THE APPLICATION OF LIOUVILLE'S THEOREM IN MASS SPECTROMETRY (*)

A. J. H. BOERBOOM

FOM — Instituut voor Atoom — en Molecuulfysica, Kruislaan 407, Amsterdam/Wgm. The Netherlands

M. F. LARANJEIRA

Laboratório de Física da Universidade de Luanda, LUANDA — Angola

SUMMARY — In an introduction Liouville's theorem is elucidated. In Part I the validity of Liouville's theorem is shown in four examples: field free space, uniform electric field, electrostatic lens and uniform magnetic field. The theory is applied on a mass spectrometer and the definition is given of «emittance».

In Part II, entry and exit pupils are defined, as well as the concept of «acceptance». Two ion optical devices are discussed in which application is made of the foregoing theory.

INTRODUCTION

Liouville [1] introduced in mechanics the concept of «phase space». This is a six-dimensional space: three coordinates give the three position coordinates of a particle, the other three coordinates represent the three components of the momentum. A certain point in phase space thus gives the position and the velocity of the particle, but these six quantities precisely deter-

(*) Received 11 June 1973.

mine the orbit of this particle in a known field of force. Each point of this orbit, together with the local velocity, reversely determines a point in phase space. This means that if one point in phase space is given, the complete orbit in real space is determined as well as the corresponding orbit in phase space.

Each individual particle out of a beam of particles will, at a certain moment, correspond with a point in phase space, and to the complete beam corresponds a cloud of points in phase space.

The propagation of the beam in real space corresponds with a change in position and shape of this cloud in phase space. Liouville's theorem now states that the point density everywehre in this cloud remains constant under this change.

This theorem is valid if the forces acting on the particle can be deduced from a Hamiltonian. If the forces change with time there still exists a Hamiltonian, if the forces are conservative, so if the total work done on the particle only depends on the initial and final positions of the particle.

I — ION BEAMS AND LIOUVILLE'S THEOREM

Often the coordinate frame can be chosen in such a way, that the displacements in the x, y, and z-directions become mutually independent. In such a case the six-dimensional phase space can be decomposed into three two-dimensional sub-spaces: (x, p_x), (y, p_y), and (z, p_z) in each of which Liouville's theorem holds.

As a first example we treat a collimator, i. e. a combination of two aligned diaphragms, constructed with the intention of limiting the divergence of a beam. First we assume the diameters of both orifices to be equal (see fig. 1). We may consider the four rays 1-4 as the outermost ones, that still can pass through the collimator. At the positions A-D we draw the two-dimensional phase-diagram (r, p_r). The points representing the rays 1 and 3 remain fixed, as the corresponding rays proceed at constant distances from the main axis and do not change direction in the field free space. The points 2 and 4 move parallel to the r-axis in phase space; their direction r' is constant, but the distance r changes. It is evident however that the area of the parallelogram

1 2 3 4 is constant through this transformation. This holds for any area, enclosed by a curve that has been laid on a number of phase points, so around every point of the phase figure the local density is constant.

After having passed the second diaphragm the beam diverges and this corresponds with a phase figure becoming more and more extended and narrow, but the area occupied by the parallelogram remains constant to the local density.

Now we want to limit this divergence of the beam by a lens and we choose its strength in such a way, that the uttermost rays 2 and 4 just become parallel, the other rays then are made converging.

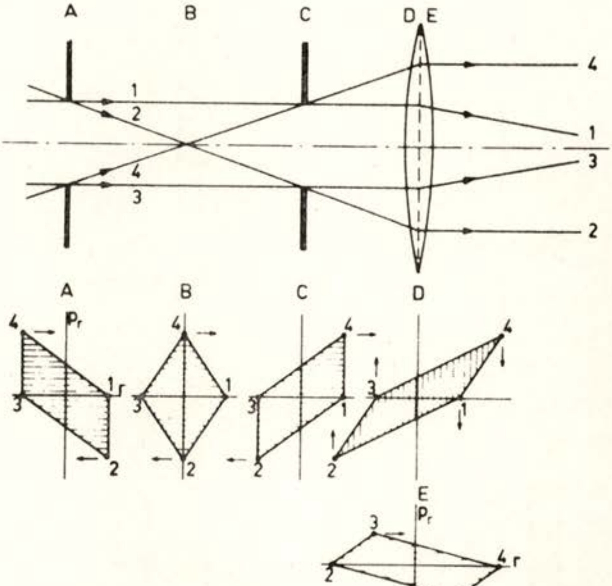

Fig. 1 — Propagation of an ion beam through a collimator and a lens, with cross sections through phase space.

When we apply the «thin lens» approximation, the orbits of the particles experience a bend on passing the lens plane, so r remains constant and r' changes. In the phase diagram all points move parallel to the p_r-axis. The points 2 and 4 arrive at the r-axis ($r' = 0$). The positions of 1 and 3 can be calculated with the well-known lens formulae, but if we apply Liouville's theorem the new positions of 1 and 3 follow from the constancy of the enclosed area.

Comparing fig. 1E and 1D we observe that the parallelogram experienced a rotation, though with some deformation. Now after the lens the same process begins: 2 and 4 on the r-axis remain fixed, the other points move again parallel to the r-axis and after some time the phase-figure becomes again a long-shaped and narrow parallelogram. By continuously applying lenses the beam can be kept limited but it is impossible to create a really parallel beam.

Two diaphragms with different diameters are shown in fig. 2. We have taken the case that the first diaphragm is smaller than

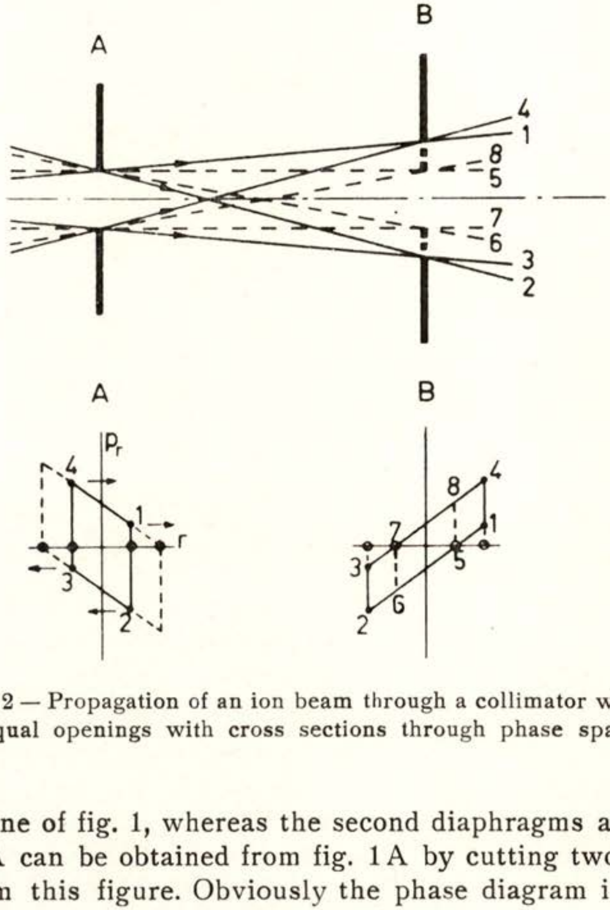

Fig. 2 — Propagation of an ion beam through a collimator with unequal openings with cross sections through phase space.

the first one of fig. 1, whereas the second diaphragms are equal. So fig. 2A can be obtained from fig. 1A by cutting two vertical slices from this figure. Obviously the phase diagram is again a parallelogram with moving sides (see fig. 2).

Both sets of parallel sides pass through fixed points on the r-axis, the four vertexes of the parallelogram move along lines parallel to the r-axis.

A so-called «point-source» emitting in a certain solid angle is the limiting case: an infinitely narrow parallelogram through the origin, extending in the p_r-direction from some $p_{r,\max}$ through $p_{r,\min}$ (see fig. 3).

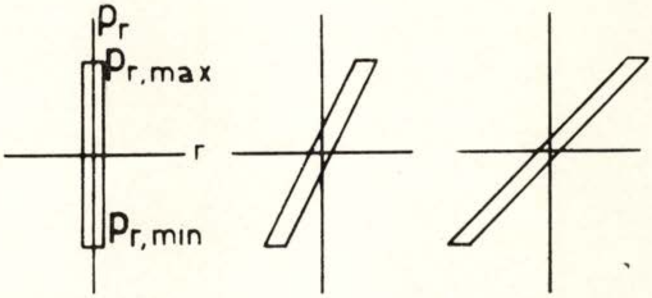

Fig. 3 — Cross sections through phase space for a point source.

If we also decrease the second diaphragm in fig. 2 (dotted lines) we have collimated the beam of fig. 1. In the phase diagram this corresponds with cutting two vertical slices from the parallelogram in fig. 2 B. We now have obtained in phase space a parallelogram smaller than in fig. 1 but similar, in real space a less diverging beam, of considerably smaller intensity. Later on in this paper we will discuss a collimating system (fig. 11) where the same decrease in divergence has been obtained, but with less loss in intensity.

As a second example we take propagation of ions in a uniform electric field along the z-axis. The orbits then are parabolas

$$\begin{cases} r = r_0 + p_r t/m \\ z = z_0 + p_z(o)\, t/m + (e\,\mathrm{E}/2\,m)\, t^2 \end{cases} \qquad \begin{cases} p_r(t) = p_r(o) = p_r \\ p_z(t) = p_z(o) + e\,\mathrm{E}\, t . \end{cases}$$

In the (r, p_r)-subspace the same happens as in the first example: a shifting parallelogram: two vertexes are fixed on the r-axis and the other ones move parallel with the r-axis.

In the (z, p_z)-subspace the four vertexes of the phase diagram move along congruent parabolas

$$z - z_0 = (p_z^2 - p_z(o)^2)/(2\,e\,\mathrm{E}\,m) .$$

As can be seen from fig. 4, for a certain value of t and constant z we have $p_{max} - p_{min} = (p_{max} - p_{min})_{t=0} = \Delta p_{z,0}$ as well as for constant p_z we have

$$z_{max} - z_{min} = \Delta z ,$$

the phase diagram remains a parallelogram with a constant base and a constant height, so with a constant area.

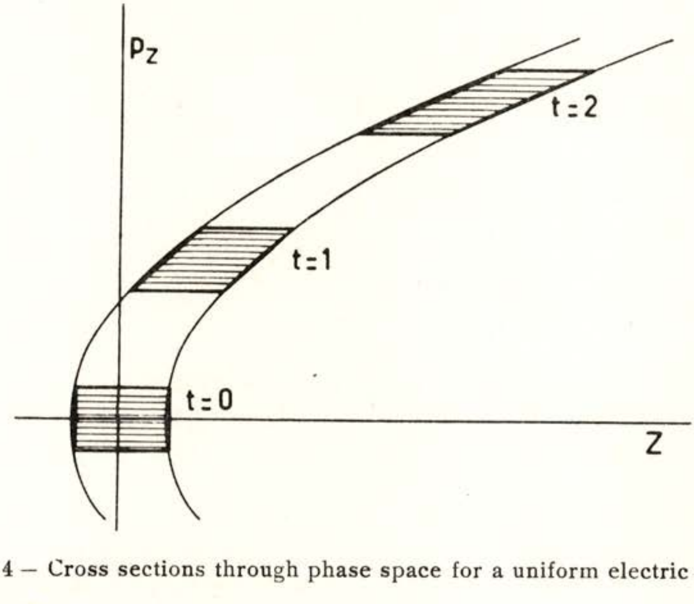

Fig. 4 — Cross sections through phase space for a uniform electric field.

So both in the (r, p_r)- as well as in the (z, p_z)-subspaces the phase areas are constant.

Now frequently we are less interested in the position and momentum of the ion, but more in the ion orbit, i. e. the position and direction. This direction is given through the angle between the orbit and the main axis: $\alpha_r = \arctan p_r/p_z$. Now p_r is a constant, whereas p_z continuously increases, so in the (r, α_r)-diagram the area decreases, viz. with the square root of the energy of the particles.

So, by accelerating the ions, the product $\Delta r \times \Delta \alpha_r$ decreases and this is in general application in ion-optical apparatuses.

In the case an image is produced, the foregoing theory can be somewhat more concretized (fig. 5).

We call $l_2\ l_1 = M_l$ = the linear magnification,
and $\alpha_2/\alpha_1 = M_\alpha$ = the angular magnification.

Assuming the energy of the particles to be respectively eV_1 and eV_2 we can state that

$$M_l\, M_\alpha \sqrt{V_2/V_1} = 1 \quad \text{or} \quad l_1\, \alpha_1 \sqrt{V_1} = l_2\, \alpha_2 \sqrt{V_2}.$$

This is Lagrange's law.

As the next example we take an accelerating lens, consisting of two colinear tubes at different potentials V_1 and V_2 (with

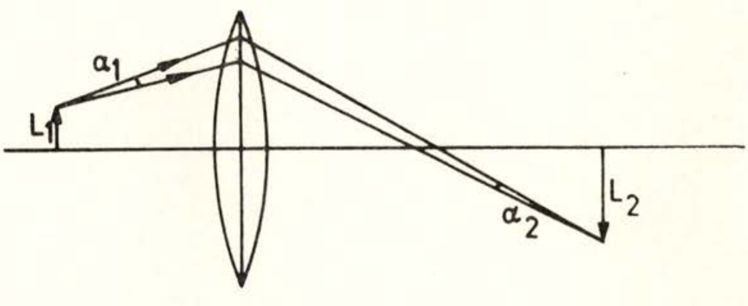

Fig. 5 — Lagrange's law.

respect to the ion source). We chose $V_2 = 5\,V_1$ and constructed the ion orbits [2].

0 is the object emitting ions over a certain length and into a certain solid angle. Nine orbits $1 \cdots 9$ have been drawn, I being the image.

In the lower part of fig. 6 the shape of the beam is given in the (r, α_r)-space at several positions along the main orbit. At the site 0 the area occupied in phase space is a rectangle, if we assume that all points of the object emit into the same solid angle. In the field free space this rectangle transforms into a parallelogram, as is shown at the site of the first focus F_1 and the first principal plane H_1. The area of the parallelogram remains constant, as shown before.

Between the first and the second principal planes the acceleration takes place, at least in the Gaussian description of the ion orbits; in reality the acceleration happens gradually between both tubes.

After this acceleration the area in the (r, α_r)-space has decreased with a factor $\sqrt{V_2/V_1}$. From the second principal plane the area remains constant again.

The area in the (r, α_r)-space multiplied by $\sqrt{V}$ and divided by a conventional factor of π is called the «*normalized emittance*». This quantity is an invariant of the beam. The factor π has been introduced, because in beam physics the phase figure is often an ellips.

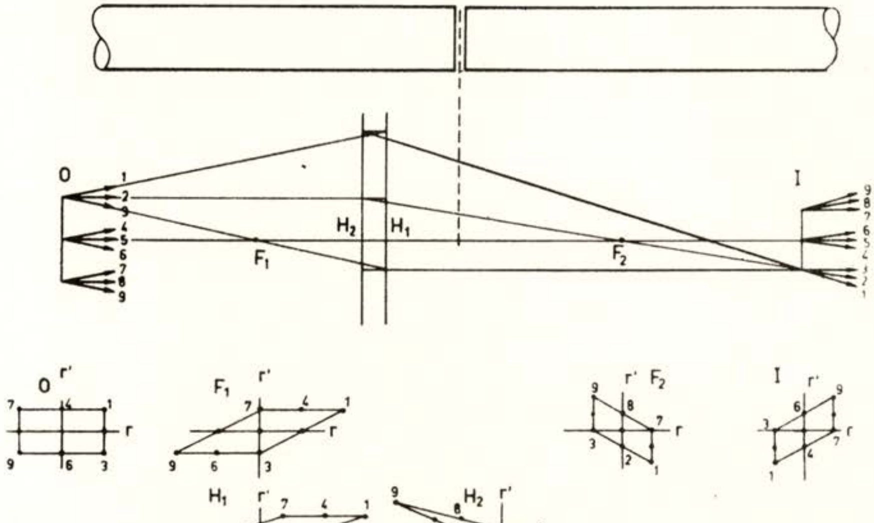

Fig. 6 — Image formation and cross sections through phase space for a two tube lens.

Our last example is the 180° uniform magnetic field. The ion orbits in this field can in first order very well be represented by

$$(1) \qquad \text{so} \qquad \begin{cases} r = R_0 + A\cos\Theta + B\sin\Theta \\ r' = \quad - A\sin\Theta + B\cos\Theta . \end{cases}$$

In the plane $\Theta = 0$ we have

$$\begin{cases} r(o) = R_0 + A & -s/2 \leq A \leq s/2 \\ r'(o) = \quad B & -\alpha \leq B \leq \alpha \end{cases}$$

where R_0 = radius of the main orbit,
s = slit width,
α = half opening angle.

So, for $\Theta = 0$, the phase diagram is a rectangle. But the equations (1) represent a pure rotation of this rectangle and obviously the area is constant. See fig. 7.

We make an application of the foregoing theory on a mass spectrometer, though any other ion-optical apparatus will do as well.

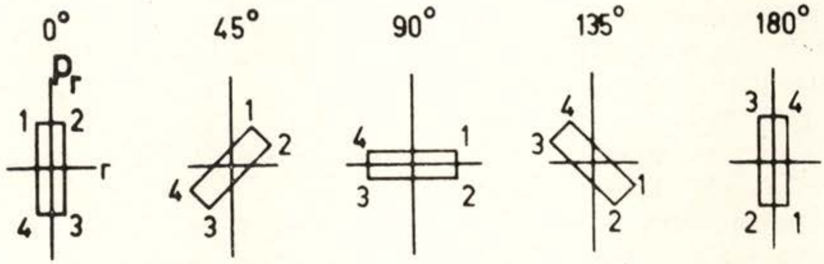

Fig. 7 — Cross sections through phase space for a uniform magnetic field.

In the ionization chamber ions are produced by an electron beam of a certain size. Parent ions have very small initial energies, i. e. $0.1\,eV$ at most, as at the ionization process no kinetic energy is transferred. The momentum vector of these ions can be pointed into any direction. The size of the electron beam and the velocity distribution of the molecules when being ionized determine the emittance of the beam of parent ions.

A repeller electrode or an extraction field causes the ions to move towards the exit slit of the ionization chamber.

Supposing for example that the electron beam width is 1 mm and that the ions have a kinetic energy of $5\,eV$ when leaving the ionization chamber, we have simply

$$1\,\text{mm} \times 180^\circ \times \sqrt{0.1} = b \times \alpha \times \sqrt{5} \quad \text{so} \quad b \times \alpha = 25\,\text{mm}^\circ,$$

where b is a beam width and α an opening angle.

If the exit slit is, for example, 1 mm, then this result means, that the ions will leave the ionization chamber with an opening angle of 25°, if one succeeds in applying the right field shape. If now one narrows the slit width to $\frac{1}{2}$ mm, then the opening angle does not automatically become 50°, but half of the ions will be lost, unless one adapts the field shape.

After having left the ionization chamber, the ions experience the main acceleration, for example through 2 kV. The product of the slit width and opening angle then becomes $\sqrt{2000/5} = 20$ times smaller, so that with 0.1 mm slit width the entry angle into the analyzing magnetic field becomes $12\frac{1}{2}^{\circ}$, provided the right fields are applied.

This all concerned the parent ions, having small initial kinetic energies. If the ionization process leads to a dissociation of the ion, fragment ions can appear sometimes with appreciable kinetic energies, up to some eV. This means that one has to apply wider slits, otherwise these ions will be lost.

In the ion source of a mass spectrometer mostly slit lenses are applied. These lenses do not have a focal action in the slit direction. Because of the relatively large acceleration over a relatively small distance, there is almost no increase in beam height, so in our case the final opening angle in the slit direction will be about 180°: $\sqrt{2000/0.1} \approx 1\frac{1}{4}^{\circ}$ for parent ions and considerably more for fragment ions.

In the accelerating field of the ion source all ions gain almost equal amounts of energy, so they will have almost the same Hamiltonian and the orbits will not differ much. In the magnetic field, however, a momentum-depending term enters in the Hamiltonian and the orbits of ions of different mass will deviate. In fig. 8 the (r, p_r)-diagram is drawn for ions of two different momenta, passing through a 180° uniform magnetic field. In the source plane, $\theta = 0$. Both phase diagrams partly coincide, though the ions with the larger mass extend over a large area. The phase diagram of the main mass m_1 rotates around the point $r = R_0$, $p_r = 0$, whereas the centre of rotation for the mass m_2 moves. In the r-direction the displacement is given by

$$\frac{R_1 - R_2}{R_1} = \frac{\sqrt{m_1} - \sqrt{m_2}}{\sqrt{m_1}} (1 - \cos \theta)$$

and in the p_r-direction by

$$\frac{p_{r,1} - p_{r,2}}{p_{r,1}} = \frac{\sqrt{m_1} - \sqrt{m_1}}{\sqrt{m_1}} \sin \theta .$$

In the circumstances (slit width and relative mass difference) of fig. 8 a separation of both masses in phase space occurs already before $\theta = 135^\circ$, though both ion beams in real space still overlap. At the first order focus, $\theta = 180^\circ$, the best separation is obtained (*).

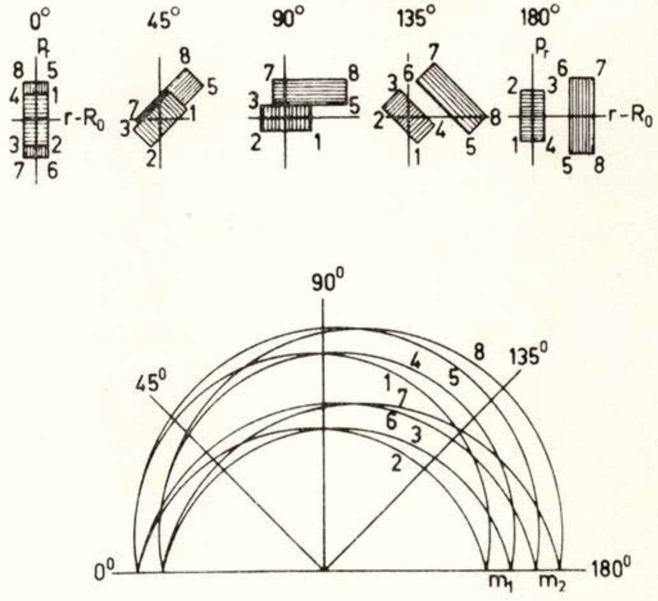

Fig. 8 — The separation of ions of two different momenta in a 180° uniform magnetic field and in phase space.

Liouville's theorem gives the best obtainable condition: the minimum slit width and, in connection with this, the maximum obtainable resolution without loss of particles. But the theorem can also be applied in the reversed sense: just as well as it is not possible to use narrower slits, it is not necessary to apply wider slits. And here a contradiction seems to exist with practice, when at the detector side of the mass spectrometer image aberrations appear. It is a wellknown custom in mass spectrometry to have the exit slit of the analyser tube somewhat wider than the entry slit in order to avoid loss of ions.

(*) See insert, page 260.

The explanation is the occurrence of non-linear effects, causing a distorsion of the volume element in phase space. Indeed the volume remains constant, but it looses its rectangular or parallelogram shape, so it fits only in a larger parallelogram.

Let us take for example the 180° uniform magnetic field; then ions entering the field under an angle α will have a first order focus at 180° (eq. 1), but in second approximation an aberration term $- R_1 \alpha^2$ has to be added.

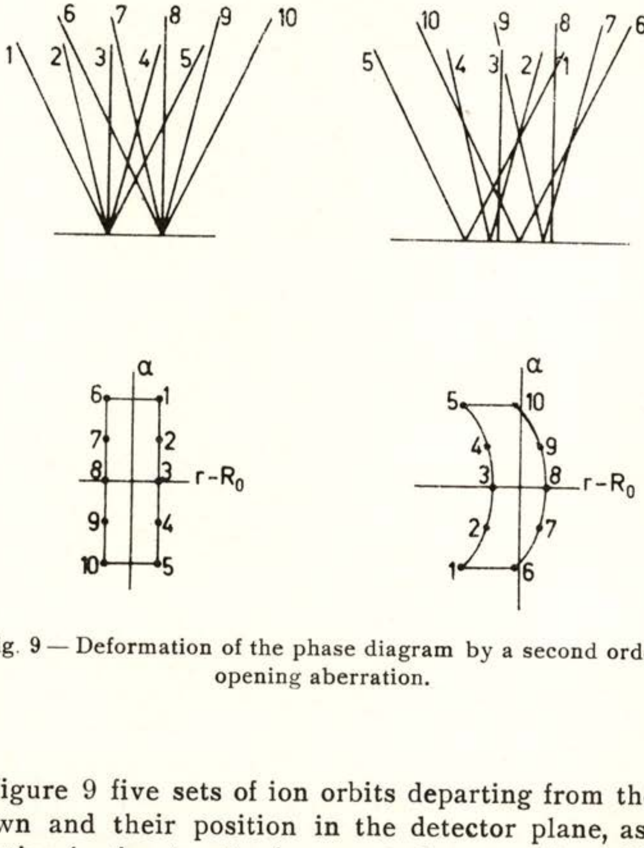

Fig. 9 — Deformation of the phase diagram by a second order opening aberration.

In figure 9 five sets of ion orbits departing from the source are shown and their position in the detector plane, as well as the situation in the (r, α_r)-subspace at the same sites. Obviously the area again remains constant, but a broader exit slit is necessary. It is the task of ion-optics to shape such fields, that these non-linear effects are minimized.

II. ION-OPTICAL APPARATUSES AND LIOUVILLE'S THEOREM

Another concept that we take from light optics are *entry* and *exit pupils*. We will use also the language of optics.

We consider an object that is imaged by an optical system, consisting of several lenses (see fig. 10). In this system the beam

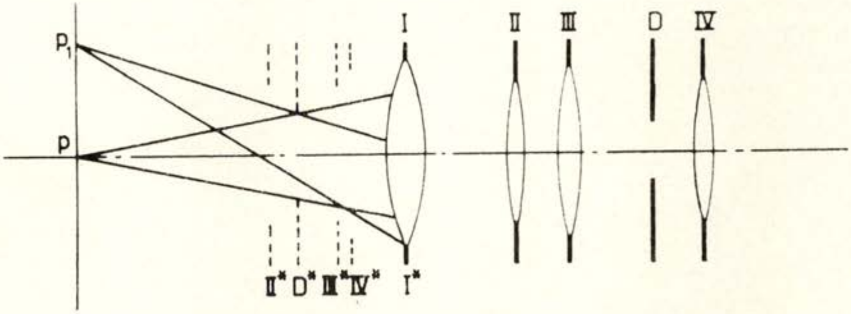

Fig. 10 — Definition of the entry pupil.

will encounter various openings, which will act as diaphragms: in the first place intentionally placed diaphragms; but every lens is bounded and this limitation acts as a diaphragm. Furthermore the beam can be intercepted by too narrow tubes or by other obstacles.

Each of these diaphragms we image by the interjacent lenses backward towards the object space and forward to the image space, as shown in fig. 10. In this way we get a number of virtual diaphragms.

Looking from a certain point P in object space, one of these diaphragms will be the smallest one. This one is called the *entry pupil*: every ion that can pass this virtual diaphragm, will pass the whole system; all ions outside the opening of this diaphragm, will be intercepted somewhere in the lens system.

In the same way at the image side, for the image P′ of P one of the diaphragms will be the smallest. This is the *exit pupil*. Obviously the exit pupil is the image of the entry pupil.

We defined the entry and exit pupils with respect to the points P and P′. Other points can have other pupils. So for P_1 in fig. 10 the pupil is much smaller than for P.

Position and size of the virtual diaphragm will depend on the index of refraction of the lens. For ions this means that they will depend on the energy and the momentum of the ion. In designing a mass spectramoter one should endeavour to make the pupils equal for all ions to avoid the so-called «mass discrimination».

An example shows how to work with pupils (see fig. 11).

Lenses A and B have equal strength, the second focus of lens A coinciding with the first focus of lens B. Diaphragm I is situated in the first focal plane of A and diaphragm II at the side of the second focus.

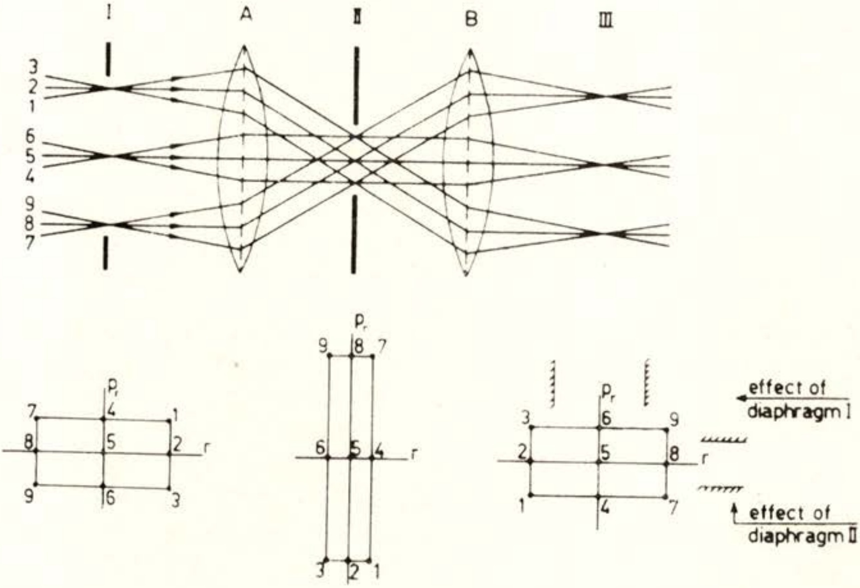

Fig. 11 — Collimating and diaphragm lens.

The phase diagram (r, p_r) is drawn for positions I, II and III, together with some rays. Apparently diaphragm I controlls the cross section of the beam at the side III, with constant divergence, whereas diaphragm II reversely controlls the divergence with constant diameter.

A system like this is much more effective than the usual collimator, consisting of two diaphragms at a certain mutual distance as discussed above (fig. 2).

In the former case on reducing the diaphragms indeed the divergence decreases, but also rays with low divergence are intercepted. Bannenberg and Boerboom [3] published and apparatus in which the above method has been applied with quadrupole lenses, so independently in two mutually perpendicular directions. Another interesting system is given in fig. 12.

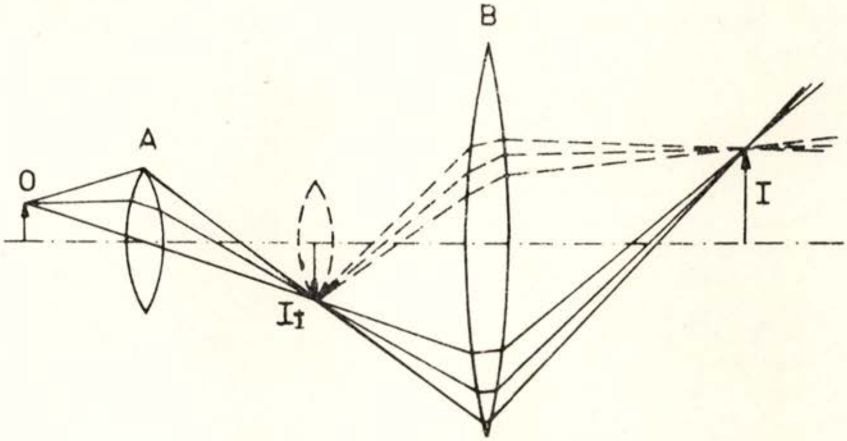

Fig. 12 — Principle of the field lens.

Object 0 is imaged by lens A onto an intermediate image I_1 and this image is re-imaged by lens B onto the final image I_2. In the situation as given in the figure lens B should be very large if we don't want to lose intensity, i. e. if we want to keep the limitation of A as the entry pupil.

Now we put an extra lens at the side of the intermediate image, in the figure indicated by dotted lines. Now a lens refracts the rays, so all rays will be broken at I_1. But I_1 is imaged onto I, what means that all rays from I_1 are focussed in I, independent of their direction. The intermediate lens therefore does change neither the position nor the magnification of the final image. It only changes the position of the pupils, so that the rays proceed closer to the main axis. In light optics this intermediate lens is called the «field lens».

In a double focusing mass spectrometer the second lens B is the magnetic analyser. A magnet with a large pole gape is expensive. It can be worthwhile to consider the application of an intermediate lens. Bannenberg and Boerboom [3] also apply this principle in a 200 kW accelerator.

Entry and exit pupils are in close connection with the «acceptance» of the apparatus. The acceptance is defined as the normalized volume of that part of phase space for which the corresponding ions can be transmitted through the apparatus. It is the complementary concept of emittance.

On designing an instrument the acceptance of the apparatus ought to be equal or larger than the emittance of the beams to be transported.

REFERENCES

[1] LIOUVILLE, *Journ. de Math.* **3**, 349 (1838).

[2] See f. e. K. R. SPANGENBERG, Vacuum Tubes, McGraw-Hill, New York, London, 1948.

[3] J. G. BANNENBERG and A. J. H. BOERBOOM, *Nucl. Instr. Meth.* **91**, 269 (1971).

[4] H. MATSUDA, S. FUKUMOTO and T. MATSUO, Recent developments in Mass Spectroscopy, Ed. K. Ogata and T. Hayakawa, University of Tokyo Press, 1970.

ACKNOWLEDGEMENTS

The discussions with Dr. J. G. Bannenberg are gratefully acknowledged. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).

INSERT

As soon as in phase space the diagrams of the ions of different momentum are separated, they can be separated in real space too without further need of a magnetic field. When both phase figures have turned more than 90° a field free drift space suffices; if the separation has occurred before this 90° rotation, an electrostatic (or magnetic) lens is necessary for an additional rotation of the phase figures. So we can distinguish two functions of the magnet: the magnetic field as such separates according to momentum of the ion, and by appropriate shaping (sector angle and oblique entry or exit) it also acts as a (quadrupole) lens. Matsuda c. s. [4] have described two double focusing instruments in which they take advantage of this possibility to make use of both actions independently.