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On the Mechanism of Liquid Metal Electron and Ion Sources

R. Gomer

The James Franck Institute and The Department of Chemistry, The University of Chicago,
Chicago, IL 60637, USA

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Abstract. The mechanisms of electron and ion generation from Taylor cones of liquid metals are discussed. In the case of electron emission the vacuum arcing mechanism of Swanson and Schwind, which accounts for the observed high current repetitive pulsing is briefly reviewed. For ion emission mechanisms from onset to the high current regime are proposed. It is concluded that at onset ions are generated exclusively by field desorption. A theory to account for the observed emitter heating is advanced, and it is concluded that high currents result from field ionization of thermally evaporated atoms. It is shown that space charge becomes important even at very low ion currents and is instrumental in providing stabilization in all regimes of ion emission.

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Liquid metal ion sources have been studied by several investigators since at least 1967 [1–7]. These sources provide a high brightness, quasi-point source of metal ions for high-resolution ion beam lithography and other potential applications. The details of the ion generating mechanism seem very incompletely understood. Recently Swanson and Schwind [8] have also investigated liquid metal field emission sources. The mechanism in this case, as proposed by these authors, seems straightforward but will be briefly included here since it provides an interesting contrast to the ion emission case and serves to throw some light on the latter.

A liquid metal ionization or electron source typically consists of a fine tungsten capillary (0.02 to 0.002 cm in diameter) or of a capillary with a tungsten needle projecting through it, and an extraction electrode in front of this assembly. The tungsten assembly is cleaned, for instance by sputtering, so that it is wetted by the liquid metal used, which is then forced into the capillary by a suitable arrangement. When a critical voltage, generally 5–10 kV, is applied between capillary and extractor the liquid metal is pulled outward by the electrostatic forces at its surface. It was shown in 1964 by Taylor [9] that the balance between electric and surface tension stresses leads to the formation of a cone of half-angle 49.3°, at a critical voltage V_c which depends on the electrode configuration and the surface tension. In principle, this cone should become infinitely sharp at its apex. Under some conditions dynamic instabilities occur and jetting with the ejection of liquid droplets is observed. For many liquid metals of low ionization potential it is possible however to minimize droplet formation. If the liquid metal electrode is made positive with respect to the extractor relatively stable, dc ion emission results for such metals with currents ranging from a few microamperes to milliamperes. For Ga at currents $> 10^5$ amperes Swanson [10] has observed incandescence of the liquid cone itself, and at slightly higher currents a glow is seen in front of the liquid cone; the glow region increases in size with increasing current. Its size seems to be ~ 1 μm or slightly larger. These effects seem to occur with all metals. Ion emission has been reported for Ga [4], alkali metals [2, 4, 5], Au [6], Bi-Sn-Cd (Wood's metal) [3], Hg [6], and others [6]. Some authors [4] mention energy spreads of ~ 10 eV for ions. For alkali ions both singly and to a lesser extent doubly charged ions, as well as dimer and multimer ions have been reported [3]. In one instance a space charge limited, i.e. $i - V^{3/2}$ current voltage relation has been reported [2].

If the polarity is reversed Swanson and Schwind [8] find, with an applied dc voltage that emission consists

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of nano-second pulses, the current per pulse reaching values of 200–300 amperes (!). The pulse repetition rate appears to be limited by the charging time of the power supply.

Since the formation of the emitter cone depends on electric forces, ion sources of this kind have also been called EHD (electrohydrodynamic) ion sources, and presumably the same, rather misleading, designation could also be applied to these configurations when used for electron emission.

1. Mechanism of Electron Emission

The mechanism proposed by Swanson and Schwind [8] seems to explain the phenomenon and is here given very briefly. On application of the critical Taylor voltage a liquid cone of very high curvature at its apex is formed and since the field near this apex is of the correct sign for field emission, electron tunneling occurs. The current initially emitted (as seen in oscilloscope traces) is of the order of several milliamperes. This leads to heating of the apex region, thermal evaporation of metal atoms, and their ionization by field emitted electrons, which gain sufficient kinetic energy at very small distances from the cone (10–100 Å). The resultant positive ions are attracted toward the cone where they (a) reduce electron space charge thus increasing field emission and (b) cause the sputter desorption of additional ions and neutrals. The result is an explosive increase in net current and destruction, literally blowing apart, of the cone apex. This phenomenon, vacuum arcing [11], can be observed equally well with solid metal field emitters but is then a single event, requiring the preparation of a new tip for its repetition. In the present case, on the other hand, the cone apex reforms very quickly under the electric stress on the liquid conductor and the process repeats itself.

2. Ion Emission

We turn next to the case where the cone is made positive and ion emission is observed. The principal questions are:

1) What is the mechanism of ion generation?
2) Why is it stable, unlike the electron emission case?
3) Why is heating of the cone observed at quite small currents?
4) Is the "plasma" region in front of the cone incidental to or central to the ion generating mechanism(s)?

2.1 The Taylor Cone

We start by considering briefly the Taylor voltage, the electric field near the cone apex, and the forces acting on the cone. The condition for stress equilibrium on the surface of a curved conducting liquid with an electric field E at its surface is

$$\gamma(1/r_1+1/r_2)=(E/300)^2/8\pi\,, \tag{1}$$

where γ is surface tension of the liquid in dynes/cm, r_1 and r_2 the principal radii of curvature and E the field in volts/cm. For a sphere $r_1=r_2$ and the left side of (1) takes the familiar form $2\gamma/r$, while for a cone there is only one radius, which increases linearly with distance from the cone apex. Taylor [9] showed that (1) could be met by an electric potential of the form

$$V=Ar^{1/2}\mathrm{P}_{1/2}(\cos\theta)\,, \tag{2}$$

where r is the radius vector in spherical polar coordinates and $\mathrm{P}_{1/2}$ the Legendre polynomial of order 1/2 and A a constant; this potential gives an outward normal field with the required r dependence and satisfies Laplace's equation. In order to satisfy the requirement that $V=0$ on the cone surface, $\mathrm{P}_{1/2}(\cos\theta)$ must be 0 on the cone, which is the case for $(0\leqq\theta<\pi)$ $\theta=130.7°$, giving a cone half-angle of 49.3°. The outward normal field on the cone turns out to be [9]

$$\begin{aligned}E&=(1/r)dV/d\theta=Ar^{-1/2}(d\mathrm{P}_{1/2}/d\theta)_{130°}\\&=0.974Ar^{-1/2}\end{aligned} \tag{3}$$

and thus from (1) the critical cone-forming voltage is given by

$$V_c=1.432\times10^3\gamma^{1/2}R_0^{1/2}\,, \tag{4}$$

where R_0 is the value of r at $\theta=0$ for the counter electrode (extractor) assuming that the latter has the idealized shape

$$r=R_0[(\mathrm{P}_{1/2}(\cos\theta)]^{-2}\,. \tag{5}$$

For actual geometries which do not conform to this shape R_0 can be thought of as a form factor of the order of the electrode spacing. To get some feeling for V_c let us assume $R_0\sim0.1$ cm, $\gamma=700$ dynes/cm (a value appropriate for liquid Ga, but typical of most of the metals under consideration). We then find $V_c=11$ kV in good agreement with the observed values, considering the uncertainty in R_0.

For voltages less than V_c no cone will be formed and for voltages in excess of V_c the net electric force exceeds the surface tension force so that the cone will be unstable. In reality it seems possible to exceed V_c considerably without the formation of droplets or the ejection of liquid jets in the case of ionization in vacuum. This point will be considered in more detail later.

It is evident from the Taylor argument that a rounded cone apex must be unstable at V_c relative to elongation into a true cone since the electrostatic forces will

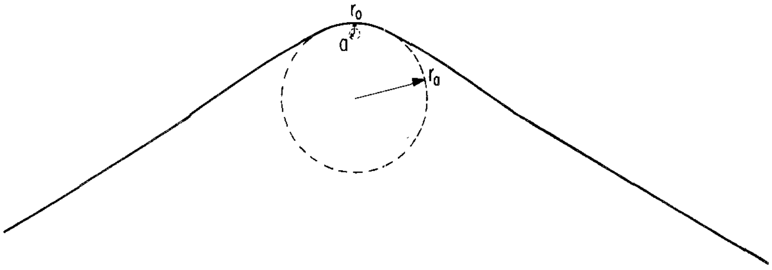

Fig. 1. Equipotential simulating shape of cone terminated by spherical apex cap based on (7) with $k=0.5$. a radius of core-sphere; r_0 distance from origin to equipotential at $\theta=0$; r_a radius of best inscribable sphere

always exceed the surface tension forces. Thus any rounding will either have to be the result of a balance between the rate of removal of atoms and ions at the apex and the rate of supply of liquid, or must result from a reduction in apex field by space charge effects.

2.2 Apex Field

It is important to know the electric field at the (rounded) cone apex. This can be obtained by the method of Dyke et al. [12]: A "core" consisting of a conducting sphere on a conducting cone is chosen. For this geometry the potential is given by

$$V(r,\theta)=(V_R/R_0^n)(r^n-a^{2n+1}r^{-(n+1)})\,\mathrm{P}_n(\cos\theta), \tag{6}$$

where r is the radius vector in polar coordinates, R_0 has the same meaning as in (4) and a is the radius of the core-sphere. n is chosen to make $V=0$ along the cone, i.e. $n=1/2$ in the present case. One then constructs an equipotential surface by picking a value of $V=$constant in such a way that this equipotential approximates the real geometry, in our case a cone of half-angle 49.3° terminated by a spherical cap. Using $n=1/2$ and (6) one obtains

$$\mathrm{P}_{1/2}(\cos\theta)=\frac{1-k^2}{x^{1/2}(1-k^2/x^2)} \tag{7}$$

as the equation of an equipotential, where use has been made of the fact that $\mathrm{P}_{1/2}(\theta=0)=1$. k and x are defined by

$$k=a/r_0 \tag{8}$$

$$x=r/r_0 \tag{9}$$

and r_0 is the distance from the origin to the equipotential at $\theta=0$. Equation (7) can easily be solved for pairs of (θ, r) values once a given k has been picked, so that a polar plot of the equipotential can be constructed. It was found that a good approximation to the desired geometry was obtained by the choice $k=0.5$, as shown in Fig. 1. The best sphere inscribable does not however have radius r_0 but $7.0r_0$. We designate this as the apex radius r_a

$$r_a=7r_0\,. \tag{10}$$

The field-voltage proportionality constant for $\theta=0$, $\beta_0=E(r_0,0)/V_{\text{applied}}$ is then given by

$$\beta_0=\tfrac{1}{2}\frac{(1+3k^2)}{R_0^{1/2}r_0^{1/2}}\cdot\frac{1}{1-\left(\dfrac{r_0}{R_0}\right)^{1/2}(1-k^2)}\,. \tag{11}$$

For $r_0/R_0 \ll 1$ the last term on the right side of (11) is 1 and, in terms of r_a, and for $k=0.5$

$$\beta_0 \cong 2.32(R_0 r_a)^{-1/2}\,. \tag{12}$$

It is interesting to compare this value with β for a sphere of the same radius r_a

$$\beta_{\text{sphere}}=1/r_a \tag{13}$$

so that we have

$$\beta_{0\,\text{cone}}/\beta_{\text{sphere}}=2.32(r_a/R_0)^{1/2}\,. \tag{14}$$

Using (4) for V_c and (12) for β_0 we find for $V=V_c$ an apex field E_0

$$E_0=3322(\gamma/r_a)^{1/2}\,[\text{volts/cm}]\,. \tag{15}$$

If $\gamma=700$ dynes/cm, $r_a=2\times10^{-7}$ cm, $E_0=2\times10^8$ volts/cm. It will be shown presently that this is of the order required for field desorption.

2.3 Force on the Cone

In the absence of space charge the steady state configuration of the apex region would be determined by balance between the removal of atoms and ions and their resupply under the unbalanced electrostatic force. The latter is therefore of some interest. The net outward force along the cone axis of symmetry is given in the absence of space charge by the net outward force over the truncated region of the cone, since along the cone electric and surface tension forces balance at $V=V_c$.

Assuming a spherical cap tangent to the cone where sphere and cone join the force F would be given by

$$\begin{aligned} F&=0.6\pi r_a^2(\varepsilon_0^2-2\gamma/r_a)\\ &=0.6\pi r_a^2\left[\frac{(E_0/300)^2}{8\pi}-\frac{2\gamma}{r_a}\right]\\ &=5.43 r_a\gamma\,[\text{dynes}]\,, \end{aligned} \tag{16}$$

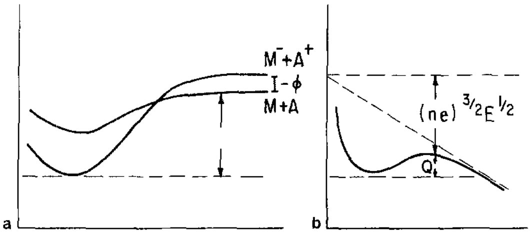

Fig. 2. Potential energy diagram for field evaporation when $I-\phi$ is small. (a) No applied field; (b) applied field E. The diagrams drawn assume that the ground state is actually ionic, but this is not essential, as long as the field deformed curve at the maximum of the potential barrier is ionic. M + A neutral curve, $\mathrm{M}^- + \mathrm{A}^+$ ionic curve. H_a heat of adsorption (or vaporization) relative to neutral metal + neutral atom in the absence of applied field. Q activation energy of field evaporation

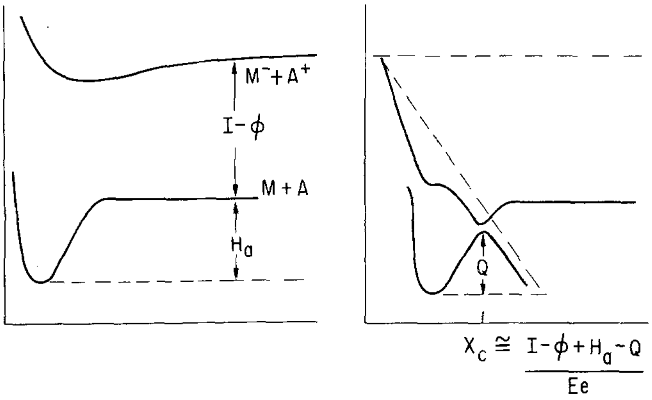

Fig. 3. Potential energy diagrams illustrating field desorption. (a) Field free case, (b) applied field E. M + A neutral curve, $\mathrm{M}^- + \mathrm{A}^+$ ionic curve, H_a heat of vaporization, I ionization potential, of atom A, ϕ work function of metal, Q activation energy of desorption, x_c crossover of field deformed ionic and neutral curves

where use of (1) and (15) has been made. For $\gamma = 700$ dynes/cm, $r_a = 2 \times 10^{-7}$ cm, $F = 7.6 \times 10^{-4}$ *dynes.*

2.4 Supply of Liquid

If viscous forces within the cone itself can be neglected the mass flow dv/dt under this force would be given by the net negative pressure acting on the supply capillary of radius r_c from Poiseuille's equation

$$dv/dt = r_c^2 F/(8\eta l)\,[\mathrm{cm}^3/\mathrm{s}]\,. \tag{17}$$

If F is taken as 8×10^{-4} dynes and $r_c^2 = 10^{-2}$ cm, $\eta \cong 0.01$ poise, $l = 0.1$ cm one finds $dv/dt = 10^{-5}\,\mathrm{cm}^3/\mathrm{s}$. Converted into current, using $\sim 3 \times 10^{-23}\,\mathrm{cm}^3$ as the volume of an atom and the fact that 1 ion/s $= 1.6 \times 10^{-19}$ amperes we find an equivalent current of 0.05 amperes. This value is much larger than the ion currents just beyond onset which are $\sim 10^{-5}$ amperes and would predict essentially no blunting by desorption since supply exceeds desorption by a factor of $\sim 10^3$. The electric field falls off from the $\theta = 0$ value with increasing polar angle and this may reduce the total force by a factor of ~ 5. It is also possible that the effective length of the supply capillary has been underestimated. However it is still impossible to explain appreciable blunting on the basis of the above considerations alone. It will turn out that there is in fact some slight blunting and that this results from a reduction in E by space charge, rather than by supply limitation. Thus the conclusion of this section is that supply will always be adequate to provide the observed ion currents.

2.5 Mechanism of Ion Formation

We consider next the mechanism of ion formation, starting at current onset. It seems clear that at least the initial step of ion emission is field evaporation or field desorption [13–15]. Two mechanisms for this have been proposed. Müller [13] assumed that under conditions of very high field the "ionic" potential curve corresponding to the state Metal⁻ + Ion fell below the "neutral" curve Metal + Atom with desorption occurring by the atom moving outward, being adiabatically ionized and desorbing over the Schottky barrier of the field-deformed ionic curve (Fig. 2). At sufficiently high field the latter would present a negligible barrier and under these conditions the field required for desorption is obtainable from the relation

$$H_a + I_n - n\phi = (n^3 e^3 E)^{1/2} - \tfrac{1}{2}(\alpha_a - \alpha_i)E^2\,, \tag{18}$$

essentially an energy balance equation, where E is field, H_a the atomic binding energy, I_n the appropriate sum of ionization potentials to produce an ion of charge n, ϕ the work function, and α_a and α_i atomic and ionic polarizabilities. This mechanism probably applies when $I-\phi$ is small. When $I \gg \phi$ Gomer and Swanson [14, 15] have proposed a mechanism depicted schematically in Fig. 3, which consists of the intersection of neutral and ionic curves in such a way that (again for zero barrier height for desorption)

$$H_a + I_n - n\phi - n^2 e^2/4x_c = Eex_c - \tfrac{1}{2}(\alpha_a - \alpha_i)E^2\,. \tag{19}$$

Here x_c is the distance from the surface at which the intersection of the curves occurs, i.e. ~ 2 Å. Both models indicate that fields of the order of one to several volts/Angstrom are required, depending on H_a, I and ϕ and this is confirmed by experiments on solid field emitters.

Since the quantitative validity of the image potential law at the fields involved is not clear, since x_c is increased from its zero field value by field penetration

[15], and since the effective polarizability of an atom in a metal surface is difficult to calculate, it is not easy to go beyond semiquantitative estimates of desorption fields. This has nevertheless been attempted by Brandon [16] who concludes that for Ga $E=1.16$ volts/Å, i.e. 1.16×10^8 volts/cm.

It will turn out that a related phenomenon, field ionization [17] probably contributes most to current generation at high currents. This can be understood by analogy with field desorption, as indicated by Fig. 4, and consists of the intersection of an ionic and neutral curve at distances where the potential of the latter is sensibly zero. Looked at in terms of electrons, it amounts to tunneling of an electron out of a field deformed atomic potential.

In general the fields required for field desorption of an atom are considerably higher than those for field ionization of the same gas phase atom as is obvious from Figs. 3 and 4.

2.6 Space Charge Effects

We next consider space charge effects. For electron emission these become appreciable only at much higher currents than those involved here, but because of their mass ion velocities are less by a factor of ~300 and space charge becomes important in the microampere range. An exact solution to the space charge problem for the cone is very difficult and we limit ourselves to the case of concentric spheres, that is, we replace emitter and collector by small and large spheres, respectively. An approximate connection with the cone will be made via a scaling argument. Unlike the classical, thermionic, case treated by Langmuir [18] it is not permissible to set the field at the emitter equal to zero since, as we have seen, fields of the order of volts/Å are in fact required there.

The basic equations are

$$\tilde{V}^2 V = 4\pi\varrho \tag{20}$$

with

$$\varrho = \frac{i}{4\pi r^2 v} \tag{21}$$

and

$$v = (2Ve/m)^{1/2} + v_T \tag{22}$$

$$v_T \cong (2kT/m)^{1/2} \tag{23}$$

so that

$$r^2\frac{d^2V}{dr^2} + 2r\frac{dV}{dr} = i\left[\left(\frac{2e}{m}\right)^{1/2} V^{1/2} + (kT/m)^{1/2}\right]^{-1}. \tag{24}$$

Let $x=r/r_a$ where r_a is the emitter radius. Define V_0 as the applied voltage required, if there were no space charge, to produce the necessary field E_0 at r_a:

$$E_0 = V_0/r_a. \tag{25}$$

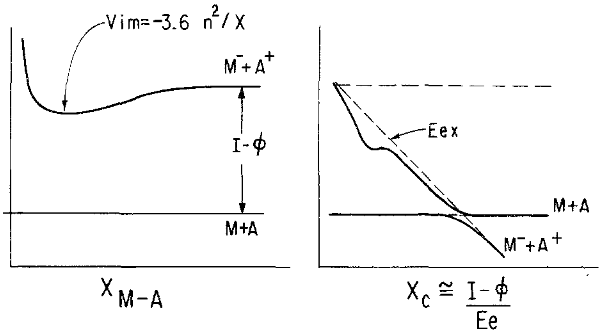

Fig. 4. Potential energy diagrams illustrating field ionization. All symbols as in Fig. 3. Correspondence with Fig. 3 can be made by assuming, in Fig. 3, a field so weak that intersection occurs in the flat portion of the neutral curve, i.e. to the right of the intersection shown there

Let $V/V_0=y$. Equation (24) then becomes

$$x^2\frac{d^2y}{dx^2} + 2x\frac{dy}{dx} = \left(\frac{m}{2e}\right)^{1/2} iV_0^{-3/2} \cdot [y^{1/2} + (v_T/v_0)]^{-1}, \tag{26}$$

where

$$v_0 \equiv (2V_0 e/m)^{1/2}. \tag{27}$$

For V in volts, i in amperes and m expressed as molecular weight M, (26) becomes

$$x^2y'' + 2xy' = 6.49\times10^5 iM^{1/2}V_0^{-3/2} \cdot [y^{1/2} + (kT/V_0 e)^{1/2}]^{-1} \tag{28}$$

with initial conditions

$$y(1) = 0 \tag{29}$$

$$y'(1) = 1. \tag{30}$$

If it were not for the appearance of V_0 in the term $(kT/V_0e)^{1/2}$ in (28), the latter could be solved numerically without further ado for various values of $iM^{1/2}V_0^{-3/2}$, the integration being carried out until such values of x as yield a constant value of $y\equiv y(\infty)$ (or until $y'\cong0$). By assuming a value, or values, of V_0 the current would then be determined and also the voltage required to produce it, namely $V_0 y(\infty)$. The presence of the term $(kT/V_0e)^{1/2}$ forces us however to make some more explicit assumptions about the emission process. Specifically we first assume that the field is sufficiently high to make the lifetime of a surface atom with respect to ion desorption constant at a value τ. The current is then given by

$$i = 4\pi r_a^2\, 10^{15}/\tau \text{ ions/s}, \tag{31}$$

where the number of atoms/cm^2 is taken as 10^{15}. In units of amperes (31) becomes

$$i = 2.01\times10^{-3} r_a^2/\tau \text{ [amperes]}. \tag{32}$$

Table 1. Solutions of (36) in tabular form. Symbols as in text. For $V_0 \leqq 1$ the term $0.16\,V_0^{-1/2}$ in (36) was calculated as if $V_0=20$ in that term

V_0 [volts]	V [volts]	i [amperes]	V/V_0	$V^{3/2}/i$
0.01	0.0154	1.2×10^{-11}	1.54	1.6×10^8
0.5	1.81	3.13×10^{-8}	3.62	7.8×10^7
1.0	4.61	1.25×10^{-7}	4.61	7.9×10^7
5.0	40.5	3.13×10^{-6}	8.1	8.2×10^7
10.0	102	1.25×10^{-5}	10.2	8.2×10^7
20	258	5×10^{-5}	12.9	8.3×10^7
50	875	3.13×10^{-4}	17.5	8.3×10^7
100	2,280	1.25×10^{-3}	22.8	8.7×10^7
500	16,750	0.031	33.5	7×10^7

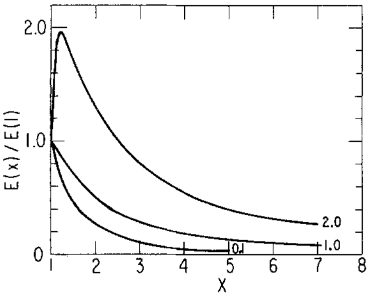

Fig. 6. $E(x)/E(1)$ vs. x for various values of V_0, based on solutions of (36). Note that for $V_0=20$ the field E peaks at $x=1.2$, and is almost $2E(1)$ at that point

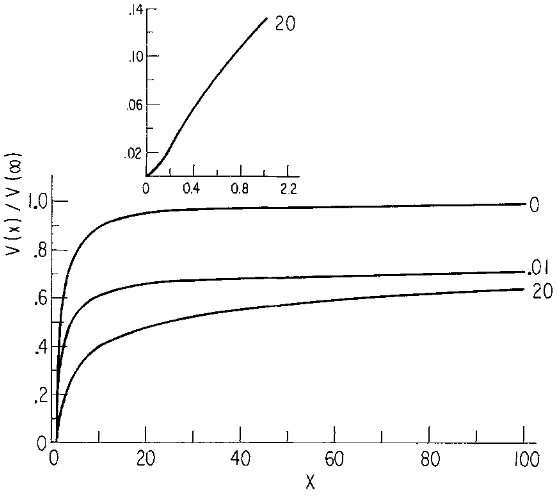

Fig. 5. Plots of $V(x)/V(\infty)$ vs. x for various values of V_0, based on solutions of (36). Insert shows region for $1 \leqq x \leqq 2$ for $V_0=20$, to illustrate the fact that for appreciable space charge the field E will have its maximum at $x>1$

If we now pick a fixed value for E_0 we can eliminate r_a from (32) by (25) and have

$$i=2\times 10^{-3} V_0^2/(E_0^2 \tau). \tag{33}$$

Substitution of this expression for i in (28) yields

$$6.49\times 10^5 i M^{1/2} V_0^{-3/2} = 1.30\times 10^3 M^{1/2} V_0^{1/2}/(E_0^2\tau) \tag{34}$$

and (28) becomes

$$x^2 y'' + 2xy' = 1.30\times 10^3 M^{1/2} V_0^{1/2}/(E_0^2\tau) \cdot \left[y^{1/2} + \left(\frac{kT}{e}\right)^{1/2} V_0^{-1/2} \right]^{-1}. \tag{35}$$

This procedure is equivalent to assuming that changes in i result from increases in r_a if τ and E_0 are considered to stay constant. With the explicit (and slightly arbitrary) choice $E_0=4\times 10^8$ volts/cm, $\tau=10^{-13}$ s, $M=70$ (corresponding to Ga), (35) finally becomes

$$x^2 y'' + 2xy' = 0.68 V_0^{1/2} (y^{1/2} + 0.16 V_0^{-1/2})^{-1}, \tag{36}$$

where $T=300$ K has been used. Equation (36) was solved numerically for various values of V_0 until y no longer increased appreciably with increasing x. The arbitrary cutoff was made at $x=10^4$. The applied voltage V can now be found as $V_0 \cdot y(\infty)$, where ∞ is taken to be equivalent to $x=10^4$ and i can be obtained from (33). Table 1 shows the values of i vs. the corresponding applied voltage V for various values of V_0 as well as $V/V_0 \equiv y(\infty)$. Also shown are values of $V^{3/2}/i$. These are sensibly constant until $i<10^{-11}$ indicating space charge behavior, for which i should be proportional to $V^{3/2}$. Figure 5 shows plots of $V(x)/V(\infty)$ vs. x for some selected values of V_0. It is clear that the potential rises much less rapidly than in the absence of space charge. Figure 6 shows the field, relative to that at $x=1$, vs. x.

If we now shed our scruples about the term $(kT/V_0 e)^{1/2}$ in (28) or (36) and assume that its exact magnitude is relatively unimportant so long as it is finite and thus prevents $\nabla^2 V$ from becoming infinite at $x=1$[1], we can also interpret the results in terms of fixed r_a, if we assume that the variation in E_0 required to increase i is so small that a constant value of E_0 can be assumed even when i is varied. In that case a fixed choice of $V_0^{\text{true}} = E_0 r_a$ suffices to obtain i, the values of V_0 shown in Table 1 being now considered simply as numbers required to vary i. We call these V_0 (parameter).

We have from (34) and the values of E_0 and τ used to obtain (36)

$$i=1.26\times 10^{-7} V_0^{3/2} V_0^{1/2}(\text{param}) \tag{37}$$

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[1] This point was confirmed by direct calculation, using $V_0=20$ volts and $T=300$ and 900 K, for $i=0.1$, 1, and 10 microamperes. The results do not differ from those shown in Fig. 7, obtained as described in the text.

and

$$V = V_0 \cdot y(\infty). \tag{38}$$

For a particular choice of V_0 i is now obtained as a function of applied voltage V by picking a value of V_0 (param) from Table 1, using the appropriate value of $y(\infty)$ to obtain V from (38) and the value of i from (37). A plot of $\log i$ vs. $y(\infty) \equiv V/V_0$ for $V_0 = 20$ volts, obtained in this way, is shown in Fig. 7; space charge effects are still appreciable when $i \cong 10^{-6}$ amperes, where $V/V_0 = 1.5$. The choice $V_0 = 20$ volts corresponds to $E_0 = 1 \times 10^8$ v/cm for $r_a = 2 \times 10^{-1}$ cm, or to 2×10^8 v/cm for $r_a = 10^{-7}$ cm.

It should be emphasized that the smallness of r_a is crucial to this result, although this is not directly obvious. An example will illustrate this. Suppose we choose $E_0 = 2 \times 10^8$ volt/cm and $r_a = 10^{-6}$ rather than 10^{-7} cm. We then have $V_0 = 200$ volts, instead of 20 volts and from (37) we see that the ratio $V/V_0 = 1.5$ now corresponds to $i = 3 \times 10^{-5}$ amperes, or 30 times higher than for $r_a = 10^{-7}$ cm. The physical reason is that higher currents are now required to produce the same current density.

We now adapt these results to the Taylor cone in a rough way by assuming (a) that the values of current for the sphere of same radius r_a as the cone apex must be divided by ~ 4 to give the equivalent cone current, since the emitting area of the latter is $\sim \pi r_a^2$ rather than $4\pi r_a^2$ as for the sphere, and (b) that once this correction has been made the same *ratio* of V/V_0 can be used for the cone as for the sphere. Table II lists some representative assumptions of r_a, E_0, and values of i and V based on these assumptions, calculated by means of (14), (37), (38) and the solutions of (36).

The numerical values of V listed in Table 2 depend not only on the quantitative validity of our extrapolation from sphere to cone but also on the exact value of R_0 and must therefore be considered at best semiquantitative estimates. Despite this fact several conclusions emerge rather clearly: 1) Apex fields of $\gtrsim 10^8$ volts/cm can only be obtained with very small apex radii, even in the absence of space charge, and 2) space charge effects become significant at currents of $\gtrsim 10^{-7}$ amperes. There is some trade-off between apex radius and V/V_0, as already pointed out, and also $V_{\text{cone}}/V_{\text{sphere}}$ decreases with increasing r_a, as indicated by (14). Nevertheless it seems clear that r_a values much in excess of 100 Å would require voltages in considerable excess of experimentally observed values to produce the required apex fields. This conclusion is of considerable significance for ion-optic applications, since it implies a very small effective source size and consequent high brightness, as is in fact observed experimentally. Since the apex is probably spheroidal rather than spherical, the effective source size is dependent on actual apex size.

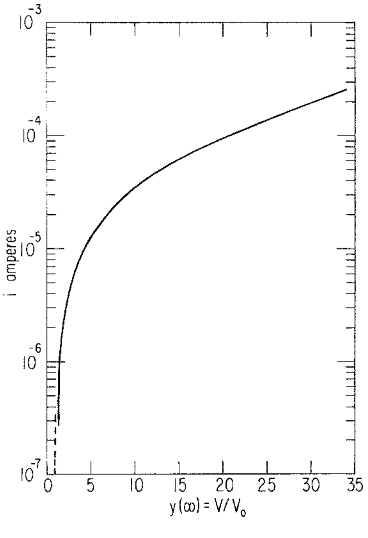

Fig. 7. Log i vs. $y(\infty) = V(\infty)/V_0$ for $V_0 = 20$, based on (37)

Table 2. Various combinations of r, E_0, i, and V. The values for i refer to a sphere and should be divided by ~ 4 for the cone. The values of V_0 correspond to the voltage required to produce the field E_0 at the surface of a sphere of radius r_a in the absence of space charge

r_a [cm]	E_0 [volts/cm]	V_0 [volts]	i [amperes]	V_{sphere} [volts]	V_{cone} [volts]
10^{-7}	10^8	10	4×10^{-7}	15	6,450
10^{-7}	10^8	10	2.8×10^{-6}	36	15,566
10^{-7}	2×10^8	20	1.1×10^{-6}	30	9,302
10^{-7}	2×10^8	20	8×10^{-6}	72	21,900
2×10^{-7}	10^8	20	1.16×10^{-6}	30	9,120
3×10^{-7}	10^8	30	2.1×10^{-6}	45	11,200
4×10^{-7}	10^8	40	3.2×10^{-6}	60	12,930
8×10^{-7}	10^8	80	9×10^{-6}	75	18,430
8×10^{-7}	10^8	80	1.6×10^{-6}	96	14,600

We are also able now to estimate to what extent space charge can contribute to relaxation of the cone apex from infinite sharpness. From (1) we find for example if $r_a = 2\,10^{-7}$ cm and $\gamma = 700$ dynes/cm that the equilibrium field is $E = 1.26 \times 10^8$ volts/cm. It is clear from Table 2 that even a modest current can suffice to reduce E_0 to this value from that which would be present at V_c in the absence of space charge, say 2×10^8 volts/cm. Thus such blunting as occurs seems to result entirely from reduction in apex field by space charge, rather than from any limitations on liquid supply, as already stated in an earlier section.

2.7 *Mechanisms of Current Generation and Stabilization*

We are now ready to consider ion current formation from onset to high currents, as voltage is increased from 0. Clearly there can be no current at all below V_c since cone formation is a prerequisite. If the apex field at V_c (in the absence of ion current and hence space charge effects) is too small to allow field desorption, no ion current will be observed at V_c. Increases in V will then lead to droplet formation, possibly with concomitant ionization. This will be discussed in slightly greater detail in the next section. Assuming however that the apex field at V_c suffices for appreciable ion generation there will be a sharp onset of current at V_c. In the case of Ga, for instance, the experimental onset value [10] appears to be 2–3 microamperes, and this implies that there will already be some space charge effects at onset. The cone apex will consequently assume a form corresponding to equilibrium between surface tension and electrostatic stress, the latter being reduced by space charge in the current generating region from the value which would obtain in the absence of current. As already pointed out the effective apex radius must be of the order of 10–50 Å to account for the observed voltages required. In the current regime just beyond onset the mechanism of ionization must correspond to pure field desorption or evaporation, and consequently ion energy distributions will be narrow, and principally determined by quantum effects, i.e. uncertainties in the locus of ionization. These probably amount to ~1 eV.

Emission in this current-voltage regime will be stable since space charge provides negative, i.e., stabilizing, feedback: If through some fluctuation r_a increases, E will decrease, and hence i will decrease. This causes a reduction in space charge so that E (for fixed V) increases, pulls the apex into a sharper configuration (i.e., decreases r_a), thereby causing more i and also more space charge screening, this causing relaxation, etc.

We must consider next what happens as V is increased so that i increases to $\geqq 10^{-5}$ amperes. It is found experimentally [10] for Ga, for instance, that the liquid cone is heated to $\geqq 1000\,°\mathrm{C}$ at such currents. It is easy to show that ohmic heating at 10^{-5} amperes is unimportant. (See, for instance, [8].) On the other hand, field desorption with short desorption times can lead to heating through an effect analogous to that observed when a solid is cleaved. The separation energy in that case always exceeds the surface energy of the surfaces created because the breaking of bonds can never be performed adiabatically and some energy is always imparted to the separated solids through "snapping back". In the present case, if the departing ion leaves very rapidly, the remanent liquid will not have time to assume its equilibrium configuration as the ion leaves. Thus the work of removing an ion exceeds the adiabatic value and the difference appears eventually as heat in the liquid. It turns out that only a very small amount of energy per ion formed is required to account for the temperature rises in fact observed at $>10^{-5}$ amperes. Very approximately we have a steady state

$$K\frac{\Delta T}{x} = Q/\pi r_a^2 = \bar{Q}\,, \tag{39}$$

where K is thermal conductivity, ΔT the temperature rise at the apex, x a mean distance over which this rise decays, Q the heat generated per unit time and $\bar{Q}$ the heat per unit time per unit area. Equation (39) applies strictly speaking to a cylinder, not a truncated cone, but the correction factor will not exceed an order of magnitude. Taking liquid Ga as an example, $K \cong 0.3$ watt cm^{-1} deg^{-1}. Taking $x = 0.01$ cm we see that the required heat becomes, for $\Delta T = 1000$ K

$$\bar{Q} \cong 3\times 10^4 = 10^{15} q/\tau\ [\mathrm{watt/cm^2}]\,, \tag{40}$$

where q is the heat generated per ion. Thus

$$\begin{aligned} q &= 3\times 10^{-4}\tau\ [\mathrm{ergs/atom}] \\ &= 2\times 10^{8}\tau\ [\mathrm{eV}]\,. \end{aligned} \tag{41}$$

If $\tau = 10^{-12}$ s, $q = 2\times 10^{-4}$ eV. Alternately (but equivalently, since i, r_a and τ are related by (32))

$$q \cong \frac{K\Delta T}{xi}\pi r_a^2 \times 1.6\times 10^{-19}\,, \tag{42}$$

where i is ion current. Taking $i = 10^{-5}$ amperes we find

$$q = 10^{10} r_a^2\ [\mathrm{eV}] \tag{43}$$

for r_a in cm. If $r_a = 2\times 10^{-7}$ cm $q = 4\times 10^{-4}$ eV and for smaller radii q will be correspondingly smaller. This heating mechanism was pointed out to the author by Prof. W. Kohn.

In the case of solids the relaxation can involve only elastic deformations. In the case of liquids on the other hand there is in addition an analogue to plastic deformation which can occur on the time scale of interest. If an atom were plucked out of a liquid surface by field evaporation the surface area would increase by $\sim \pi r_{\mathrm{atom}}^2 \cong 7\times 10^{-16}\,\mathrm{cm}^2$ and the liquid would quickly get rid of this "hole", but not in the time of desorption. Thus there would be a relaxation energy of $\gamma \pi r_{\mathrm{atom}}^2$ ergs/ion, or for $\gamma = 700$ ergs/cm^2, 5×10^{-13} ergs/ion or 0.3 eV. This value is probably an overestimate because of partial relaxation during field desorption. Further it should be remembered that the estimate of the required heat refers to a cylinder not a very blunt cone. Finally it must also be recalled that, if the field is not high enough to allow field desorption with zero activation energy, the activation energy, which amounts to heat carried away by the desorbing particle, must be subtracted from the above value.

It is clear in any case that the effect just discussed can lead to sufficient heating to cause appreciable desorption of neutral atoms. The discussion of space charge limited field desorption also indicates that the high currents obtained experimentally at voltages of order 1.5–2V_c simply could not be obtained by field evaporation, since very much higher voltages would be needed to provide the required fields. Thus it seems clear that the high currents obtained at voltages above V_c must come from neutral atoms desorbed thermally and then ionized in some manner. It is easy to find some limits on the product of area which must supply this vapor and the (equilibrium) vapor pressure involved. The evaporating flux from a surface at temperature T such that the equilibrium vapor pressure is P is given by $\dot{N}/A$

$$\begin{aligned}\dot{N}/A &= P(2\pi mkT)^{-1/2}\\ &= 1.3\times10^{20}P_{\text{torr}}\,[\text{atoms/cm}^2/\text{s}]\end{aligned} \tag{44}$$

for Ga at 1300 K where A is area and P pressure. Thus if every evaporated atom were somehow ionized the resultant current would be

$$i_{\max}=21P_{\text{torr}}\cdot A\,[\text{amperes}]\,. \tag{45}$$

Thus for $i=10^{-4}$ amperes, $P\cdot A=4.7\times10^{-6}$ torr-cm^2. If $P=1$ torr, corresponding to $T=1350\,^\circ\text{C}$ for Ga, $A=4.7\times10^{-6}\,\text{cm}^2$, or if it assumed to be given by πr^2, $r=1.2\times10^{-3}$ cm. If $P=760$ torr a value of $r=4\times10^{-5}$ cm would result. Thus it is clear that an area much bigger than the hemispherical apex cap must contribute to current generation.

We show next that the ionization mechanism cannot be impact ionization of vapor by field desorbed ions. Let us assume for the moment that the pressure of vapor is uniform (which is, of course, incorrect) in order to estimate the mean free path with respect to excitation (or ionization). The cross section σ_i for inelastic collisions, i.e. electronic excitations in ion-atom collisions is $\sigma_i=10^{-19}-10^{-20}\,\text{cm}^2$ for ion energies in the range 1–5 KeV [19]. Since ions gain $\sim50\%$ of their final kinetic energy in $\sim10r_a$ as indicated by Fig. 5 energies of the order of 0.1–5 KeV are obviously the only ones of relevance. The mean free path for excitation is then λ_i

$$\lambda_i=(\varrho\sigma_i)^{-1}=kT/(P\sigma_i)\,, \tag{46}$$

where ϱ is gas density, or if P is expressed in torr

$$\lambda_i=1.4\times10^{-16}/(\sigma P_{\text{torr}})\,, \tag{47}$$

where $T=1400$ K has been used. Thus, for $\sigma=10^{-19}\,\text{cm}^2$ we find, at $P=10^3$ torr (a value not likely to be achievable) $\lambda_i=1.4$ cm. If we assume that the region where vapor pressure is appreciable is of dimensions 10^{-4} cm, we see that 10^{-4} ionizing collisions per field desorbed ion would occur. The situation would not be improved if P could somehow be raised: The cross section for elastic collisions σ_e in which ion kinetic energy will be efficiently lost is $\sigma_e\cong10^{-15}\,\text{cm}^2$, so that at $P=10^3$ torr the mean free path for elastic collisions is $\lambda_e\cong10^{-4}$ cm. Increasing P would correspondingly decrease λ_e and thus ion kinetic energy, thereby decreasing λ_i. Ion-atom collisions could therefore lead to substantial current increases only if every electron thereby released ionized on average 10^5 vapor atoms by avalanching. Since the cross section for electron excitation is of order $10^{-15}-10^{-16}\,\text{cm}^2$ (for electron energies of ~100 eV) and hence the mean free path for electron ionizing events also of order 10^{-4} cm at $P=10^3$ torr this seems impossible. Although the pressures to be expected in front of the apex can be substantially increased by polarization effects, it seems impossible to attain the values necessary for impact ionization over a sufficient region of space to make this mechanism likely as a major contributor to current generation. At very high currents however, if secondary electrons from the cathode are able to reach the cone and its vicinity, electron impact ionization of metal vapor probably contributes substantially. Under these conditions however ion energies will show a wide spread, and the effective source size will also have increased substantially so that this regime is of little interest for ion-optical applications.

The most likely mechanism for current generation under conditions where space charge limited field evaporation cannot account for more than a fraction of the current is probably field ionization. The overall mechanism can be envisaged as follows. Metal atoms evaporating from the cone in the vicinity of the apex are drawn into the high field region by the polarization force, $\frac{1}{2}\alpha\,\text{grad}\,E^2$ and are there field ionized. Thus supply from a region much larger than that corresponding to the immediate cone apex is utilized, and since impact ionization is not involved low steady state vapor densities present no difficulty. The electrons liberated by field ionization are accelerated to the cone and serve to heat it. The energy supplied in this way overcompensates that withdrawn by vaporization. The latter is ~5 eV/atom; since the distances at which field ionization occurs probably lie between $0.1r_a$ and r_a from the surface the energy delivered per electron is necessarily much greater. The reason that runaway heating does not occur is probably that the total number of atoms evaporating exceeds those being ionized by a sufficient factor. Under conditions where field ionization predominates, the field at the cone apex is probably reduced to the point where field desorption no longer occurs. Under conditions of appreciable space charge the potential drop between emitter and cathode is not concentrated near the emitter as in the absence of space charge but distributed over a larger distance (Fig. 5). Consequently high fields are also maintained over much larger distances, (Fig. 6) and are sufficient for field ionization still to occur at 1–5r_a in front of the cone apex. The lifetime with respect to field ionization can be estimated very crudely [17] from

$$1/\tau = v_e e^{-6.8\times10^7 I^{3/2}/E}, \qquad (47)$$

where v_e is an electronic frequency, $\sim 10^{15}\,\mathrm{s}^{-1}$ and I the ionization potential of the atom being field ionized. For Ga $I = 6\,\mathrm{eV}$ and for $E = 10^8$ volts/cm $\tau \cong 2\times10^{-11}$ s. In this time an atom moving with thermal velocity moves ~ 100 Å. In this distance the high field is not changing very much under space charge conditions and consequently the probability of field ionization is high.

Although the probability of impact ionization or excitations by ions is small as we have seen it should nevertheless suffice to account for the visible light seen for $i \geqq 10$ microamperes. At very high voltages and currents it is conceivable that pressures in the apex region are sufficiently high to allow enough multiplication of electron ionization to make field ionization the minor and electron impact ionization the major current generating mechanism. As already indicated the primary source of electrons under these conditions may be secondaries released from the cathode under ion impact.

Unlike the electron emission case runaway is not observed for ion emission. The reason is that unlike the electron emission case there is sufficient negative feedback present in all regimes of ion emission. This is provided by space charge and by the fact that a decrease in apex field leads to an increase in apex radius, hence a further decrease in field and thus to decreases in emission which in turn reduce space charge thus lead to increase in field etc. The reason space charge is effective in ion but not in electron emission is of course that the primary charge carriers in ion generation are massive and the counter charge carriers, which reduce space charge are light, with the opposite situation occurring in electron emission.

Although it seems certain that ion-atom collisions cannot contribute appreciably to ion current, such collisions may nevertheless lead to appreciable broadening of the ion energy distribution, since elastic and charge exchange collisions have very high cross sections. Considerable broadening is also known to occur in field ionization [17] at high fields, since then the locus of ionization is distributed over an appreciable region of space, and hence of potential.

We must finally consider why it is possible to exceed the Taylor cone voltage V_c without destroying the cone. The answer can be given only qualitatively, but must be that under space charge conditions the field is concentrated in the space charge region, i.e. lines of force are so concentrated that the field on the cone surface does not appreciably exceed the Taylor field. It is obviously not practical to attempt a calculation of equilibrium shape under space charge conditions without far more detailed knowledge of the actual current distribution than is available at present.

2.8. Droplet Formation

Finally droplet formation must be discussed since its occurence is undesirable for ion formation but desirable if the object is "atomization", that is the deliberate formation of small droplets. It is clear that droplets *must* form if the field at the cone apex and down-shank from it exceeds the critical field. Thus, if at V_c the field in the apex region is insufficient for enough field evaporation to produce appreciable space charge, the cone apex will be pulled out into a jet and when the length of the latter exceeds $2\pi r$, where r is the jet radius, necking off and hence droplet formation will occur in accordance with well known classical theory [20]. It should be noted that the field at the apex is (in theory) infinite but of course this region has dimension of less than a single atom. Thus the criterion just spelled out applies to the region immediately adjacent to the theoretical cone apex. Formally we may write from (2), (3) and (4) that droplets will form if

$$1394\gamma^{1/2}/r^{1/2} < E_c, \qquad (48)$$

where E_c is the field for sufficient field desorption to give adequate space charge, i.e. to give a current of say 10^{-6} amperes, and r is the radius of curvature of the cone slightly below its theoretical apex. If r is chosen as 10^{-7} cm and $\gamma = 700$ dynes/cm the left-hand side of inequality (48) gives $E_c \leqq 1.17\,10^8$ volts/cm. Thus very roughly we expect no droplet formation for metals for which the desorption field is of order 1 V/Å and would expect droplet formation for metals with appreciably higher evaporation fields.

3. Conclusion

The foregoing indicates that the processes entering into the operation of a liquid metal ion source are by no means simple and that at best a semiquantitative description of the various phenomena is possible. Nevertheless even a qualitative understanding of these sources is of some interest because of the potential applications of these sources as in ion optical applications of various kinds.

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