Scanning Microscopy

Volume 10 | Number 4 Article 1

9-22-1996

Ion and Electron Emission from Liquid Metal Sources

H. Niedrig
Technische Universitat Berlin, nied0432@mailszrz.zrz.tu-berlin.de

Scanning Microscopy Vol. 10, No. 4, 1996 (Pages 919-935) 0891-7035/96$5.00+.25
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

ION AND ELECTRON EMISSION FROM LIQUID METAL SOURCES

H. Niedrig

Optisches Institut, Technische Universität Berlin
Hardenbergstr. 36 A, D-10623 Berlin, Germany
Phone number: 49-30-314 22735 / FAX number: 49-30-314 26888 / E-mail: nied0432@mailszrz.zrz.tu-berlin.de

(Received for publication March 7, 1996 and in revised form September 22, 1996)

Abstract

In liquid metal ion sources, the emission is located at the apex of a liquid cone (the often so-called Taylor cone), formed by electrostatic forces and surface tension. Reversal of the extraction voltage polarity results in electron emission from the liquid metal surface. For small apex radii, ≤ 1 μm, steady field emission of electrons has been observed, whereas for apex radii ≥ 10 μm, explosive pulsed emission occurs. Since the onset voltage for electron emission has been found to be considerably lower than the critical voltage for the formation of the Taylor cone, it has been concluded that dc (direct current) electron emission from a field stabilized cone is not possible. *In situ* high-voltage transmission electron microscopy observations seem to confirm this conclusion, although in one case, a field-stabilized liquid micro-cone during electron emission has been observed for a liquid-gallium-indium-tin source. The literature on liquid metal ion and electron sources is reviewed. From *in situ* transmission electron microscopy observations of the cone formation, relations for cone angle and jet length dependent on ion emission current are derived. Growth and emission of microdroplets at liquid indium ion sources have been imaged. In the case of electron field emission from liquid indium sources, no liquid cone formation has been observed.

Key Words: Liquid metal electron sources (LMES), liquid metal ion sources (LMIS), Taylor-Gilbert cone, micro-droplet emission, *in situ* high-voltage transmission electron microscopy, emission electron microscopy.

Introduction

In the sixties, ion emission from liquid-metal-filled capillary tubes in high electric fields, called electrohydrodynamic ion sources, was investigated for applications in space thruster propulsion systems (Krohn, 1961, 1974; Mahoney *et al.*, 1969). In the seventies, these ion sources, now called liquid metal ion sources (LMIS), gained new interest for their use in focused ion beam applications such as scanning ion microscopy {e.g., Anazawa *et al.*, 1982; Sternberg *et al.*, 1988; Knapp *et al.*, 1991, [for a review, see Levi-Setti (1983) or Mair and Mulvey (1985a)]}; secondary ion mass spectroscopy (SIMS; Bayly *et al.*, 1983; Gnaser and Rüdenauer, 1983); imaging-SIMS (e.g., Mair and Mulvey, 1985a; Levi-Setti *et al.*, 1988, 1993) and ion beam lithography (e.g., Orloff, 1984, 1991; Mair and Mulvey, 1985b; Dudnikov, 1996). Besides the capillary type mentioned above, the needle type LMIS was developed (Clampitt and Jefferies, 1978a,b; Clampitt, 1981; Mair and Mulvey, 1984a,b), consisting of a fine tungsten needle covered by a liquid metal film. In both cases, the application of a voltage of several kilovolts causes the liquid surface to form a liquid cone, as the equilibrium surface between the electric field forces and surface tension. The ion emission takes place at the apex of the cone due to the increased electric field strength caused by the small apex radius.

Taylor (1964) showed that, for the static equilibrium problem, given certain constraints (for example, that the counter-electrode should have an appropriate shape), there was a mathematical solution in the form of a cone of half-angle 49.3°. In a carefully designed apparatus, he verified this experimentally for oil water interfaces subjected to an electric field. Therefore, later on such cones were often called "Taylor cones." However, as pointed out by Forbes (see **Note added in proofs**, and Ljepojevic and Forbes, 1995) such liquid cones, formed under electric stress, were already described by Gilbert (1600)! Forbes, therefore, suggests to call the experimentally observed cones "Taylor-Gilbert" cones, and Taylor's calculated cone shape "Taylor's mathematical

List of Symbols

T	:	temperature (Kelvins)
T_F	:	melting temperature (Kelvins)
U_{ext}	:	extraction voltage (V or kV)
U_0	:	onset voltage for emission (kV)
$U_{0\text{-ion}}$	:	onset voltage for ion emission = critical voltage for cone formation (kV)
$U_{0\text{-el}}$	:	onset voltage for electron emission (kV)
U_a	:	acceleration voltage (kV) of electron microscope
I_e	:	emission current (A, mA, or μA)
ϑ	:	half-angle of liquid cone (degrees)
ϑ_0	:	half-angle of liquid cone for $I_e = 0$ (degrees)
l	:	length of cusp or jet (μm)
l_0	:	length of cusp or jet for $I_e = 0$ (μm)
r_t	:	radius of curvature of solid tip (μm)
γ	:	surface tension (kg/s^2 = N/m = J/m^2)
E_0, E	:	electric field strength (V/m)
m	:	mass of ions (kg)
e	:	1.602 x 10^{-19} A·s (coulomb), electron charge
v	:	flow velocity of liquid metal film (m/s)

cone." For clarity, this terminology will be adopted from here on.

There has been some theoretical discussion on the exact shape of an operating source (Chung *et al.*, 1984a,b,c, 1986; Kingham and Bell, 1984; Cutler *et al.*, 1986). The truth of the situation seems to be that the practical circumstances of operation of liquid-metal field emission sources never conform exactly to Taylor's constraints, so Taylor's mathematical solution is never strictly applicable; however, as shown by Kingham and Bell (1984), it is often a good approximation at low emission currents, particularly at points well away from the cone apex.

There has also been theoretical discussion about the emission mechanism, whether this is field ionization (of thermally evaporated atoms) or field evaporation, and about the role of space-charge effects (Gomer, 1979; Swanson *et al.*, 1980; Kingham, 1982; Prewett *et al.*, 1982; Swanson, 1983; Swanson and Kingham, 1986). Further contributions to these aspects have been published by Forbes and Mair (1982), Ptitsin and Shevchenko (1992), Ptitsin (1993), and Ljepojevic and Forbes (1995).

The cone model has then been improved by assuming a conical or cusp-like protrusion at the apex of the liquid (Taylor-Gilbert) cone (Kang and Swanson, 1983, Kingham and Swanson, 1984, 1986; Chung *et al.*, 1987, 1991; Miskowsky *et al.*, 1989; Swanson and Bell, 1989; Forbes and Ljepojevic, 1989, 1991, 1992). The protrusion length increases with the ion emission current (Mair and Forbes, 1991, 1992; Mair, 1994; Liu and Forbes, 1995). Experimental evidence for this model, i.e., a jet-like protrusion at the apex of the liquid cone was presented by Aitken (1976) and by Clampitt and Jefferies (1978b) with *in situ* scanning electron microscopy, by Gaubi *et al.* (1982) using *in situ* transmission electron microscopy (300 keV) and by Ben Assayag *et al.* (1985) with *in situ* high-voltage transmission electron microscopy. Cui Zheng and Tong Linsu (1988) have described a numerical approach to determine the liquid emitter shape and the liquid flow on the needle surface.

Current-voltage characteristics have been calculated by Kingham and Swanson (1984), Mair (1984a,b, 1994), Mair and Mulvey (1986), Ljepojevic and Forbes (1992), and Miskovsky *et al.* (1994). Wagner and Hall (1979) found an influence of the liquid flow impedance on the current-voltage characteristics. This effect has been theoretically confirmed by Forbes *et al.* (1995).

The energy distribution and the broadening of energy width of LMIS beams due to beam current and temperature was analyzed by Sudraud *et al.* (1979), Swanson *et al.* (1979a,b, 1980), Knauer (1981), Mair *et al.* (1983, 1984), Ben Assayag and Sudraud (1984), Papadopoulos *et al.* (1984), Mayer (1985), Rüdenauer *et al.* (1987), Hornsey (1991), Hesse *et al.* (1995), and Kruit *et al.* (1995).

The optics of an LMIS gun have been studied by Orloff and Swanson (1979), and the ion trajectories in the extraction region of LMIS have been calculated by Ward and Seliger (1981). Light emission from the region close to the tip of an emitting LMIS (Krohn, 1961) has been measured versus beam current and source temperature by Hornsey and Marriott (1989), following earlier work by Kuk *et al.* (1980) and Venkatesan *et al.* (1981).

Apart from ion emission, microdroplet emission from LMIS (Krohn, 1961, 1974; Wagner *et al.*, 1981; Hornsey and Ishitani, 1990a,b; Vladimirov *et al.*, 1992) and emission of metallic clusters (e.g., Joyes *et al.*, 1986) have been observed and investigated theoretically (Miskowsky *et al.*, 1988). New time-dependent calculations by Forbes *et al.* (1995) indicate that, "under the combined influence of gravitational and electrostatic forces, the surface of a conducting liquid can develop into a highly disorganized state" with surface shapes which remind of recently published electron micrographs of the liquid cone of an operating LMIS (Praprotnik *et al.*, 1994b).

The heating of the emitter tip by secondary electrons from the extracting electrode has been considered by Czarczynski and Znamirowski (1993, 1995), and the

X-rays excited on the emitter by these secondaries have been used by these authors (1995) to take X-ray photographs from the emitter tip and its surrounding by means of a camera obscura.

For reviews on LMIS see Gabovich (1983); Mair and Mulvey (1984a); Melngailis (1987); Swanson and Bell (1989); Mackenzie and Smith (1990); Prewett and Mair (1991); Czarczynski and Znamirowski (1993); and Swanson (1994). The paper by Mackenzie and Smith (1990) contains a complete bibliography with about 1100 references of earlier work on liquid-metal ion sources and their applications.

Reversal of the extraction voltage polarity should result in electron emission from the liquid metal surface, thus creating a liquid metal electron source: LMES. This effect was first observed by Swanson and Schwind (1978), although they only found a **pulsed** electron emission mode with pulse rise times of 2 to 3 nanoseconds for both capillary-type and needle-type liquid metal sources of diameters between 50 and 200 μm. Hata *et al.* (1986, 1987a,b) obtained **stable** dc (direct current) field emission of electrons from Ga-In-Sn liquid alloy sources for apex radii of the underlying tungsten tips of approximately 1 μm and an extraction voltage of about -2 kV. By raising the voltage to -4 kV, the tip exploded, and pulsed emission was observed. The destroyed tungsten tip had a tip radius of about 10 μm, and such an emitter never showed dc field emission in agreement with the observations of Swanson and Schwind (1978). By observing emission patterns from LMES in the dc mode, Hata *et al.* (1988) concluded that different stable protrusions are formed on the emitter tip, the number of which could be reduced with cleaning by field evaporation of liquid metal.

In all cases, the onset voltage for field electron emission was found to be considerably smaller than the onset voltage for ion emission (Mitterauer, 1984). Therefore, it was concluded that dc electron emission from a field stabilized Taylor-Gilbert cone is not possible regardless of the substrate's tip radius (Rao *et al.*, 1989).

However, a liquid metal electron source and, in particular, a source developing a Taylor-Gilbert cone during electron emission would represent a field emission electron source that can be operated without the necessity of ultrahigh vacuum conditions, because the liquid surface reforms itself under the ion bombardment from the residual gas. Also, the capability of a liquid metal source to emit either ions or electrons, only by reversing the polarity of the extraction voltage, is of particular interest for analytical instruments (Rao *et al.*, 1989; Driesel, 1990; Sawaragi *et al.*, 1990). Therefore, it seems worthwhile to investigate the surface formation and the dynamics at the ion and electron emitting liquid surface by *in situ* imaging in an electron microscope during emission of the source. Until now this has been done only by a few authors. Their findings, including our own results, will be presented in the following sections.

In Situ Observation of Liquid Metal Ion Emission

The first *in situ* (light optical) micrographs of an operating liquid metal ion source of the capillary type were published by Swatik and Hendricks (1968), showing the end of a 250 μm capillary filled with gallium-indium eutectic fluid at different extraction voltages. Near the onset voltage, the original liquid hemisphere deformed into an ellipsoidal surface. At a reproducible critical voltage (onset voltage), the ellipsoidal surface abruptly changed to a pointed, cone-like geometry, and ion emission commenced from the tip.

In situ scanning electron micrographs of a liquid caesium ion source of the needle type were published by Aitken (1976); Clampitt and Jefferies (1978b). The images, with a resolution of about 1 μm, display a cusp-like protrusion of liquid caesium with an apex radius of approximately 2 μm at the tip of the needle.

From *in situ* transmission electron microscopy (TEM) observations and by means of a TV camera and video tape recording, Sudraud *et al.* (1979) and Gaubi *et al.* (1982) could estimate a radius of curvature of about 3 μm at the apex of the Taylor-Gilbert cone on a liquid gold ion source during ion emission. Therefrom, they estimated an electrostatic field strength at the ion emitting surface to be of the order of 5×10^8 V/m. However, the observed value of curvature was later assumed to be overestimated because of imaging errors due to the strong electric field at the operating ion emitting tip (Ben Assayag *et al.*, 1985).

More detailed observations were done by Wagner *et al.* (1981), who operated liquid indium ion sources in a 200 keV transmission electron microscope (TEM). The formation of a Taylor-Gilbert cone was directly observed during source operation. On the needle shank below the liquid cone, the formation of liquid droplets was observed; the droplets grew in size and left the shank. The Taylor-Gilbert cone itself remained free of droplet formation. No droplet growth and emission from the needle shank was observed until the Taylor-Gilbert cone was formed, with the associated emission of ions. Wagner *et al.* qualitatively explained the formation of the droplets by the increased field strength at the edges of the etched grooves on the tungsten tip, which is more pronounced during ion emission, when the liquid is drained from the grooves.

To avoid too large a deviation of the imaging electrons in the TEM caused by the strong electric field at

the apex of the liquid tip, it is advisable to use a high-voltage transmission electron microscope (HV-TEM). Therefore, Ben Assayag and Sudraud (1984) and Ben-Assayag *et al.* (1985), used the Toulouse 3 MeV HV-TEM for their further *in situ* observations. For a gallium LMIS, they found an oscillating regime between ellipsoidal and conical shapes around the onset voltage within a small voltage range of typically 10 volts, accompanied by ion current oscillations. For a slightly higher voltage, the cone remained stable. The micrographs demonstrate different conical shapes in the low and high current regimes. For low ion currents $\leq$ 1 μA, the apex half-angle of the liquid metal cone was near the Taylor value of 49.3°. At intermediate currents between 1 and 70 μA, the cone walls became more and more concave with increasing current, transforming into a cuspidal shape with a liquid-jet-like protrusion. At 70-80 μA, oscillations of the cone appeared until at 100 μA, the apex exploded, and ion emission spread over a large area of the cone walls.

Pure copper tips spot-welded on the apex of a tungsten hairpin filament were used by Denizart *et al.* (1991) for *in situ* observations within the 3 MeV HV-TEM in Toulouse. By electrolysis in orthophosphoric acid, copper tips with a radius of curvature at the apex of about 100 nm have been obtained. When the base of the tip was heated to a temperature around the melting temperature T_F of copper (T_F = 1356 K), a thin liquid copper film appeared. The application of a few hundred volts then induced a diffusion of the viscous liquid along the surface of the tip towards its apex where the electrostatic field had its maximum value. At the tip apex, the temperature T was smaller than at the base. The authors identified three different regimes:

(i). In the **intermediate regime** ($T \approx 0.7\ T_F$), an increasing number of protuberances were formed at the tip apex with increasing voltage.

(ii). In the **drops regime** ($T \approx 0.8\ T_F$), with increasing voltage, slow vibrations of the liquid meniscus at the tip apex appeared with a period of about 20 seconds, first between spherical and ellipsoidal shape, then (in less than 0.1 second), between ellipsoidal and conical shape, all within a range of about ten volts. Surprisingly, for a further slight increase of the voltage beyond the critical value, the cone was divided first into two "drops," then into four, and into a further increasing number of drops with the applied voltage. The drops diffused along the solid tip and exploded at the apex. This phenomenon probably has to do with an insufficient matter flow to the apex, which does not compensate for the emitted ionized matter rapidly enough. Some of these features seem to be related to the observations of Ben Assayag *et al.* (1985) with a liquid gallium source at high emission currents, as described above.

(iii). The **LMIS regime** was obtained when the temperature T at the tip apex had nearly reached the melting temperature T_F. The thickness of the liquid film was now greater and more liquid metal could reach the tip apex. For a voltage just below the critical value, again an oscillation between a spherical and an ellipsoidal shape occurred. As soon as the voltage approached the critical value, the meniscus oscillated between the ellipsoidal and the conical shape accompanied by an oscillation of the ion current. When the critical value of the voltage was reached, the oscillations stopped and a conical equilibrium configuration appeared with a half-angle of about 45°, not reaching Taylor's value of 49.3°. The radius of curvature at the cone apex was estimated to be about 2 nm.

These observations demonstrate the complexity of the dynamics occurring at the tip of an LMIS, and also the need for further *in situ* observations of the ion emitting process for different materials and configurations. An exact knowledge of these processes is also required for the understanding of the conditions for electron field emission from liquid metal sources. Therefore, one purpose of this paper is to present *in situ* images of the surface dynamics of indium liquid metal ion emitters obtained by the 1 MeV TEM (JEOL JEM HV, Tokyo, Japan) at the Max-Planck-Institut für Mikrostrukturphysik in Halle. For these *in situ* experiments, a special specimen holder has been constructed which permits the installation of the emitter with electrical connections into the object level of the HV-TEM (Fig. 1a). Tungsten tips electrolytically etched in KOH (Müller and Tsong, 1969) were used, which were bonded to a 0.2 mm tungsten hairpin heater. From the investigations by Hata *et al.* (1986), it is known that stable dc electron field emission can be obtained for emitter tip radii $\leq$ 1 μm. Therefore, tip radii of 0.5 to 2 μm have been used. As a reservoir for the liquid metal, a steel capsule is mounted around the hairpin heater. The emitter was electrolytically coated with indium. Then, small pieces of indium were placed into the reservoir and melted in high vacuum until the whole tip was wetted (Fig. 1b). A plane extraction electrode is positioned opposite the emitter with an adjustable distance of 0 to 1 mm. Both are mounted on ceramic holders, thus allowing the measurement of the extraction voltage U_{ext} between emitter and extraction electrode and the emission current I_e. The electron micrographs of the LMIS surface shape were taken at an acceleration voltage U_a = 1 MV. The *in situ* images in Figures 2, 3, 5, and 8 are taken from video films originally made to record variations with time; this explains the reduced image quality (Praprotnik, 1994; Praprotnik *et al.*, 1994a,b; Niedrig *et al.*, 1995). Corresponding investigations have also been

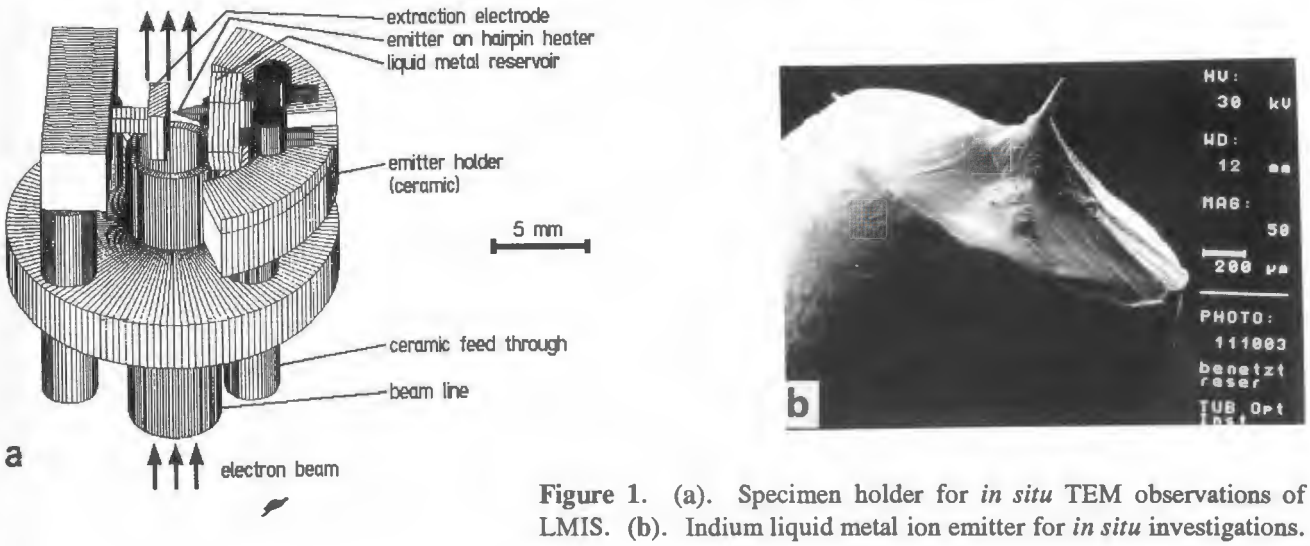

Figure 1. (a). Specimen holder for *in situ* TEM observations of LMIS. (b). Indium liquid metal ion emitter for *in situ* investigations.

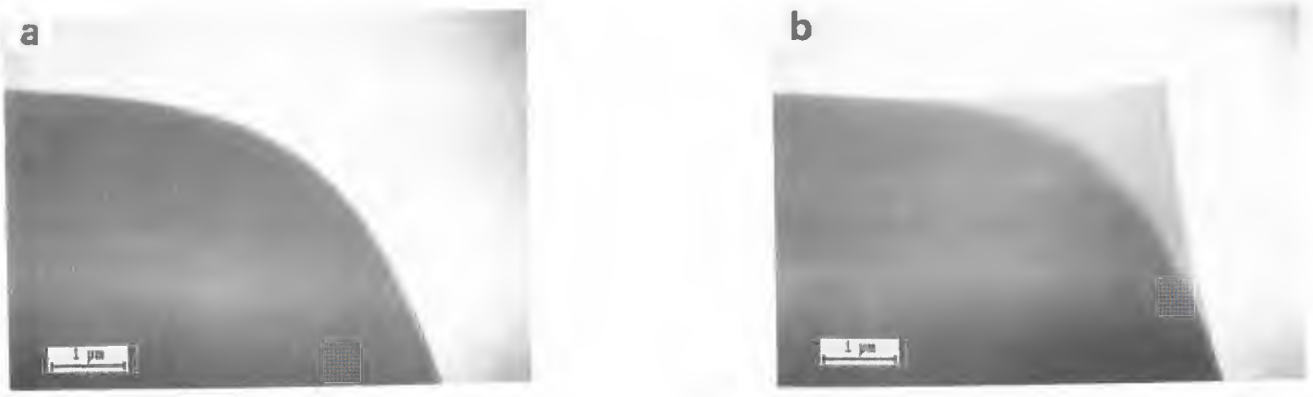

Figure 2. (a). Shape of liquid indium surface below the onset voltage for ion emission. (b). Shape of surface above the onset voltage: a Taylor-Gilbert cone has been formed.

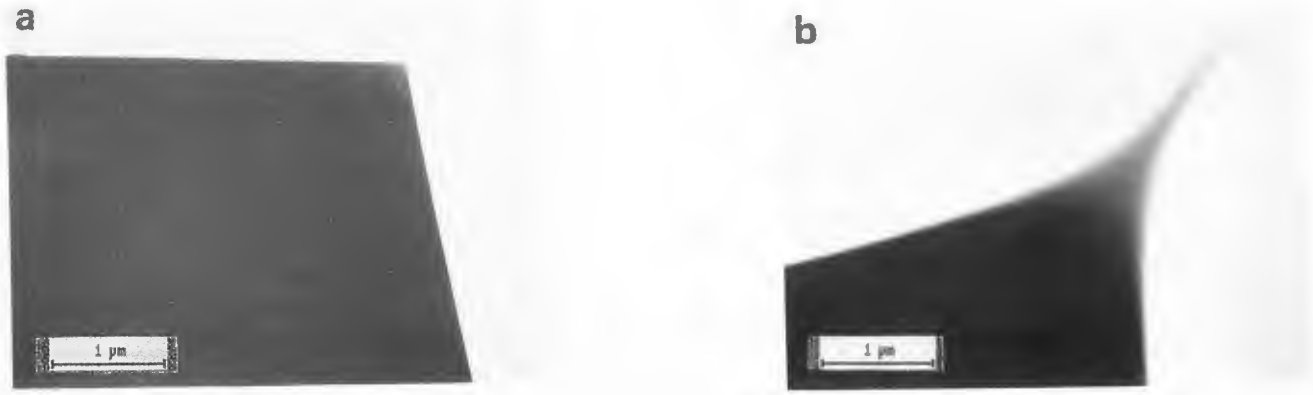

Figure 3. (a). Shape of the Taylor-Gilbert cone for an emission current of 2.8 μA. (b). Taylor-Gilbert cone for an emission current of 38.5 μA. A cusp or jet has been formed (Figures 1-3: Praprotnik, 1994).

been done with liquid gallium emitters (Driesel *et al.*, 1995b) and liquid gold-silicon alloy emitters (Driesel *et al.*, 1995a).

With increasing extraction voltage, ion emission starts at a well defined onset voltage connected with the abrupt formation of a Taylor-Gilbert cone (Fig. 2). Near the onset voltage, the cone is not stable. Within very short time intervals (below 0.02 seconds), the cone can form and vanish again, and can move on the liquid surface; even several cones can form, uniting themselves at higher voltages. However, this phenomenon appeared accidentally and not in a regular geometrical arrangement like a division of the cone into several "drops" at the tip as has been observed by Denizart *et al.* (1991) and already described above.

The cone half-angle ϑ is not exactly equal to the Taylor value of 49.3° but varies between 50.8° for an emission current I_e = 2.8 μA (Fig. 3a) and 40.4° for I_e = 38.5 μA (Fig. 3b) according to the empirical relation

$$\vartheta = \vartheta_0 - \frac{d\vartheta}{dI_e} I_e \,, \qquad (1)$$

with

$$\vartheta_0 = (51.1 \pm 0.6)°,\ d\vartheta/dI_e = (300 \pm 30) \times 10^{-3}\ °/\mu A.$$

The variation of the cone angle observed for indium is of the same order of magnitude as that calculated by Forbes and Ljepojevic (1991) for gallium. For gallium as well as for tin, however, Driesel *et al.* (1995b) and Driesel and Dietzsch (1996) obtained the variation of ϑ being smaller by a factor of about 2.

For emission currents $I_e \geq 10$ μA a cusp or jet with growing length l develops at the apex of the cone (Fig. 3b) corresponding to the empirical relation

$$l = l_0 + \frac{dl}{dI_e} I_e \,, \qquad (2)$$

with

$$l_0 = (-0.23 \pm 0.09)\ \mu m, \text{ and}$$
$$dl/dI_e = (39 \pm 4) \times 10^{-3}\ \mu m/\mu A$$

for In.

The definition of the jet length l is given in Figure 4b, showing detail I of the schematic drawing of the effects at the tip of an LMIS (Fig. 4a).

Calculations of Ptitsin and Shevchenko (1992) showed that at the observed onset voltages the electric field strength at a blunt cone (for instance, of a hyperboloid shape) without a jet extension is much less than the field strength needed for emission of ions from the LMIS surface. Also, the space charge at the emitter tip is high because of the low velocity of the ions during emission. The jet extension overcomes these hindrances and allows a stable emission because of the increased electric field strength at its apex and because of the thereby reduced space charge. A higher emission current causes an increased jet length. An analytical treatment by Mair and Forbes (1991, 1992) yields a linear dependence of the jet length l on the emission current I_e

$$l \approx \frac{2}{3\pi\gamma} \sqrt{\frac{m}{2e} U_0}\ I_e, \qquad (3)$$

where e/m is the specific charge of the emitted ions, γ is the surface tension, and U_0 is the onset voltage for the formation of the Taylor-Gilbert cone and for the ion emission. Apart from l_0 in Equation 2, there is an approximate agreement between the jet lengths calculated from Equations 2 and 3 up to emission currents of about 20 μA. Above this value, the concave shape of the "cone" and jet no longer allows an exact determination of the jet length.

The observed variation of the jet length for indium is about one order of magnitude higher than that calculated by Forbes and Ljepojevic (1991), which roughly agrees with the observed values for gallium (Driesel *et al.*, 1995b). New extended calculations by Liu and Forbes (1995) based on the modelling program developed by Forbes and Ljepojevic (1991) exhibit a surprisingly good agreement with the experimental results of Praprotnik *et al.* (1994a,b). The differences between the results for gallium and indium, for example, demonstrate that the Taylor-Gilbert cone shape strongly depends on the liquid material due to different surface tension, hydrostatic pressure, viscosity, and space charge effects.

On the liquid metal surface in the region surrounding the liquid cone, spherical microdroplets (radius 0.2 to 10 μm) appear, growing as long as ion emission occurs at the cone tip. Finally the droplets are emitted (Fig. 5). Lowering the extraction voltage, the growth of the microdroplets comes to rest when the ion emission reduces to zero, together with the vanishing of the Taylor-Gilbert cone at the onset voltage. In this case, the liquid metal flow along the shaft of the emitter needle, which evidently is a condition for the droplet growth, also comes to rest.

Vladimirov *et al.* (1992, 1995) have discussed different mechanisms for the formation of droplets: the Rayleigh instability (Rayleigh, 1879, 1882) leads to the formation of small droplets and to the fragmentation of the jet (Zeleny, 1915, 1917). This instability also causes a periodic pressure modulation in the liquid and thereby excites capillary waves in the liquid film (Faraday, 1831). Further analyses on this phenomenon have been done, for instance, by Gabovich (1983) and by Cutler,

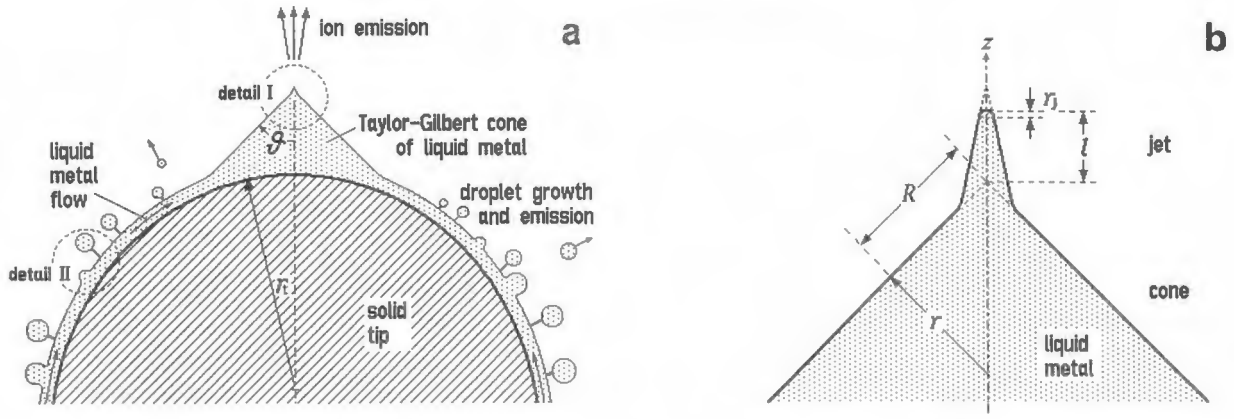

Figure 4. (a). Liquid Taylor-Gilbert cone on a solid tip and droplet emission from an LMIS. (b). Detail I of Figure 4a: definition of geometric quantities of cone and jet.

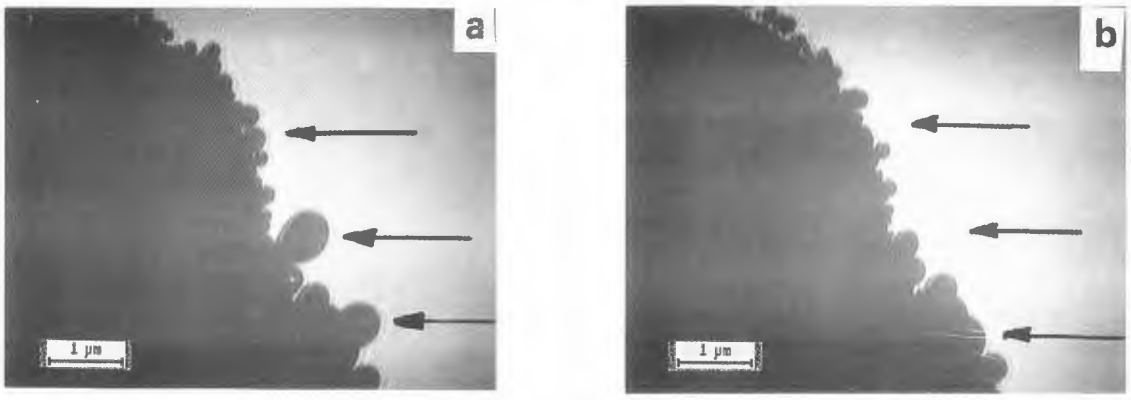

Figure 5. Microdroplet emission from the liquid metal surface surrounding the Taylor-Gilbert cone. The image on the right was taken 5 seconds after the left-hand image (Praprotnik, 1994).

Miskowsky and coworkers (Chung *et al.*, 1987; Miskovsky *et al.*, 1988). According to Vladimirov *et al.*, the Faraday instability leads to the formation of larger droplets tearing off the peaks of the capillary waves on the surface of the Taylor-Gilbert cone.

Experimentally, Vladimirov *et al.*, found small droplets in the central emission direction, and larger droplets in peripheral areas, in agreement with the discussed mechanisms. D'Cruz *et al.* (1985) claimed for gold LMIS that the emission of clusters and droplets is confined to the tip of the Taylor-Gilbert cone and that emission from the shank is negligible.

However, in our *in situ* experiments, the Taylor-Gilbert cone was always completely free of droplet formation, in agreement with the micrographs published by Wagner *et al.* (1981) and Ben Assayag *et al.* (1985). The droplet formation as shown in Figure 5 at the tip surface surrounding the Taylor cone can be understood qualitatively by regarding the equilibrium of electric stress and surface tension at the surface of the liquid

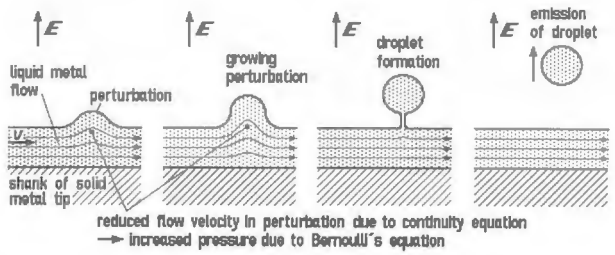

Figure 6. Detail II of Figure 4a: formation and emission of droplets from the surface of a flowing metal film under electric stress. *E*: electric field strength.

---

metal flow (Fig. 6) along the shaft of the emitter needle during ion emission (Fig. 4a: detail II). The surface of the flowing film exhibits an instability (Frenkel, 1935; Tonks, 1935; Gabovich, 1983) which arises because a small perturbation of the surface (like a small "hump") causes an increased static pressure within the liquid flow

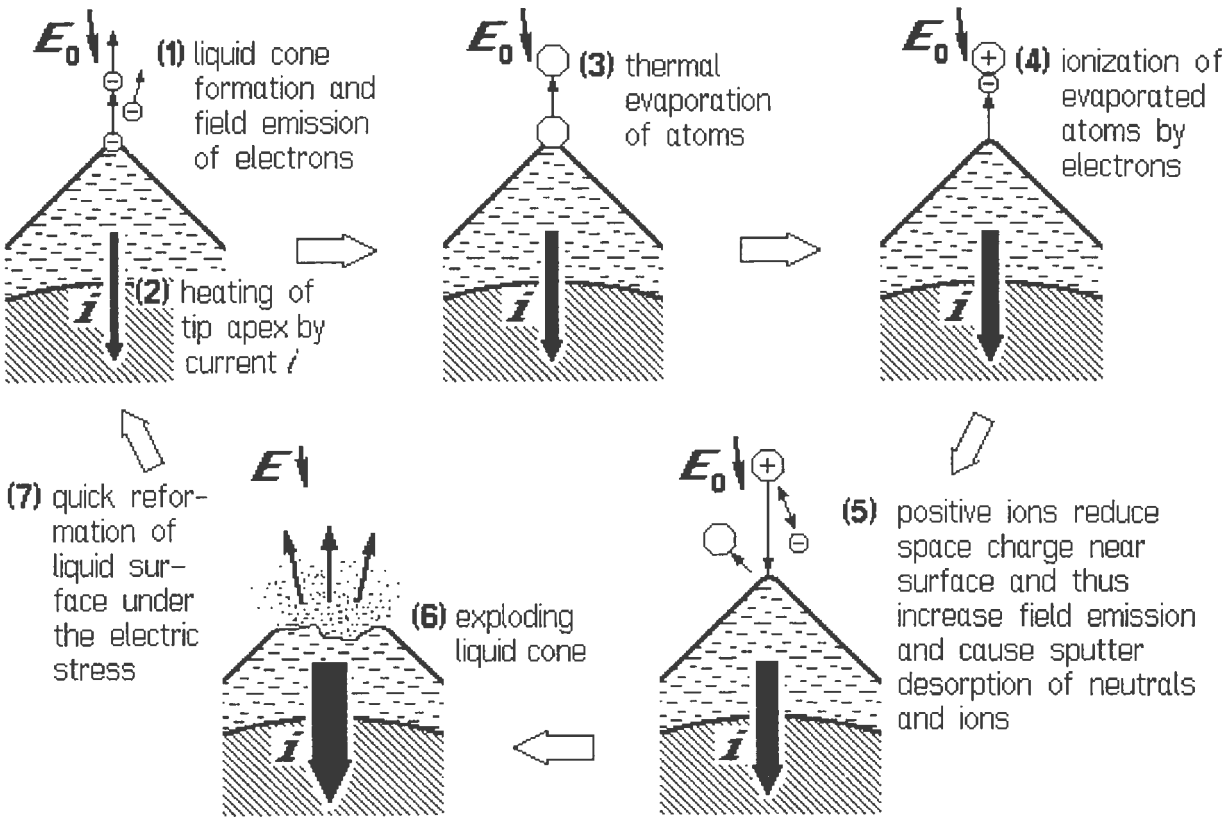

Figure 7. Model of explosive emission mode of a liquid metal electron source (LMES) after Swanson and Schwind (1978), and Gomer (1979): one period of pulsed emission. E, E_0: electric field strength.

---

at the hump, resulting in a growth of the initial perturbation (Fig. 6). This follows from the reduced flow velocity v at the increased flow cross-section at the hump due to the continuity equation, which then causes an increased static pressure due to the Bernoulli equation. The growing surface perturbation transforms into a sphere, connected to the liquid flow by a very thin filament, and finally leads to the emission of a droplet. The initial perturbations may arise by underlying perturbations of the solid needle surface, or by Faraday capillary waves excited by the Rayleigh instability at the jet extension apex, as discussed above. When the flow comes to rest, the described instability vanishes and droplet growth and emission stop.

We observed that the droplet size increases with the distance from the Taylor-Gilbert cone, which is plausible because of the decreasing field. From the micrographs published by Wagner *et al.* (1981), one can deduce a similar behaviour, which is also confirmed by recent observations at tin LMIS by Driesel and Dietzsch (1996).

Fehringer *et al.* (1994) showed for indium LMIS that redeposition of sputtered electrode material can lead

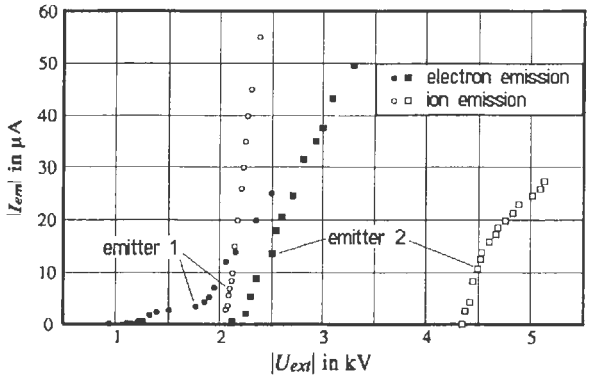

Figure 8. *I-U* characteristics of two different liquid indium emitters which can be switched from ion emission to electron emission by voltage reversal (Praprotnik, 1994).

---

to the formation of a solid surface film below the apex region, consisting of crystalline platelets, which do not move during ion emission. Corresponding observations

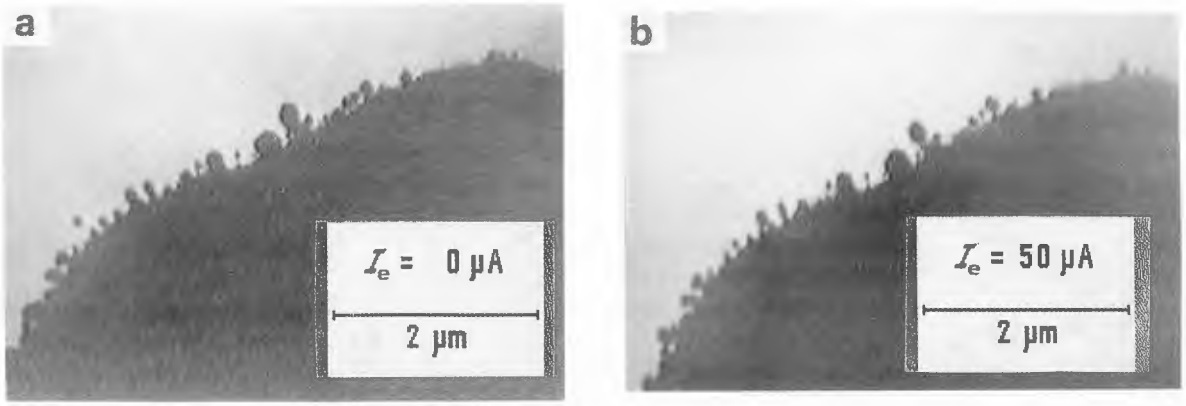

Figure 9. *In situ* TEM observation of the surface of an indium liquid emitter (Praprotnik, 1994). (a). Just below the onset voltage for electron emission: $I_e = 0$ μA. (b). In the electron emitting mode $I_e = 50$ μA.

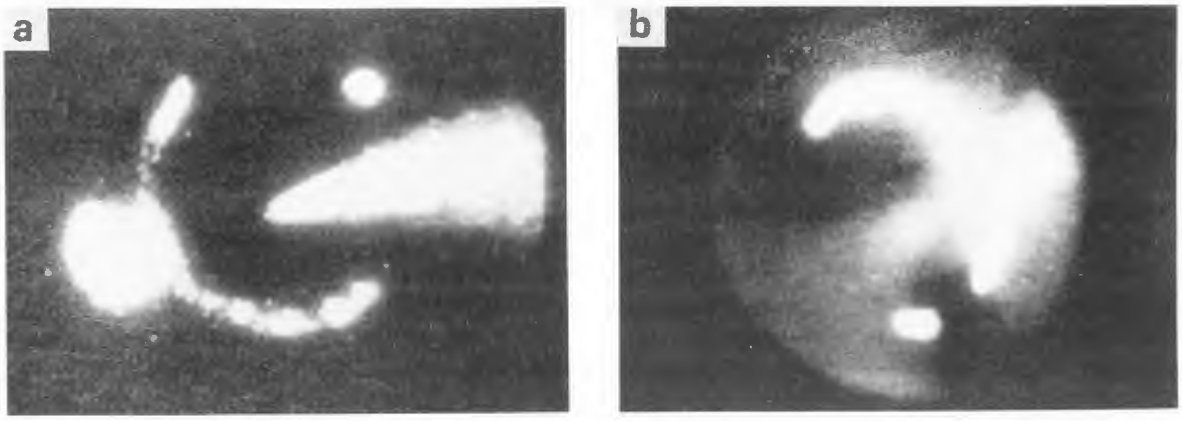

Figure 10. Electron emission patterns of two different indium liquid metal emitters, observed in an electron emission microscope (Praprotnik, 1994).

---

were made by Galovich (1988) for gallium LMIS. Under these circumstances, liquid indium is therefore flowing towards the needle apex in an annular gap between the solid contamination film on the liquid surface and the central needle.

In Situ Observations of Liquid Metal Electron Emission

At a first view, a reversal of the voltage polarity should not change the equilibrium geometry of the Taylor-Gilbert cone, if the same field strength could be applied, but it should result in electron emission from the tip, as has been pointed out in the **Introduction.** This would create an attractive field emission electron source with the capability to operate in normal high vacuum.

Pulsed electron emission was first observed by Swanson and Schwind (1978). They proposed a model (Fig. 7) where, by applying the critical Taylor voltage, a liquid cone is formed and electron tunneling occurs at its apex, causing a field emission electron current of milliamperes or even amperes. This leads to heating of the apex region, thermal evaporation of metal atoms, and their ionization by field emitted electrons within a distance of 1 to 10 nm from the cone. The resultant positive ions are attracted towards the cone where they reduce the electron space charge and thereby increase electron field emission. They furthermore cause sputter desorption of additional ions and neutrals. Finally, an explosive increase in current and destruction of the cone apex occurs within nanoseconds. The cone apex then reforms quickly under the electric stress on the liquid metal surface (Gomer, 1979), and the process repeats itself with a repetition rate of 40 to 80,000 pps (pulses per second). Swanson and Schwind have measured corresponding average currents of 4 μA to 6.5 mA.

Stable field emission of electrons was found by Hata *et al.* (1986, 1987a,b) for apex radii $r_t \leq 1$ μm of the underlying tungsten tip, whereas for $r_t \geq 10$ μm, pulsed electron emission occurred as in the experiments of Swanson and Schwind. From Fowler-Nordheim plots: $\log(I_e/U_{ext}^2)$ versus $1/U_{ext}$ (Fowler and Nordheim, 1928; Gadzuk and Plummer, 1973) Hata *et al.* (1987a,b) concluded a strong dependence on the volume of liquid metal adhered to the tungsten tip and on the distance between the tip and the extraction electrode. From experimental Fowler-Nordheim plots, Hata *et al.* (1987a) estimated the emission area ranging from 1 to 10^4 nm^2. Praprotnik (1994) obtained emission areas ranging from 0.3 to 60 nm^2. Although the calculation from such plots is not very accurate, the emission areas seem to be in both cases much smaller than the tip surface πr_t^2. This is important for the discussion about field electron emission from liquid metal tips (see below).

Figure 8 shows the I_e-U_{ext} characteristics of two different emitters, with tip radii $r_t \leq 2$ μm, in the electron emission mode (full symbols) and in the ion emission mode (open symbols). As was found also by Mitterauer (1984), Hata *et al.* (1988), and by Rao *et al.* (1989), we observed that the onset voltage for electron emission $U_{0\text{-el}}$ is considerably smaller than that for ion emission ($U_{0\text{-ion}}$). We obtain from Figure 8,

$$\frac{U_{0-ion}}{U_{0-el}} \approx 2 \qquad (4)$$

The conditions for the formation of a Taylor-Gilbert cone are therefore not fulfilled for moderate electron emission currents. Field electron emission apparently occurs already at extraction voltages where the formation of a Taylor-Gilbert cone is not yet possible. This is confirmed by Figure 9, showing a liquid metal electron emitter in situ below and above the onset voltage for electron emission. The surface shape does not change when the emission starts. Also, for higher emission currents no Taylor-Gilbert cone was observed.

Emission images of the liquid metal emitters inserted into an electron emission microscope (Schäfer, 1994) revealed that electron emission occurs simultaneously at different points of the liquid metal surface (Fig. 10), presumably because of surface roughness structures. That means that the electron emission area is much smaller than the tip surface area πr_t^2, as was already stated from the Fowler-Nordheim plots. Surface structures such as small stable droplets, which appear very similar to those observed in the ion emission mode (Fig. 5), were observed below and above the onset voltage for electron emission (Fig. 9). These droplets developed during the preparation of the liquid metal emitter, when the surface was cleaned by thermal evaporation of the surface contamination film. The emission patterns were different for different emitters. For constant emission conditions they did not vary strongly with the emission time. After discharges, however, the patterns changed. These observations agree with those of Hata *et al.* (1988) who concluded from corresponding emission patterns that a number of stable protrusions are formed at the emitter tip, which lead to field electron emission at voltages far below the onset voltage for Taylor-Gilbert cone formation and ion emission. Figure 9 reveals such protrusions.

For a liquid gallium emitter with a tip radius of r_t = 20 μm, Driesel *et al.* (1995b) found an onset voltage for electron emission roughly equal to that for ion emission leading to the assumption that in this case a liquid cone could be formed. However, for such tip radii a cone seems to be formed and destroyed within nanoseconds and with repetition rates of some 10^4 s^{-1}, as described above (Swanson and Schwind, 1978). Such short processes could not be visualized in the TEM. For gold-silicon alloy liquid metal ion emitters Driesel *et al.* (1995a) found a lack of droplet emission and a very smooth liquid surface at the beginning of the operating time. However, in the electron emission mode no formation of a stable liquid cone was observed.

Recently, for the first time, Hata *et al.* (1994) observed microcone formation for high electron emission currents of 300 μA from a liquid gallium-indium-tin alloy source in a 1 MeV high voltage TEM. The microcone had a much smaller base radius than the Taylor-Gilbert cone in the ion emission mode. Its apex half-angle was determined to about 60°, and the radius of curvature at the cone apex was estimated to be less than 10 nm. This gives an emission current density at the apex of more than 10^{11} A/m^2, comparable to the emission current density of ordinary solid field emitters. Hata *et al.* (1995, 1996), also found hints for the existence of a maximum critical value of the film thickness for the liquid cone formation, when using single-crystal tungsten tips coated with a liquid lithium film. From electron field emission patterns and from the corresponding *I-U* characteristics, it was concluded that liquid cones form on the facets of the tungsten crystal surface for lithium film thicknesses below 120 nm. For higher thicknesses, only pulsed explosive emission was observed.

Conclusions

Ion emission from liquid metal emitters has been investigated by many authors. It occurs at the apex of a liquid cone formed as the equilibrium surface by electric field forces and surface tension: Taylor-Gilbert cone. Its shape corresponds approximately to that calculated by

Taylor (the so-called Taylor cone), but varies with increasing ion emission current (formation of a jet at the apex), as shown by theoretical calculations and by *in situ* HV-TEM images for various liquid metals. Our own observations in a 1 MeV-TEM confirmed this for liquid indium. Also micro-droplet growth and emission at the shank of the emitting indium tip was demonstrated.

Reversing the voltage polarity results in electron field emission. For radii of the underlying solid tip $\geq$ 10 μm, pulsed electron emission was found (Swanson and Schwind, 1978, and others). Stable dc electron emission has been observed and investigated for emitters with tip radii $\leq$ 1-2 μm (Hata *et al.*, 1986, 1987 a,b). Our own *in situ* investigations at an indium LMES with a HV-TEM proved that the electron field emission apparently occurs at micro-roughness structures at the liquid metal surface, for voltages far below the critical voltage for Taylor-Gilbert cone formation. Emission pattern images and Fowler-Nordheim plots confirm that concept. So far, the formation of a stable Taylor-Gilbert cone in the electron emission mode has been observed only in one case (Hata *et al.*, 1994), but has not yet been explained theoretically.

Liquid metal electron emitters do not need ultra high vacuum conditions and, therefore, offer the possibility of electron field emission sources operating in the medium high vacuum of an electron microscope. Therefore, further *in situ* investigations on the tip topography during emission, on the influence of the liquid film thickness and of the material of the metallic liquid (viscosity and atomic mass) seem to be necessary. Also, the long-term behaviour of the liquid metal electron emitters has to be investigated further.

Acknowledgements

The cited experiments of my co-worker Dr. B. Praprotnik have been supported by a grant of the Deutsche Forschungsgemeinschaft. They were done in collaboration with the Max-Planck-Institut für Mikrostrukturphysik in Halle. We thank Prof. Heydenreich for the allowance to use their 1 MeV TEM and Dr. W. Driesel for the collaboration. Special thanks are due to all the reviewers for their numerous hints and comments which were extremely helpful for improving the paper.

References

Aitken KL (1976) Mechanisms of ion emission from liquid caesium. In: Field Emission Day: Proceedings of a meeting held at ESTEC, Noordwijk, on 9 April 1976 (Report No. ESA SP 119). European Space Agency, 75738 Paris 15, France. pp. 23-39.

Anazawa N, Aihara R, Okunuki M, Shimizu R (1982) Development of a gallium ion source scanning ion microscope and its applications. Scanning Electron Microsc. **1982**; IV: 1443-1451.

Bayly AR, Waugh AR, Anderson K (1983) SIMS micro-analysis with a gallium ion microprobe. Nucl. Instrum. Meth. Phys. Res. **218**: 375-382.

Ben Assayag G, Sudraud P (1984) LMIS energy broadening interpretation supported by HV-TEM observations. J. Physique, Coll. **C9** (Suppl. au No. 12, 45): 223-226.

Ben Assayag G, Sudraud P, Jouffrey B (1985) *In situ* high voltage TEM observation of an electrohydrodynamic (EHD) ion source. Ultramicroscopy **16**: 1-8.

Chung M, Cutler PH, Feuchtwang TE, Miskovsky NM (1984a) Solution of Laplace's equation for a rigid conducting cone and planar counter-electrode: Comparison with the solution to the Taylor conical model of a field emission LMIS. J. Physique, Coll. **C9** (Suppl. au No. 12, 45): 145-152.

Chung M, Cutler PH, Feuchtwang TE, Kazes E, Miskovsky NM (1984b) Use of variational equations to analyze equilibrium and stability of an electrically stressed conducting fluid: Application to a cuspidal model of an LMIS. J. Physique. Coll. **C9** (Suppl. au No. 12, 45): 153-159.

Chung M, Cutler PH, Feuchtwang TE, Miskovsky NM Sujatha, N (1984c) On the theory of the equilibrium configuration and stability of an electrically stressed conducting fluid: Application to liquid metal ion sources. Scanning Electron Microsc. **1984**; IV: 1547-1556.

Chung M, Cutler PH, Feuchtwang TE, Kazes E, Miskovsky NM (1986) An electrohydrodynamic analysis of the equilibrium shape and stability of stressed conducting fluids: Application to LMIS. J. Physique, Coll. C7, Suppl. au No. 11, 47, **C7**: 351-358.

Chung M, Miskovsky NM, Cutler PH, Feuchtwang TE, Kazes E (1987) An electrohydrostatic analysis of equilibrium shape and stability of stressed conducting fluids: Application to liquid metal ion sources. J. Vac. Sci. Technol. **B5**: 1628-1638.

Chung M, Cutler PH, He J, Miskovsky NM (1991) A first-order electrohydrodynamic treatment of the shape and instability of liquid metal ion sources. Surf. Sci. **246**: 118-124.

Clampitt R (1981) Advances in molten metal field ion sources. Nucl. Instr. Meth. **189**: 111-116.

Clampitt R, Jefferies DK (1978a) Molten metal field ion sources. Inst. Phys. Conf. Ser. **38**: 12-17.

Clampitt R, Jefferies DK (1978b) Miniature ion sources for analytical instruments. Nucl. Instr. & Meth. **149**: 739-742.

Cui Zheng, Tong Linsu (1988) A new approach to simulating the operation of liquid metal ion sources. J. Vac. Sci. Technol. **B6**: 2104-2107.

Cutler PH, Chung M, Feuchtwang TE, Kazes E (1986) The effects of gravitational and hydrostatic pressure on the equilibrium shape of a conducting fluid in an electric field. Application to liquid metal ion sources. J. Physique, Coll. C2, Suppl. au No. 3, 47, **C2**: 87-93.

Czarczynski W, Znamirowski Z (1993) Liquid metal ion sources. Vacuum **44**: 1095-1099.

Czarczynski W, Znamirowski Z (1995) X-ray examination of liquid metal ion sources. Vacuum **46**: 781-784.

D'Cruz C, Pourrezaei K, Wagner A (1985) Ion cluster emission and deposition from liquid ion sources. J. Appl. Phys. **58**: 2724-2730.

Denizart M, Hadef B, Soum G, Verdier P (1991) Copper ion field emission source. Optik **88**: 7-10.

Driesel W (1990) Ion/electron gun for a scanning Auger microscope. Beitr. Elektronenmikroskop. Direktabb. Oberfl. **23**: 327-330 (in German).

Driesel W, Dietzsch Ch, Mühle R (1995a) Tip-shape investigation of a Au-Si alloy liquid metal ion source using a high voltage transmission electron microscope. J. Phys. D Appl. Phys. **28**: 787-793.

Driesel W, Dietzsch Ch, Niedrig H, Praprotnik B (1995b) HV TEM *in situ* investigations of the tip shape of a gallium liquid-metal ion/electron emitter. Ultramicroscopy **57**: 45-58.

Driesel W, Dietzsch Ch (1996) *In situ* HVTEM observation of the tip shape of tin liquid metal ion sources. Appl. Surf. Sci. **93**: 179-190.

Dudnikov VG (1996) Review of high brightness ion sources for microlithography. Rev. Sci. Instrum. **67**: 915-920.

Faraday M (1831) On a peculiar class of acoustical figures; and on certain forms assumed by groups of particles upon vibrating elastic surfaces. Appendix: On the forms and states assumed by fluids in contact with vibrating elastic surfaces. Philos. Trans. Roy. Soc. London, 299-340.

Fehringer M, Rüdenauer FG, Sieber A, Steiger W (1994) The state of the metal film covering the needle of a liquid metal indium ion source. Vacuum **45**: 973-976.

Forbes RG, Ljepojevic NN (1989) Recent progress in LMIS theory. J. Physique, Coll. C8, Suppl. au No. 11, 50, **C8**: 3-8.

Forbes RG, Ljepojevic NN (1991) Calculation of the shape of the liquid cone in a liquid-metal ion source, Surf. Sci. **246**: 113-117.

Forbes RG, Ljepojevic NN (1992) Liquid-metal ion source theory: Electrohydrodynamics and emitter shape. Surf. Sci. **266**: 170-175.

Forbes RG, Mair GLR (1982) Arguments about emitter shape for a liquid-metal field-ion emission source. J. Phys. D Appl. Phys. **15**: L153-L158.

Forbes RG, Mair GLR, Ljepojevic NN, Liu W (1995) New understandings in the theory of liquid metal ion sources. Appl. Surf. Sci. **87/88**: 99-105.

Fowler RH, Nordheim L (1928) Electron emission in intense electric fields. Proc. Roy. Soc. London A **119**: 173-181.

Frenkel J (1935) On Tonks' theory of liquid surface rupture by a uniform electric field. Phys. Z. Sowjetunion **8**: 675-679.

Gabovich MD (1983) Liquid-metal ion emitters. Sov. Phys. Usp. **26(5)**: 447-455.

Gadzuk JW, Plummer EW (1973) Field emission energy distribution (FEED). Rev. Mod. Phys. **45**: 487-546 (see p. 498).

Galovich CS (1988) Effects of backsputtered material on gallium liquid metal ion source behaviour. J. Appl. Phys. **63**: 4811-4818.

Gaubi H, Sudraud P, Tensé M, Van de Walle J (1982) Some new results about *in situ* TEM observations of the emission region in LMIS. In: Proc. 29th Intern. Field Emission Symp. Andrén H-O, Nordén H (eds.). Almquist and Wiksell International, Stockholm, Sweden. pp. 357-362.

Gilbert W (1600) De Magnete, magneticisque corporibus, et de magno magnete tellure. (On magnets, magnetic bodies and the large magnet earth). Translated by P.F. Mottelay. Book 2, ch. 2, p. 89. Republished by Dover, New York in 1958.

Gnaser H, Rüdenauer FG (1983) Evaluation of a liquid metal ion source for secondary ion mass spectrometry. Nucl. Instr. Meth. Phys. Res. **218**: 303-306.

Gomer R (1979) On the mechanism of liquid metal electron and ion sources. Appl. Phys. **19**: 365-375.

Hata K, Nishigaki S, Watanabe M, Noda T, Tamura H, Watanabe H (1986) Field emission of electrons from a liquid alloy surface. J. Physique, Coll. C7, Suppl. au No. 11, 47, **C7**: 375-380.

Hata K, Nishigaki S, Inoue M, Noda T, Tamura H (1987a) Steady and explosion modes in electron emission from liquid metal source. J. Physique, Coll. C6, Suppl. au No. 11, 48, **C6**: 177-182.

Hata K, Ohya R, Nishigaki S, Tamura H, Noda T (1987b) Stable field emission of electrons from liquid metal. Japan. J. Appl. Phys. **26**: L896-L898.

Hata K, Nishigaki S, Inoue M, Noda T (1988) Properties of dc mode field emission of electrons from liquid lithium cathode. J. Physique, Coll. C6, Suppl. au No. 11, 49, **C6**: 125-130.

Hata K, Saito Y, Ohshita A, Takeda M, Morita C, Noda T (1994) *In situ* HV-TEM observation of the liquid cone formation process in a liquid metal field emission gun. Appl. Surf. Sci. **76/77**: 36-40.

Hata K, Kumamura M, Yasuda T, Saito Y, Oshita A (1995) An FEM study of liquid lithium on a <011>-oriented tungsten tip. Appl. Surf. Sci. **87/88**: 117-121.

Hata K, Nakayama F, Saito Y, Oshita A (1996) Control of formation sites for liquid-Li cones on a W <100> tip by means of remolding method. Appl. Surf. Sci. **94/95**: 156-160.

Hesse E, Bischoff L, Teichert J (1995) Angular distribution and energy spread of a lithium liquid metal ion source. J. Phys. D Appl. Phys. **28**: 1707-1709.

Hornsey R (1991) Simulations of the current and temperature dependence of liquid metal ion source energy distributions. Japan. J. Appl. Phys. **30**: 366-375.

Hornsey R, Ishitani T (1990a) Droplet and cluster ion emission from Ga and In liquid metal ion sources. Japan. J. Appl. Phys. **29**: 2116-2121.

Hornsey R, Ishitani T (1990b) A new droplet brake-up model for dimer ion formation from a gallium liquid metal ion source. Japan. J. Appl. Phys. **29**: L1007-L1010.

Hornsey RI, Marriott P (1989) The effects of source temperature and characteristics on the optical emission from a gallium liquid metal ion source. J. Phys. D Appl. Phys. **22**: 699-704.

Joyes P, Van de Walle J, Colliex C (1986) About the stability and structure of metallic clusters produced by a LMIS. Ultramicroscopy **20**: 65-70.

Kang NK, Swanson LW (1983) Computer simulation of liquid metal ion source optics. Appl. Phys. A **30**: 95-104.

Kingham DR (1982) The post-ionization of field evaporated ions: A theoretical explanation of multiple charge states. Surf. Sci. **116**: 273-301.

Kingham DR, Bell AE (1984) In defense of the Taylor cone model: Application to liquid metal ion sources. J. Physique, Coll. **C9** (Suppl. au No. 12, 45) 139-144.

Kingham DR, Swanson LW (1984) Shape of a liquid metal ion source. A dynamic model including fluid flow and space-charge effects. Appl. Phys. **A34**: 123-132.

Kingham DR, Swanson LW (1986) Theoretical investigation of liquid metal ion sources: Field and temperature dependence of ion emission. Appl. Phys. **A41**: 157-169.

Knapp H, Rübesame D, Niedrig H (1991) Production of needle-type liquid-metal ion sources and their application in a scanning ion microscope. Nucl. Instr. Meth. Phys. Res. **B59/60**: 131-134.

Knauer W (1981) Energy broadening in field emitted electron and ion beams. Optik **59**: 335-354.

Krohn VE (1961) Liquid metal droplets for heavy particle propulsion. In: Progress in Astronautics and Rocketry. Vol. 5. Academic Press, NY. pp. 73-80.

Krohn VE (1974) Electrohydrodynamic capillary source of ions and charged droplets. J. Appl. Phys. **45**: 1144-1146.

Kruit P, Vijgen LJ, Xinrong J (1995) Coulomb interaction in microfocussed electron and ion beams. Nucl. Instr. Meth. Phys. Res. A **363**: 220-224.

Kuk Y, Sakurai T, Culbertson RJ, Robertson JH (1980) Optical emission from gallium ionization at a field emitter. Appl. Phys. Lett. **36**: 957-959.

Levi-Setti R (1983) Secondary electron and ion imaging in scanning ion microscopy. Scanning Electron Microsc. **1983**; I: 1-22.

Levi-Setti R, Chabala JM, Wang YL (1988) Aspects of high resolution imaging with a scanning ion microprobe. Ultramicroscopy **24**: 97-114.

Levi-Setti R, Chabala JM, Li J, Gavrilov KL, Mogilevsky R, Soni KK (1993) Imaging-SIMS (secondary ion mass spectroscopy) studies of advanced materials. Scanning Microsc. **7**: 1161-1172.

Liu W, Forbes RG (1995) Modelling the link between emission current and LMIS cusp length. Appl. Surf. Sci. **87/88**: 122-126.

Ljepojevic NN, Forbes RG (1992) A comparison of the numerical and analytical treatments of a liquid-metal ion source. Surf. Sci. **266**: 176-179.

Ljepojevic NN, Forbes RG (1995) Variational thermodynamic derivation of the formula for pressure difference across a charged conducting liquid surface and its relation to the thermodynamics of electrical capacitance. Proc. Roy. Soc. London A **450**: 177-192.

Mackenzie RAD, Smith GDW (1990) Focused ion beam technology: A bibliography. Nanotechnology **1**: 163-201.

Mahoney JF, Yahiku AY, Daley HL, Moore RD, Perel J (1969) Electrohydrodynamic ion source. J. Appl. Phys. **40**: 5101-5106.

Mair GLR (1984a) Theoretical determination of current-voltage curves for liquid metal ion sources. J. Phys. D Appl. Phys. **17**: 2323-2330.

Mair GLR (1984b) An analytical expression for the current-voltage characteristics of capillary type liquid metal ion sources. J. Physique, Coll. **C9** (Suppl. au No. 12, 45): 173-177.

Mair GLR (1994) Advances in liquid metal ion sources modelling: The analytical approach. Nucl. Instr. Meth. Phys. Res. **B88**: 435-440.

Mair GLR, Forbes RG (1991) Analytical determination of the dimensions and evolution with current of the ion-emitting jet in liquid-metal ion sources. J. Phys. D Appl. Phys. **24**: 2217-2221.

Mair GLR, Forbes RG (1992) An analytical calculation of LMIS cusp length. Surf. Sci. **266**: 180-184.

Mair GLR, Forbes RG, Latham RV, Mulvey T (1983) Energy spread measurements on a liquid metal ion source. In: Microcircuit Engineering. Vol. 83. Academic Press, London. pp. 171-178.

Mair GLR, Mulvey T (1984a) Fundamentals of liq-

uid metal ion sources: Experiment, theory and applications. Scanning Electron Microsc. **1984**; IV: 1531-1540.

Mair GLR, Mulvey T (1984b) High brightness sources for electron and ion beam microscopy and micro-lithography. Ultramicroscopy **15**: 255-260.

Mair GLR, Mulvey T (1985a) Liquid metal sources in ion microscopy and secondary ion mass spectrometry. Scanning Electron Microsc. **1985**; III: 959-971.

Mair GLR, Mulvey T (1985b) Ion beam lithography. Microelectr. Eng. **3**: 133-146.

Mair GLR, Mulvey T (1986) Some aspects of liquid metal ion sources. J. Microsc. **142**: 191-200.

Mair GLR, Mulvey T, Forbes RG (1984) Energy spreads in field evaporation and liquid-metal ion sources. J. Physique, Coll. **C9** (Suppl. au No. 12, 45): 179-182.

Mayer HP (1985) Energy spread of ions from Ga liquid metal ion sources at low emission currents. Appl. Phys. Lett. **47**: 1247-1248.

Melngailis J (1987) Focused ion beam technology and applications. J. Vac. Sci. Technol. **B5**: 469-495.

Miskovsky NM, Chung M, Cutler PH, Feuchtwang TE, Kazes E (1988) An electrohydrodynamic formalism for ion and droplet formation in stressed conducting fluids. J. Vac. Sci. Technol. **A6**: 2992-2997.

Miskovsky NM, He J, Cutler PH, Chung M (1989) A hydrodynamical study of the instability of a planar liquid metal ion source (Summary). J. Physique, Coll. C8, Suppl. au No. 11, 50, **C8**: 175-177.

Miskovsky SN, Miskovsky NM, Cutler PH (1994) Calculated *I-V* characteristics of a gold liquid metal ion source for a prototype emitter modeled as a cone-sphere. J. Vac. Sci. Technol. **B12(2)**: 737-744.

Mitterauer J (1984) Field emission and field ionization in a liquid metal cesium field-effect source. J. Physique, Coll. **C9** (Suppl. au No. 12, 45): 185-190.

Müller E, Tsong TT (1969) Field Ion Microscopy: Principles and Applications. Elsevier, NY. Chapter on Tip Fabrication.

Niedrig H, Driesel W, Praprotnik B (1995) Electron field emission from indium liquid metal emitters. Beitr. Elektronenmikroskop. Direktabb. Oberfl. (BEDO) **28**: 103-108.

Orloff J (1984) The effect of extraction voltage and beam voltage of a liquid metal ion source focused beam system on the current density in a focused spot. Scanning Electron Microsc. **1984**; IV: 1541-1546.

Orloff J (1991) Mikrotechnik mit Ionenstrahlen (Micro-technology with ion beams). Spektr. Wissensch. 138-144 (in German).

Orloff J, Swanson LW (1979) A study of some electrostatic gun lenses for field emission. Scanning Electron Microsc **1979**; I: 39-44.

Papadopoulos S, Barr D, Brown WL, Wagner A (1984) The energy spread of ions from gold liquid metal ion sources as a function of source parameters. J. Physique, Coll. **C9** (Suppl. au No. 12, 45): 217-222.

Praprotnik B (1994) Emissionsverhalten von Flüssigmetall-Ionen-/-Elektronen-Emittern (Emission behaviour of Liquid Metal Ion/Electron Emitters). Verlag, Dr. Köster, Berlin. ISBN 3-89574-070-5. pp. 46-84 (in German).

Praprotnik B, Driesel W, Dietzsch Ch, Niedrig H (1994a) HV-TEM *in situ* investigations of the surface shape and emission behaviour of liquid metal ion sources. Proc. ICEM 13 (Paris), Vol. 1. pp. 797-798.

Praprotnik B, Driesel W, Dietzsch Ch, Niedrig H (1994b) HV-TEM *in situ* investigations of the tip shape of indium liquid metal ion emitter. Surf. Sci. **314**: 353-364.

Prewett PD, Mair GLR (1991) Focused Ion Beams from Liquid Metal Ion Sources. Wiley, NY. pp. 1-148.

Prewett PD, Mair GLR, Thompson SP (1982) Some comments on the mechanism of ion emission from liquid metal ion sources. J. Phys. D **15**: 1339-1348.

Ptitsin VE (1993) Model of the mechanism of liquid metal ion source emission. Rev. Sci. Instr. **65**: 1354.

Ptitsin VE, Shevchenko SI (1992) On the mechanism of the LMIS emission. Surf. Sci. **266**: 191-196.

Rao KA, Bell AE, Schwind GA, Swanson LW (1989) A combination electron/ion field emission source. J. Vac. Sci. Technol. B **7**: 1793-1797.

(Lord) Rayleigh (1879) On the capillary phenomena of jets. Proc. Roy. Soc. **29**: 71-97.

(Lord) Rayleigh (1882) On the equilibrium of liquid conducting masses charged with electricity. Phil. Mag. (Ser. 5) **14**: 184-186.

Rüdenauer FG, Steiger W, Studnicka H, Pollinger P (1987) Mass and energy spectra of a capillary-type indium liquid-metal ion source. Int. J. Mass Spectrom. Ion Proc. **77**: 63-74.

Sawaragi H, Mimura R, Kasahara H, Aihara R, Thompson W, Hassel Shearer M (1990) Performance of a combined focused ion and electron beam system. J. Vac. Sci. Technol. **B8**: 1848-1852.

Schäfer B (1994) Die Pulslaser-induzierte thermische Elektronenemission als intensive Quelle und oberflächensensitive Sonde in der zeitauflösenden Elektronenmikroskopie (Pulse-laser induced thermal electron emission as an intensive source and surface-sensitive probe in time-resolved electron microscopy). Ph. D. thesis, Technische Universität Berlin, D 83. (in German).

Sternberg M, Niedrig H, Bicer Y (1988) Surface imaging with a scanning focused Sn-ion beam. EUREM 88. Inst. Phys. (Bristol, U.K.) Conf. Ser. No. 93; Vol. I, Chapter 5. pp. 267-268.

Sudraud P, Colliex C, van de Walle J (1979) Energy distribution of EHD emitted gold ions. J. Physique

Lettres **40**: L207-L211.

Swanson LW (1983) Liquid metal ion sources: Mechanism and applications. Nucl. Instr. Meth. Phys. Res. **218**: 347-353.

Swanson LW (1994) Use of the liquid metal ion source for focused beam applications. Appl. Surf. Sci. **76/77**: 80-88.

Swanson LW, Bell AE (1989) Liquid metal ion sources. In: The Physics and Technology of Ion Sources. Brown IG. (ed.). Wiley, NY. pp. 313-330.

Swanson L W, Kingham DR (1986) On the mechanism of liquid metal ion sources. Appl. Phys. A **41**: 223-232.

Swanson LW, Schwind GA (1978) Electron emission from a liquid metal. J. Appl. Phys. **49**: 5655-5662.

Swanson LW, Schwind GA, Bell AE (1979a) Emission characteristics of a liquid gallium ion source. Scanning Electron Microsc. **1979**; I: 45-51.

Swanson LW, Schwind GA, Bell AE, Brady JE (1979b) Emission characteristics of gallium and bismuth liquid metal field ion sources. J. Vac. Sci. Technol. **16**: 1864-1867.

Swanson LW, Schwind GA, Bell AE (1980) Measurement of the energy distribution of a gallium liquid metal ion source. J. Appl. Phys. **51**: 3453-3455.

Swatik DS, Hendricks CD (1968) Production of ions by electrohydrodynamic spraying techniques. AIAAJ **6**: 1596-1597.

Taylor GI (1964) Disintegration of water drops in an electric field. Proc. Roy. Soc. London A **280**: 383-397.

Tonks L (1935) A theory of liquid surface rupture by a uniform electric field. Phys. Rev. **48**: 562-568.

Venkatesan T, Wagner A, Barr D (1981) Optical emission: A probe of neutral atoms in liquid metal ion sources. Appl. Phys. Lett. **38**: 943-945.

Vladimirov VV, Badran VE, Gorshkov VN (1992) Microdroplet emission and instabilities in liquid-metal ion sources, Surf. Sci. **266**: 185-190.

Vladimirov VV, Gorshkov VN, Mozyrsky DV (1995) The dynamical effects in liquid-metal ion sources. Appl. Surf. Sci. **87/88**: 112-116.

Wagner A, Hall TM (1979) Liquid gold ion source. J. Vac. Sci. Technol. **16**: 1871-1874.

Wagner A, Venkatesan T, Petroff PM, Barr D (1981) Droplet emission in liquid metal ion sources. J. Vac. Sci. Technol. **19**: 1186-1189.

Ward JW, Seliger RL (1981) Trajectory calculations of the extraction region of a liquid-metal ion source. J. Vac. Sci. Technol. **19**: 1082-1086.

Zeleny J (1915) On the conditions of instability of electrified drops, with applications to the electrical discharge from liquid points. Proc. Cambr. Phil. Soc. **18**: 71-83.

Zeleny J (1917) Instability of electrified liquid surfaces. Phys. Rev. **10**: 1-6.

Note added in proof: Recently an excellent review paper on the theory of liquid-metal ion source operation has been published by Forbes: Forbes RG (1997) Understanding how the liquid-metal ion source works. Vacuum **48**: 85-97.

Discussion with Reviewers

T. Mulvey: You say that liquid metal electron emitters do not need ultra-high vacuum conditions. This is also true of any field emitter if stability of source position and intensity is not important. How would you arrange the design for a liquid metal field electron emitter in the absence of a Taylor cone?

Author: There are two special advantages of liquid metal field electron sources: **i.** The bombardment of ions from the residual gas in normal high vacuum destroys a solid tip very quickly by sputtering. This is not the case for a liquid emitter because its shape is only determined by the equilibrium between the applied electric field strength and the surface tension of the liquid surface. However, this is only true as long as the surface remains clean. Continuous ion bombardment can cause some contamination or oxide on the liquid surface {see also, Galovich (1988) and Fehringer *et al.* (1994)}. **ii.** The other advantage is the possibility of changing from electron to ion emission simply by reversing the voltage polarity, without replacing the gun. This makes it an interesting analytical tool. A liquid metal electron field emitter in absence of a Taylor-Gilbert cone should be a needle-type one with small radius of the solid core tip.

R.G. Forbes: The story of how the "blunt needle" type of ion source was discovered may be of interest. In the early days of the needle-type ion source, "sharp" needles (with a radius somewhat less than 1 μm) were used. The blunt-needle source (with a radius of 2 to 3 μm or more) came into being at the UK Atomic Energy Authority Culham Laboratories, when an undergraduate student on industrial placement (Miss S. Ventnakesh) turned the tip voltage up too high, blew the end off the emitter, and reported that she had broken her ion source.

On checking, her supervisor (Dr. R. Clampitt), discovered that the emission current from the "broken" source was many times greater than from the original source. Since then, the conventional thinking has been as follows: ion emission from a sharp needle is from a liquid film. But on the blunt needle, a Taylor-Gilbert cone can form, and it is this that is responsible for the greatly enhanced ion emission. This hypothesis has never been challenged to my knowledge, but it raises

unanswered questions; so it is not entirely clear to me that conventional thinking about the sharp-needle source is necessarily correct.

Your results seem to show that you can get stable dc electron emission from a "sharp needle," but that you cannot normally get stable dc electron emission from a "blunt needle" (presumably because an unstable Taylor-Gilbert cone forms).

Could it be said that your results confirm that for negative polarity as well as for positive polarity, for some reason that we do not clearly understand, it is difficult for Taylor-Gilbert cones to form on small radius needles?

Author: For sharp needles with tip radii $\leq 1\ \mu m$, we have not yet enough *in situ* observations to confirm your assumption. I assume that in the case of ion emission, even for sharp needles, a Taylor-Gibert cone forms. But for needles with tip radii $\leq 2\mu m$ in the electron emission mode, the dc field emission starts at voltages well below the critical voltage for Taylor-Gilbert cone formation, and the current increases exponentially with the voltage, so that the critical voltage for cone formation could either not be reached (as you have pointed out in the following comment), or results in the periodic explosive emission mode. The field emission certainly is supported by surface protrusions due to contamination or surface roughness of the underlying solid tip. More experiments should be done with very clean liquid metal surfaces and different tip radii.

R.G. Forbes: There seems to be an assumption behind some of the work on liquid-metal field electron emission, and I would like to comment on it. This assumption is that stable, negatively-charged, Taylor-Gilbert cone-like shapes exist in principle, even though it is difficult or impossible to realize stable cones in practice.

It is not obvious to me that current theoretical thinking allows a stable negatively-charged liquid cone to exist, even in principle. N. N. Ljepojevic and I have recently shown how to derive the formula for pressure difference across a charged liquid surface from the laws of thermodynamics (Ljepojevic and Forbes, 1995). An implication of that work is that Taylor's solution is a very special form of thermodynamic equilibrium: if Taylor's constraints do not apply (they never do in a real situation) then there may be no guarantee (for a particular applied voltage) that any stable static equilibrium shape exists. This result applies to both polarities of applied voltage.

The liquid-metal (positive) ion source does, however, exhibit short-term stability. Currently, my thinking is that this is associated with the flow of material through a cusp-like shape to the emitter apex, here the metal atoms are field evaporated as positive ions. With the polarity reversed, one might perhaps expect short-term stability if negative ions could be formed at the emitter apex. But the reality is that electron emission occurs at lower field strength than negative ion emission, and electron emission will induce destabilizing effects, as the author describes. Therefore, my theoretical expectation is that a negative-polarity Taylor-Gilbert cone would be intrinsically unstable. The surprise to me is that Hata *et al.* (1994) have been able to observe an electron-emitting microcone, albeit in slightly untypical geometrical circumstances. The interesting questions are why has their microcone formed, and why is it stable. Would you agree?

Author: Completely. We have to do more experiments to find out the reasons for the existence of the unexpected microcones in electron field emission as found by Hata *et al.* at high currents. Perhaps the simultaneous electron emission from an impurity protuberance close to the microcone, as shown in the images of Hata *et al.* has some stabilizing influence.

G. Ben Assayag: The voltage necessary to observe electron emission from a liquid metal source is often lower than the threshold voltage for the Taylor cone formation. This suggests that the emission sites are different for electrons and ions.

Do you think that in this case, the electron emission mechanism is specific to liquid metal emitters or is a regular field emission for some solid micro or nano-tips present on the shank of the electrochemically sharpened tungsten needle?

Author: I think your last assumption (regular field emission from solid micro or nano-tips) could well be true.

G. Ben Assayag: The HV-TEM image is a two-dimensional projection of a three-dimensional structure (the tungsten tip), so, in spite of the observation of microdroplet on Figure 9a and b, the electron emission can occur from an area invisible to the electron microscope. Do you believe it is fully impossible for the electron beam to be emitted from a site invisible to the TEM observed area?

Author: This cannot be excluded from our images. In the case of positive ion emission, we observed cones which moved normally to the image plane, thus partially or fully vanishing behind or in front of the imaged rim of the liquid metal.

However, if in the situation of Figure 9a and b, the electron emission occurred from an invisible cone, it could be that also negative ion emission takes place. Then I would expect the droplets, to be seen in Figure 9b, to grow with time due to the liquid flow combined with ion emission. This we did not observe.

B. Jouffrey: In Figure 8, what was different in emitters 1 and 2?
Author: The emitters could not be prepared identically. So, there are differences in the tip radii and in the distances between tip and extraction electrode causing different onset voltages.

B. Jouffrey: [On droplet formation] I agree with Rayleigh instabilities. The formation of droplets has been also clearly observed in the case of copper {Jouffrey B (1985) *In Situ* Experiments with High Voltage Experiments. Fujita H (ed.). Osaka University, Japan. p. 365}. The size of the droplets varies as $1/E^2$ roughly.
Author: Thank you for this information. Your finding agrees with our observation that with decreasing field (with increasing distance from the Taylor cone), the droplet size increases.

B. Jouffrey: On Figure 5, the formation of droplets is clear. You state their size increases with the distance from the Taylor cone. But it depends, from your micrographs, on the position on the liquid surface. Related to the curvature of the interface between the liquid and the close atmosphere, it seems to appear that droplets are larger where the liquid does present a concave curvature (the electric field is smaller). In addition, droplets do evaporate or explode preferentially where the field is higher.
Author: Your interpretation is correct. The mean size of the droplets increases with the distance from the Taylor-Gilbert cone. This general tendency was observed in the TEM and was documented in video sequences. Equivalent results have recently been obtained by Driesel and Dietzsch (1996). Figure 5 only demonstrates local variations of the droplet size due to the varying electric field corresponding to the local surface curvature as you described it correctly. At high fields, the droplets are emitted before they can grow to large size.

B. Jouffrey: Do you observe a movement of droplets from low to high field areas? It is clear that the electric field is perpendicular to the surface, and therefore has a rather local complicated behaviour. If the droplets do evaporate perpendicular to the surface, it means there is no flow towards the tip of the substrate.
Author: The time for the emission (or explosion) of the droplets is much shorter than the time between subsequent video images, and therefore the flight of the droplets could not be seen. A movement of the droplets during the growth at the surface has not been observed, possibly due to some contamination or oxide on the surface of the flowing metal, similar to the findings of Galovich (1988) and Fehringer *et al.* (1994).

B. Jouffrey: What is the nature, the shape of the solid substrate? Is it rough?
Author: Yes, it is rough tungsten with etch grooves along the axial direction.

B. Jouffrey: We observed in some experiments we carried out with P. Sudraud and B. Hadef, in 1984, on a Cu substrate, the formation of droplets, the size of them being roughly inversely proportional to the square of the applied voltage (we did not calculate the exact local field close to the tip). The droplets formed far from the tip and rolled towards the apex where they exploded. It seems that this behaviour was related to a very high viscosity of the small copper layer which was formed on the copper substrate heated at about 950°C. Did you change the applied voltage, and did you observe a similar effect on the formation of droplets? Were droplets exploding close to their area of formation?
Author: In our case, where we had liquid indium or gallium on a tungsten substrate (and not copper just at the melting temperature on a solid copper substrate), no lateral movement of the droplets occurred. The droplets were emitted or exploded at the site of their growth.

B. Jouffrey: We recently observed with B. Veleva, in STM at room temperature, an effect which can be related to this field influence, even if they are not at the same scale. In studying the effect of a tip on atomic steps of gold evaporated films, we observed the formation of a pseudoperiodic array of one atomic thick layer, moving under the electric field created along the scanning path of the tip close to the atomic steps. Experiments were carried out in the atmosphere. The first atomic layer is extremely mobile, and the considerations on the electrostatic pressure and the surface tension are similar to the ones of the LMIS. There is no droplet formation, but a wavy system (festoon) under the influence of the electric field.
Author: Thank you for your comment.

B. Jouffrey: The reason of the drops as has been published by Denizart *et al.* (1991), has to be sought, it seems to me, in the role of viscosity.
Author: Yes, I agree. Denizart *et al.* (1991) assumed that this phenomenon has to do with an insufficient matter flow to the cone apex which does not compensate the emitted ionized matter rapidly enough. Viscosity is certainly one of the decisive parameters determining this effect.