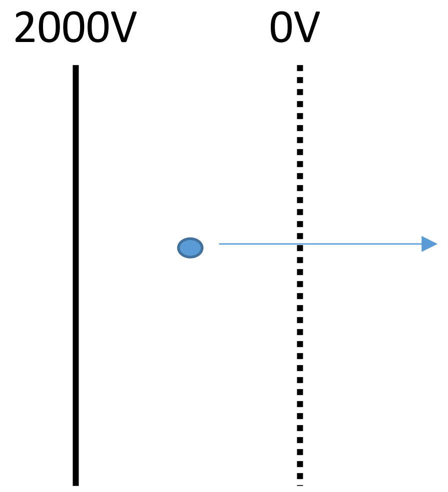
# Time-of-flight mass spectrometer (TOF)

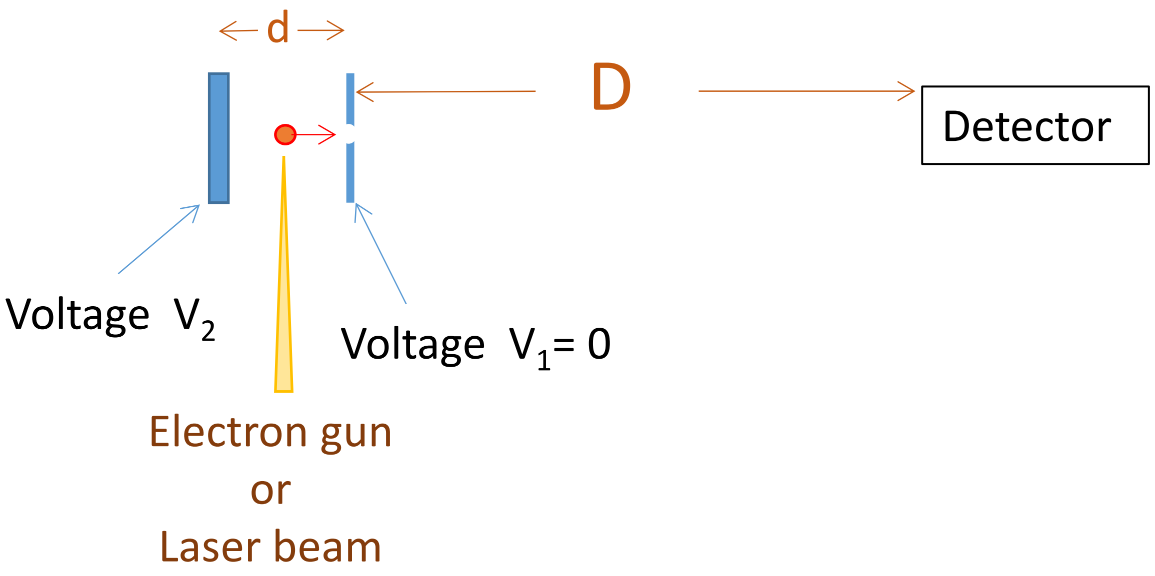
# Velocity gained from electric field

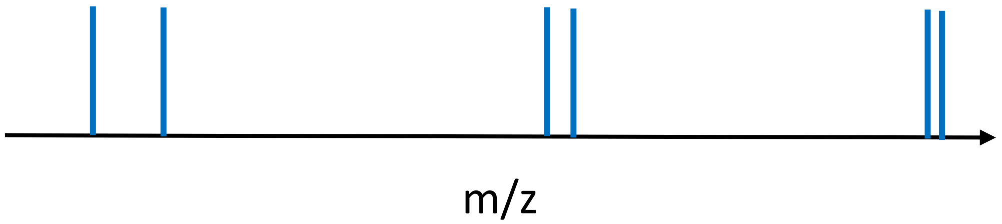
$E = 0.5mV^2$

$1000 eV \times 1.6 \times 10^{-12}$ erg/eV$= 0.5 \times [100/(6 \times 10^{23})] \times V^2$

$V = 4.4 \times 10^6$ cm/s






**Time to arrive detector**

$T = t_1 + t_2$

$0.5xd = V_0 t_1 + 0.5x(F/m)x(t_1)^2$

$d = [qx\hat{E}/m]x(t_1)^2$ (assume $V_0 = 0$)

$t_1 = \mathrm{sqrt}[dxm/(qx\hat{E})]$

$t_2 = D/V$

$V = V_0 + at_1$

$= qx\hat{E}/mxt_1$

$= \mathrm{sqrt}[(qx\hat{E})/m]$

$t_2 = Dx\mathrm{sqrt}[m/(qx\hat{E})]$

Arrival time: T = t1+ t2 ~ sqrt(m)

# Example 1

d = 2 cm = 0.02 m
D = 1 m
V1 = 2000 V

For m=100 Da

$t1 = \text{sqrt}[0.02 \times 100 \times 10^{-3}/(6.02 \times 10^{23} \times 1.6 \times 10^{-19} \times 2000)]$
$= \text{sqrt}(10^{-9}) = 3.162 \times 10^{-5}$ s

$t2 = 1 \times \text{sqrt}[100 \times 10^{-3}/(6.02 \times 10^{23} \times 1.6 \times 10^{-19} \times 2000)]$
$= \text{sqrt}(5 \times 10^{-8}) = 2.236 \times 10^{-4}$ s

T = 255.22 μs

For m=101 Da
$t1 = 3.178 \times 10^{-5}$ s
$t2 = 2.247 \times 10^{-4}$ s
T = 256.48 μs
$\Delta T$ = 1.26 μs

For m= 900 Da
$t1 = 9.486 \times 10^{-5}$ s
$t2 = 6.708 \times 10^{-4}$ s
T = 765.66 μs

Scan from m=0-900 Da takes 765 μs

For m= 901 Da
$t1 = 9.492 \times 10^{-5}$ s
$t2 = 6.712 \times 10^{-4}$ s
T = 7656.12 μs

$\Delta T$ = 0.5 μs

**Example 2**

d = 2 cm = 0.02 m
D = 2 m
V1 = 2000 V

For m=100 Da and m=101 Da

$\Delta T$ = 1.26 x sqrt(2) $\mu$s = 1.78 $\mu$s

# Time-of-flight mass spectrometer (TOF)

- No mass range (High mass range is limited by detector (detector has small response to slow particles)
- High sensitivity: most ions generated by ionization arrive detector
- Fast scan
- Easy construction

## Distance deviated by magnetic field

$S = V_0t + 0.5at^2$

$= 0.5F/m(D/v)^2$

$= 0.5qvB/m(D/v)^2$

$= 0.5qBD^2/(mv)$

$= 0.5qBD^2/\mathrm{sqrt}(2Em)$ where E is the kinetic energy

For large mass, the deviation is small.

Magnetic field has larger effect on electrons than ions

## Effect of earth magnetic field

For an single charged ion, $q = 1.6 \times 10^{-19}$ C

Assume $m = 100 \times 10^{-3}/(6 \times 10^{23})$ kg, kinetic energy = 100 eV

$100 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV} = 0.5 \times 100 \times 10^{-3} \text{kg}/(6.02 \times 10^{23}) \times v^2$

$v = 13000$ m/s

Earth magnetic field: $20\text{-}60 \times 10^{-6}$ tesla

$F = 1.6 \times 10^{-19} \text{ C} \times 13000 \text{ m/s} \times 50 \times 10^{-6} \text{ tesla} = 1.04 \times 10^{-19}$ N

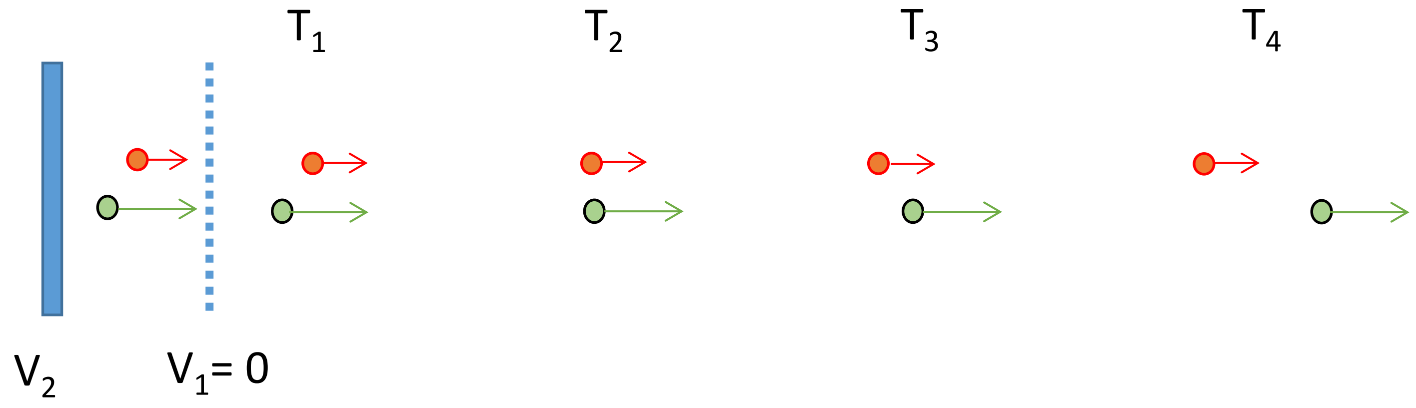
Flight distance 1 m, time $t = 1/13000 = 7.7 \times 10^{-5}$ s

$S = V_0 \times t + 0.5 \times a \times t^2$

$= 0.5 \times 1.04 \times 10^{-19} \text{ N}/[100 \times 10^{-3}/(6 \times 10^{23})] \times (7.7 \times 10^{-5})^2$

$= 1.8 \times 10^{-3}$ m

# Effects of different initial positions



# Wiley-Maclaren ToFMS

THE REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 26, NUMBER 12 DECEMBER, 1955

## Time-of-Flight Mass Spectrometer with Improved Resolution

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A new type of ion gun is described which greatly improves the resolution of a nonmagnetic time-of-flight mass spectrometer. The focusing action of this gun is discussed and analyzed mathematically. The validity of the analysis and the practicability of the gun are demonstrated by the spectra obtained. The spectrometer is capable of measuring the relative abundance of adjacent masses well beyond 100 amu.

### INTRODUCTION

THIS paper describes the improved mass resolution made possible by a new ion gun in a nonmagnetic, time-of-flight (TOF) mass spectrometer. Although the properties of this gun may make it useful for focusing electrically accelerated ion beams in other applications, the discussion will be restricted to mass spectrometers which have been tested.

Following a brief description of TOF spectrometers, their resolution is discussed. The new ion gun is then described and its focusing action is analyzed mathematically. Experimental results substantiating the general theoretical conclusions are presented. Finally, a

they have separated into bunches corresponding to $q/m$. If only singly charged ions are present, the lightest group reaches the detector first and is followed by groups of successively heavier mass. Thus, each source pulse results in a mass spectrum which can easily be displayed by connecting the ion collector to the vertical plates of an oscilloscope. An expanded portion of such a spectrum (obtained with the improved ion gun) is shown in Fig. 1.

The known abundances of the xenon isotopes displayed are 128, 2%; 129, 26.4%; 130, 4.1%; 131, 21.2%; 132, 26.9%; 134, 10.4%; 136, 8.9%.

# Wiley-Maclaren ToFMS

T = t1(V1, V2, s) + t2(V1, V2,d) + t3(V1, V2,D)

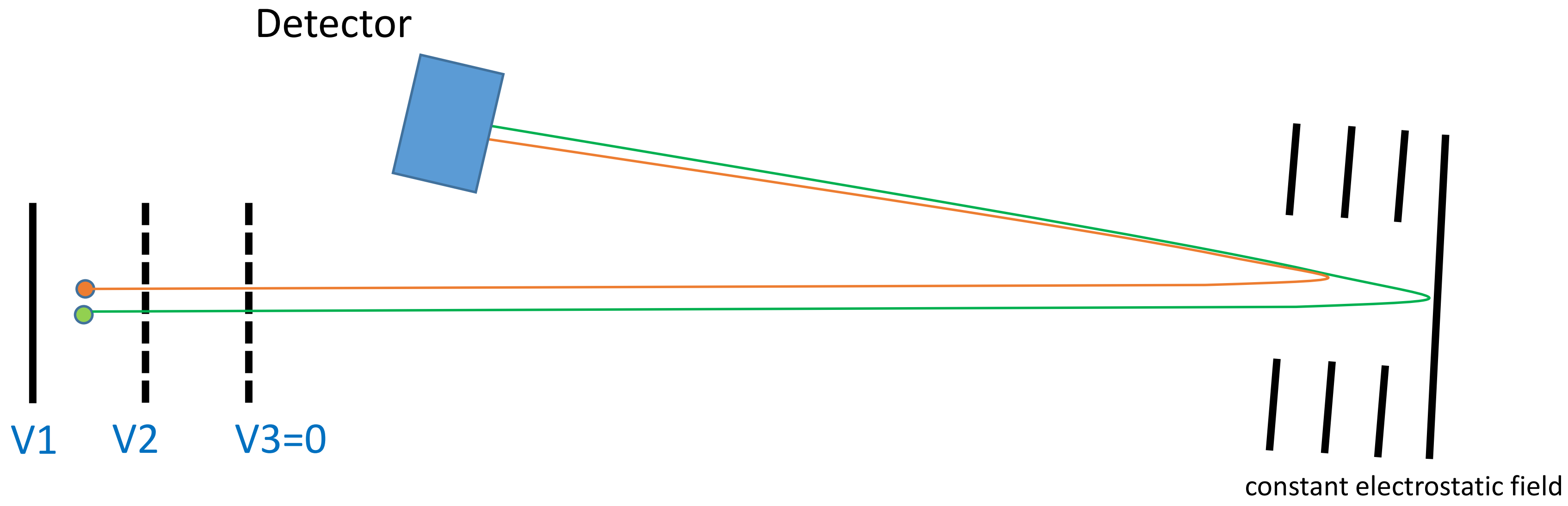
For a given s, d, D, find the V1 and v2 such that $\frac{\partial T}{\partial \Delta s} = 0$

# Delayed extraction

Ions generated from MALDI have different velocities. Ions with low velocity locate at position further away from detector, but they get more energy from electric filed. The energy turns into velocity and they catch up the other ions at the detector.

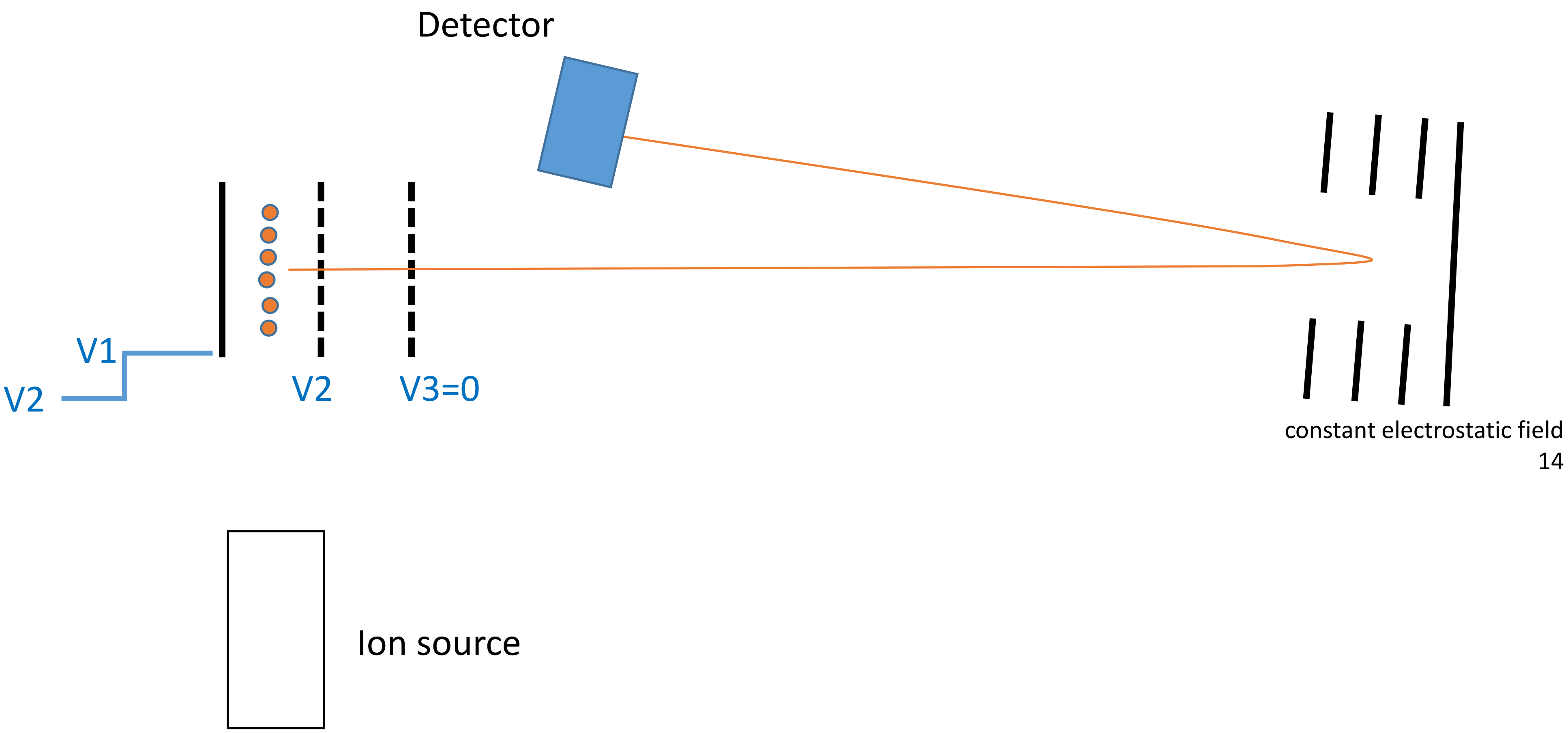
# Reflectron TOF

The kinetic energy distribution in the direction of ion flight can be corrected by using a reflectron. The more energetic ions penetrate deeper into the reflectron, and take a slightly longer path to the detector. Less energetic ions of the same mass-to-charge ratio penetrate a shorter distance into the reflectron and, correspondingly, take a shorter path to the detector. The flat surface of the ion detector (typically a microchannel plate, MCP) is placed at the plane where ions of same m/z but with different energies arrive. They arrive the detector at the same time.



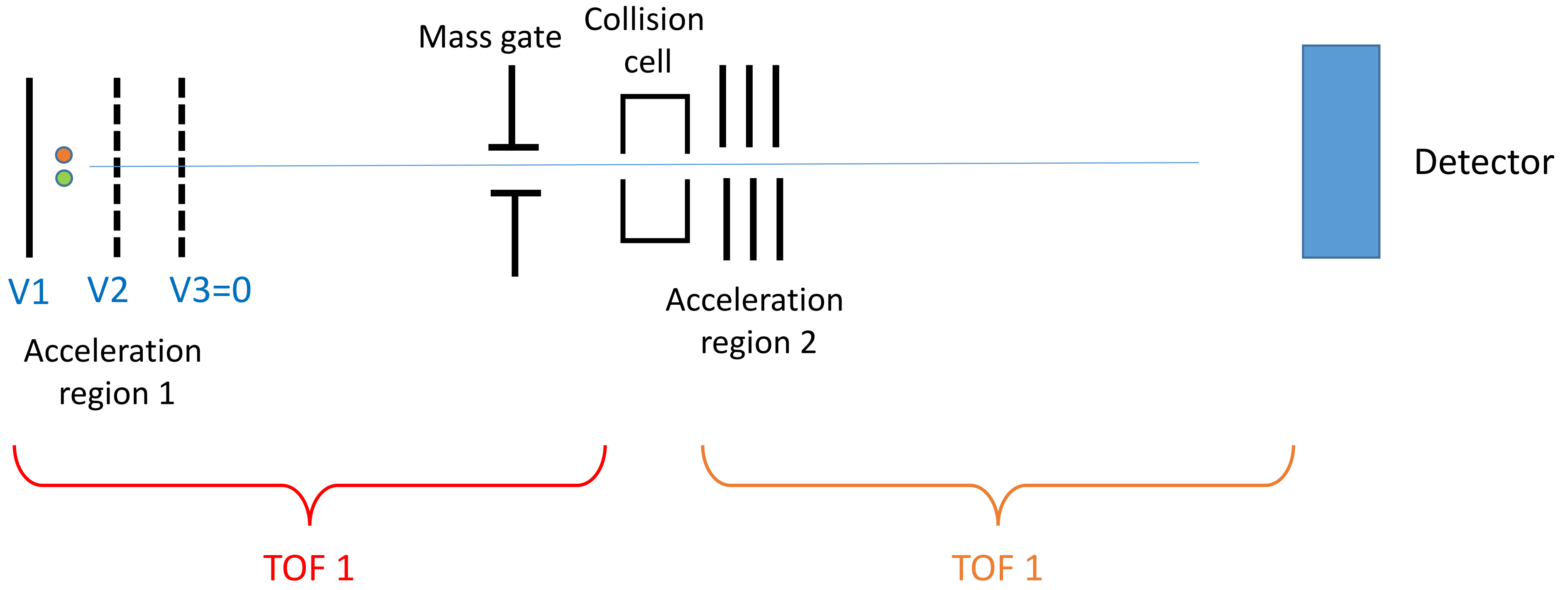
# Orthogonal acceleration time-of-flight

Ions from continuous ion sources are injected into a TOF by "orthogonal extraction" in which ions introduced into the TOF mass analyzer are accelerated along the axis perpendicular to their initial direction of motion.



# Tandem time-of-flight (TOF/TOF)

A tandem mass spectrometry method where two time-of-flight mass spectrometers are used consecutively.



# Properties of mass spectrometer

- Mass Resolution
- Mass accuracy
- Sensitivity
- Duty cycle
- Throughput

# Mass Resolution

Resolution

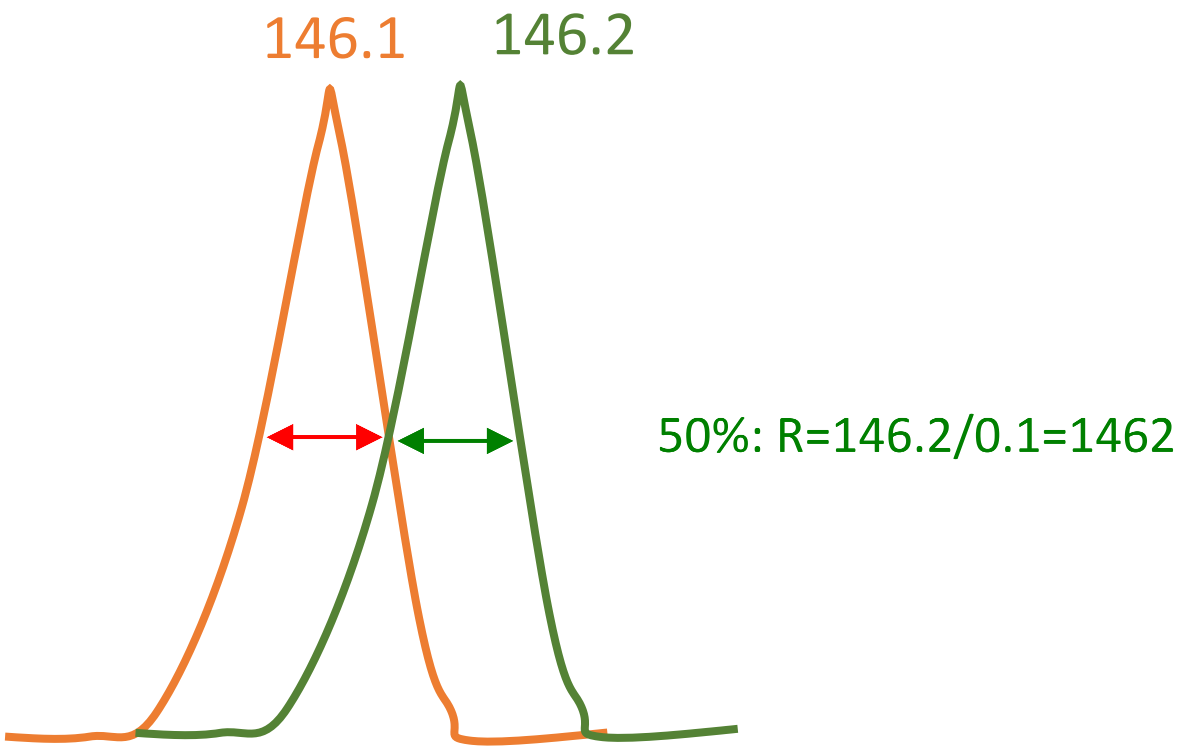
$R = M/\Delta M$

R: resolving power

M: mass of the (second) peak

$\Delta$M: Peak width

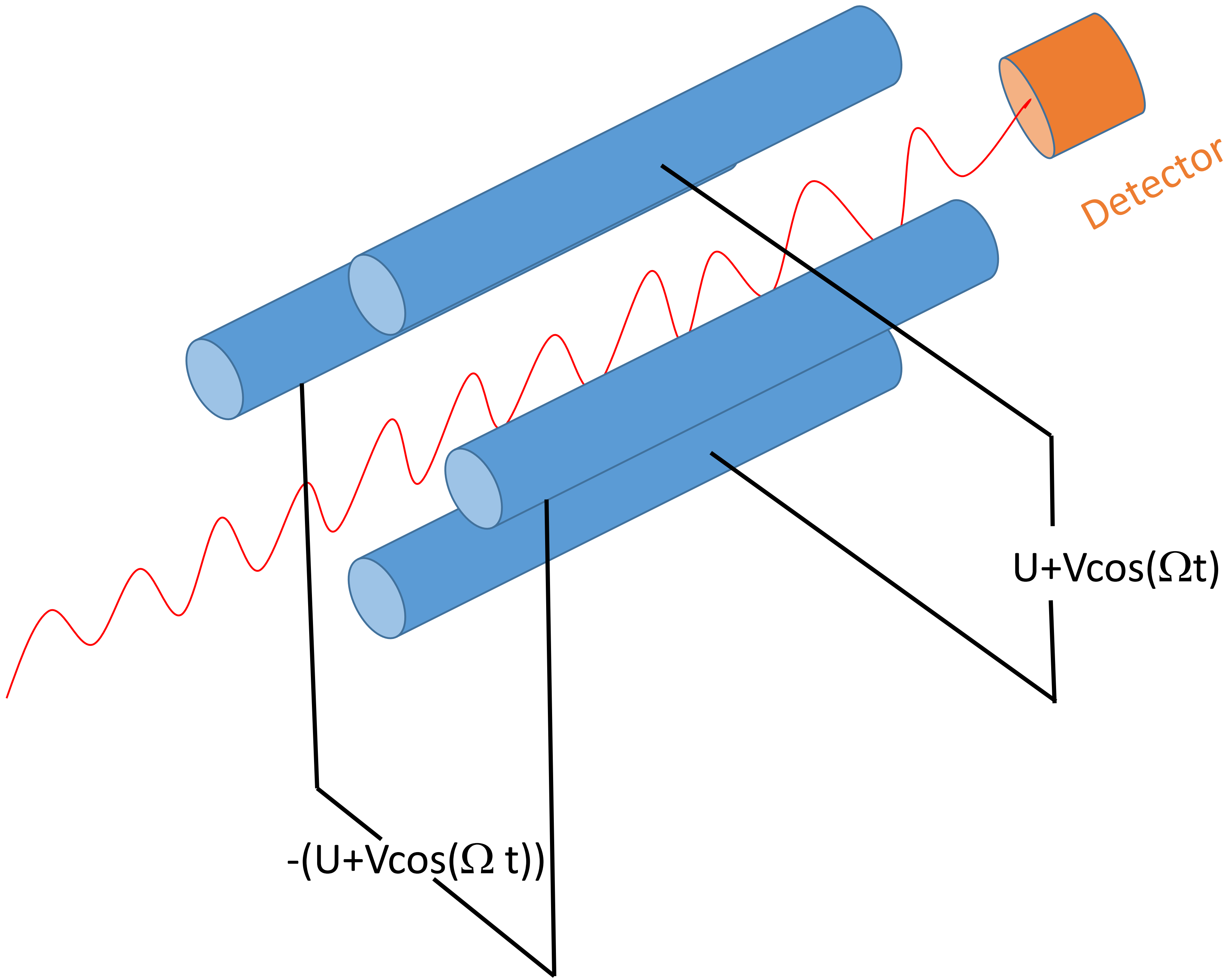
Resolution may change with M

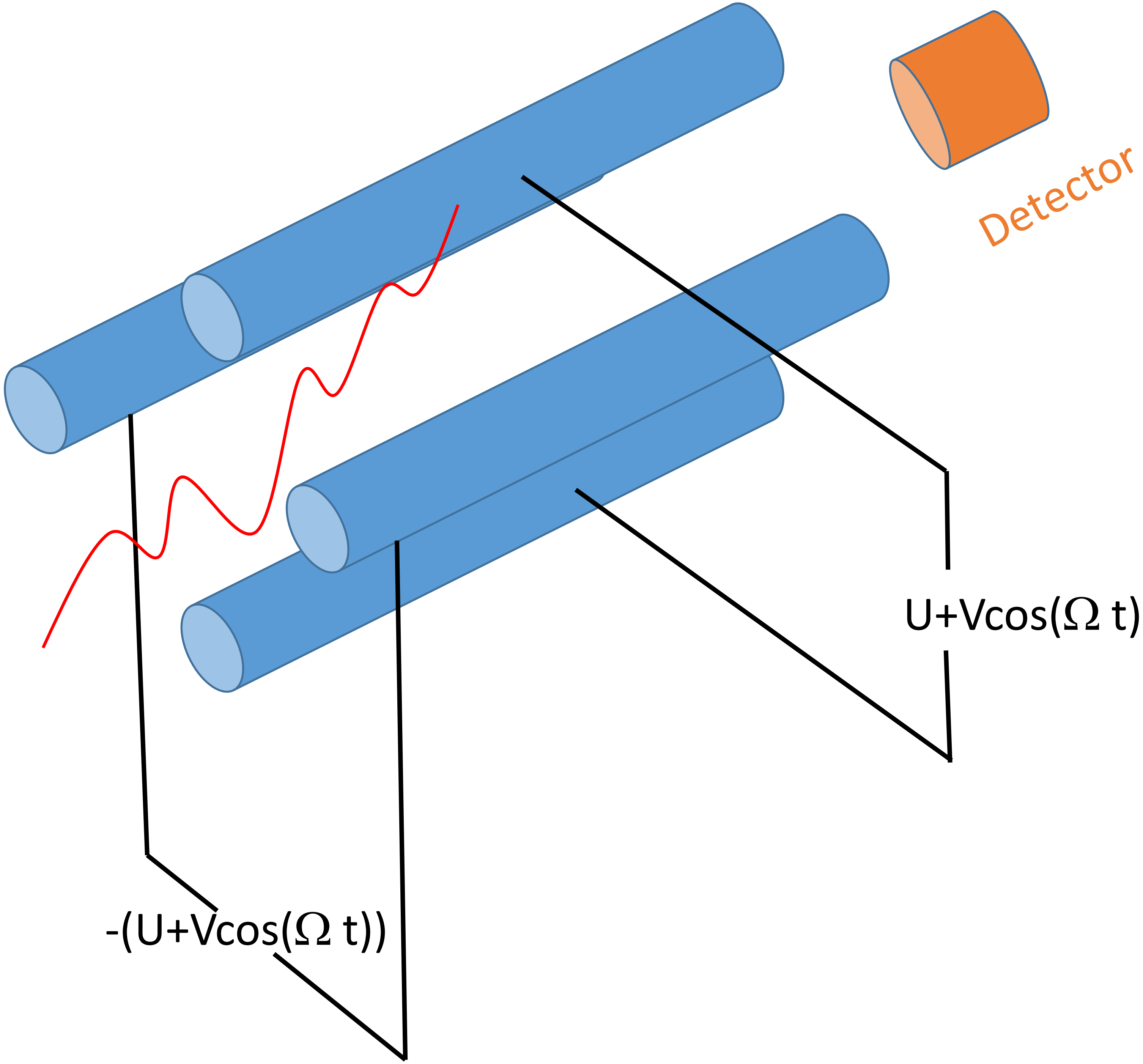


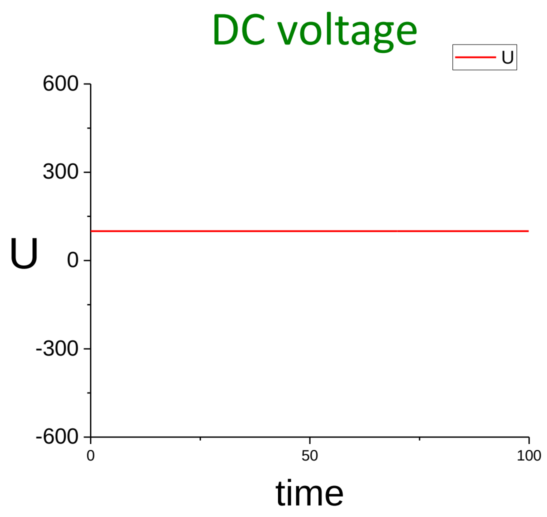
# Quadrupole mass spectrometer

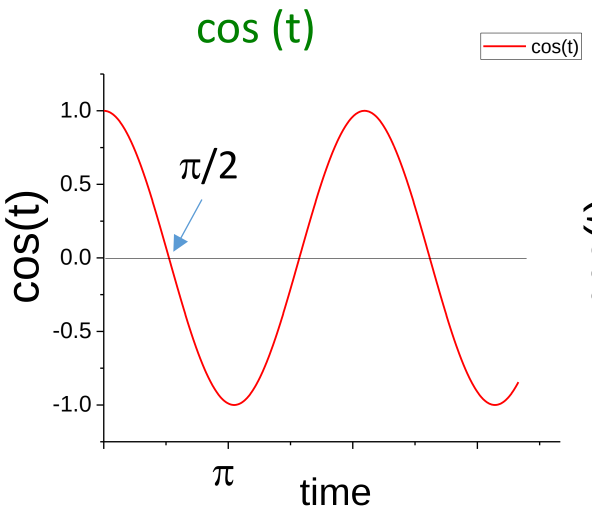
Wolfgang Paul

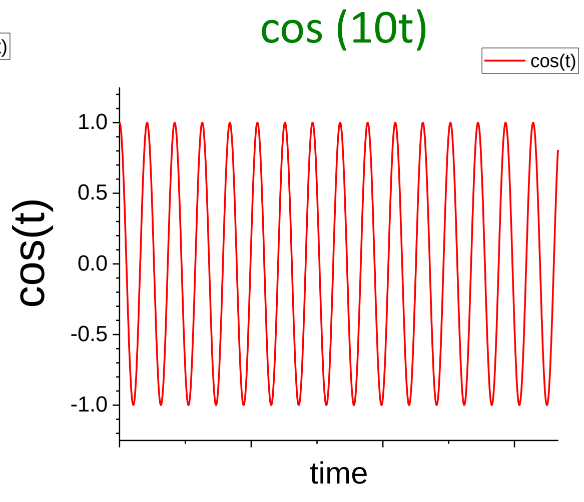
1989 Nobel prize in Physics

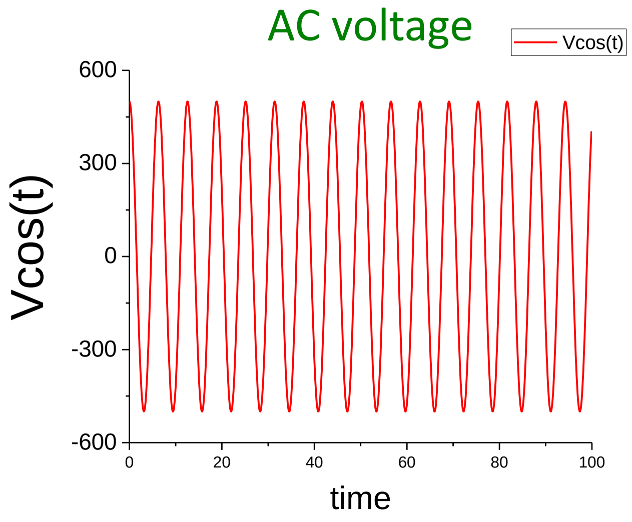

Detector
U+Vcos(Ωt)
-(U+Vcos(Ω t))

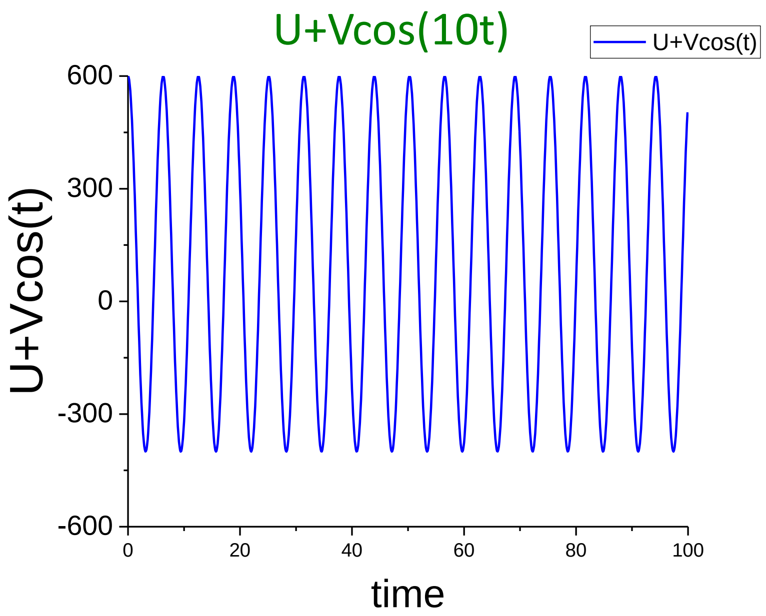

Detector
U+Vcos(Ω t)
-(U+Vcos(Ω t))

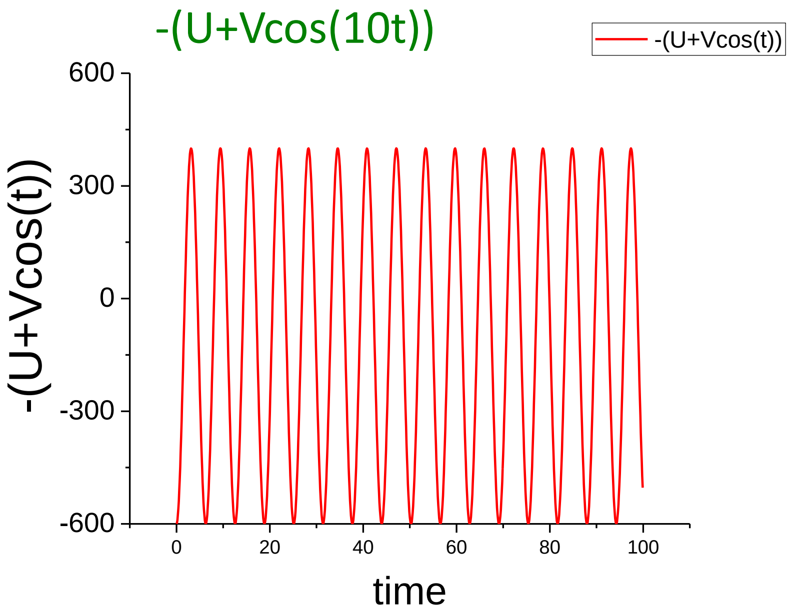

DC voltage
U
600
300
0
-300
-600
0
50
100
time

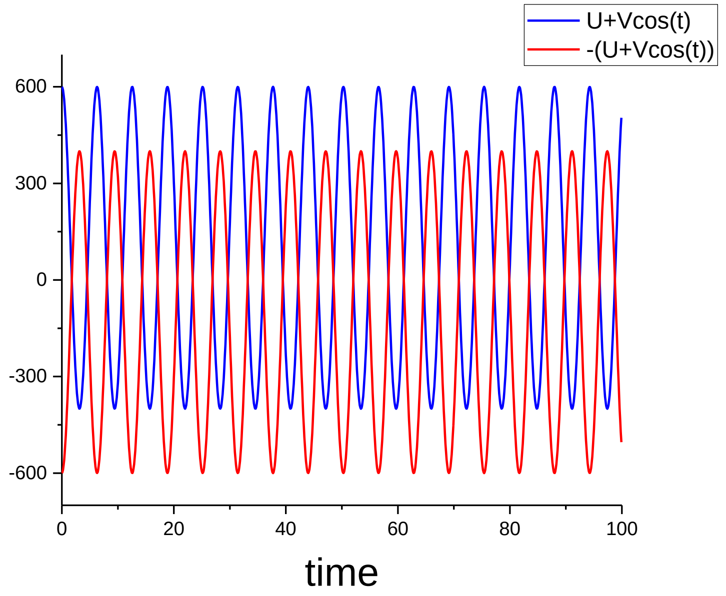

cos (t)
cos(t)
1.0
0.5
0.0
-0.5
-1.0
π/2
π
time

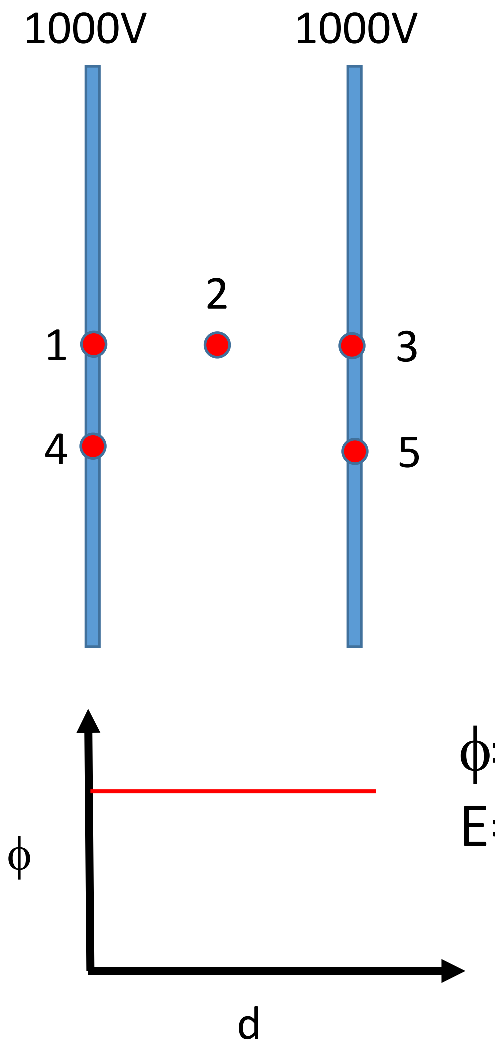

cos (10t)
cos(t)
1.0
0.5
0.0
-0.5
-1.0
time


AC voltage
Vcos(t)
600
300
0
-300
-600
0
20
40
60
80
100
time


U+Vcos(10t)
U+Vcos(t)
600
300
0
-300
-600
0
20
40
60
80
100
time


-(U+Vcos(10t))
-(U+Vcos(t))
600
300
0
-300
-600
0
20
40
60
80
100
time


U+Vcos(t)
-(U+Vcos(t))
600
300
0
-300
-600
0
20
40
60
80
100
time

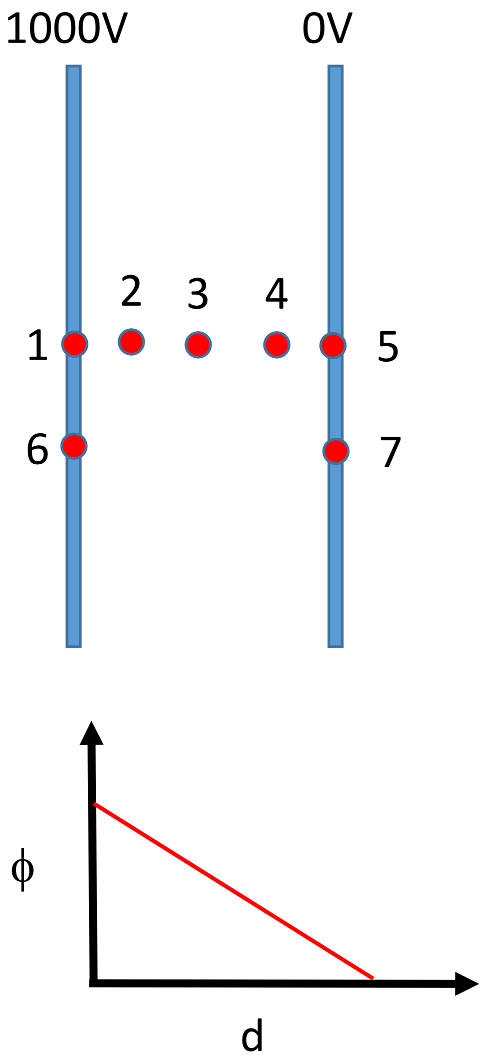



$\phi \neq 0$
E=0

$\phi_1 = \phi_2 = \phi_3 = \phi_4 = \phi_5 = 1000$ V

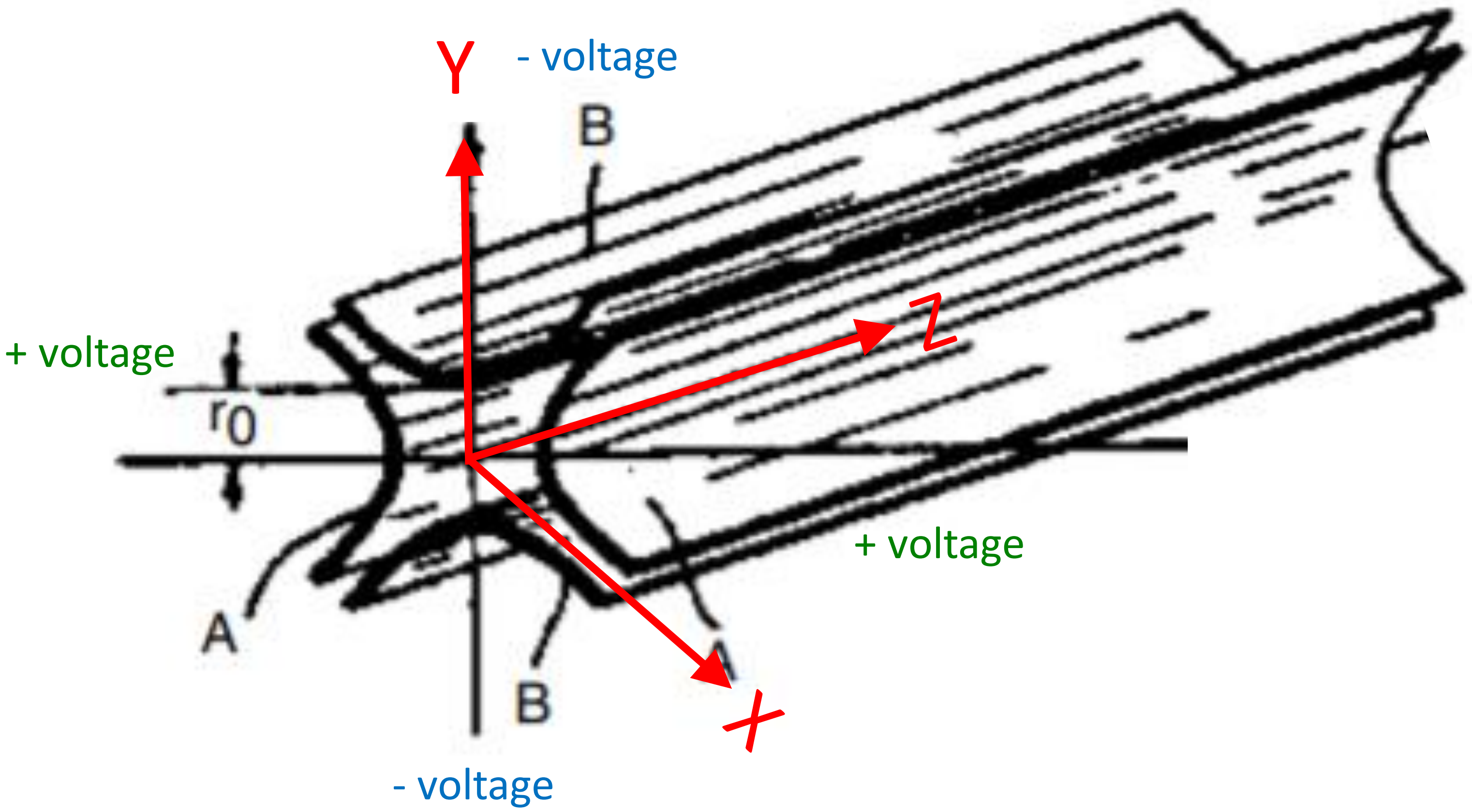
## Potential $\phi$
## &
## Electric field E

$$E = -\frac{\partial \phi}{\partial d}$$

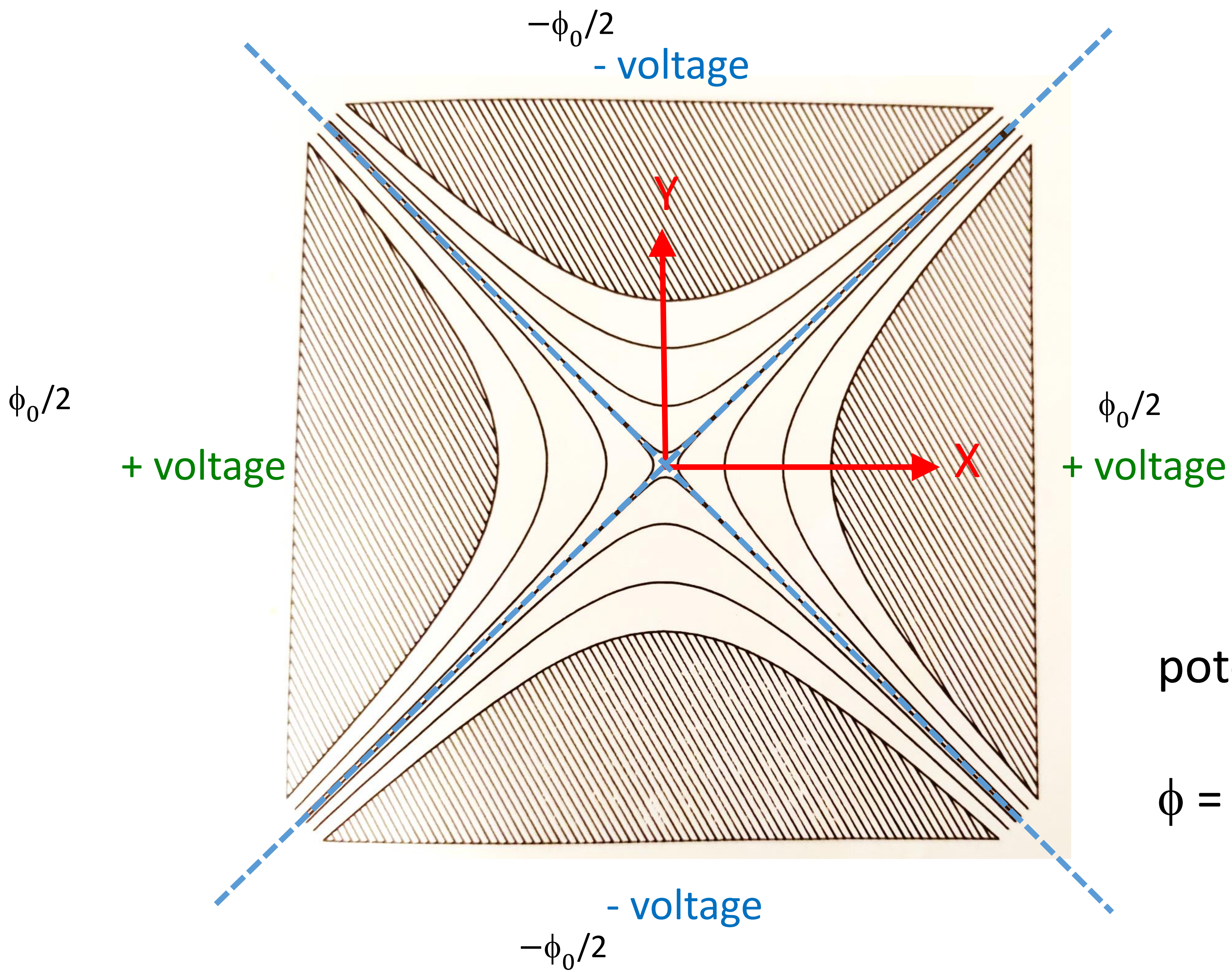



$\phi_1 = \phi_6 = 1000$ V $\quad \phi_5 = \phi_7 = 0$ V

$\phi_2 = 750$ V $\quad \phi_3 = 500$ V $\quad \phi_4 = 250$ V



Y
- voltage
B
+ voltage
$r_0$
Z
+ voltage
A
B
A
X
- voltage




potential

$$\phi = \frac{\phi_0}{2r_0^2}(x^2 - y^2)$$

$F_x$ = -e$E_x$= -e $\frac{\partial\phi}{\partial x} = -e\frac{\phi_0}{2r_0^2}(2x)$ (1)

potential

$F_y$ = -e$E_y$= -e $\frac{\partial\phi}{\partial y} = -e\frac{\phi_0}{2r_0^2}(-2y)$ (2)

$\phi = \frac{\phi_0}{2r_0^2}(x^2 - y^2)$

$F_x$ = m$a_x$= m$\frac{\partial^2 x}{\partial t^2}$ (3)

$F_y$ = m$a_y$= m$\frac{\partial^2 y}{\partial t^2}$ (4)

From (1) and (3): $m\frac{\partial^2 x}{\partial t^2} = -e\frac{\phi_0}{2r_0^2}(2x)$

From (2) and (4): $m\frac{\partial^2 y}{\partial t^2} = -e\frac{\phi_0}{2r_0^2}(-2y)$

Motions in x and y directions are independent

# What is $\phi_0$?

(1) $\phi_0 = 2(U + V\cos(\Omega t))$ Conventional method

(2) $\phi_0$ = others e.g., digital ion trap

## For conventional method:

$$m\frac{\partial^2 x}{\partial t^2} = -e\frac{\phi_0}{r_0^2}(2x) = -e\frac{2(U+V\cos(\Omega t))}{2r_0^2}(2x)$$

$$m\frac{\partial^2 y}{\partial t^2} = -e\frac{\phi_0}{r_0^2}(-2y) = -e\frac{2(U+V\cos(\Omega t))}{2r_0^2}(-2y)$$

## For conventional method:

$$m\frac{\partial^2 x}{\partial t^2} = -e\frac{\phi_0}{r_0^2}(2x) = -e\frac{2(U+V\cos(\Omega t))}{2r_0^2}(2x)$$

$$\frac{\partial^2 x}{\partial t^2} = -\frac{2e}{mr_0^2}(U + V\cos(\Omega t))\, x$$

$$m\frac{\partial^2 y}{\partial t^2} = -e\frac{\phi_0}{r_0^2}(-2y) = -e\frac{2(U+V\cos(\Omega t))}{2r_0^2}(-2y)$$

$$\frac{\partial^2 y}{\partial t^2} = \frac{2e}{mr_0^2}(U + V\cos(\Omega t))\, y$$

$$\frac{\partial^2 x}{\partial t^2} = -\frac{2e}{mr_0^2}(U + V cos(\Omega t))\ x$$

$$\frac{\partial^2 y}{\partial t^2} = \frac{2e}{mr_0^2}(U + V cos(\Omega t))\ y$$

$$\frac{\partial^2 x}{\partial t^2} + (\frac{2e}{mr_0^2}U + \frac{2e}{mr_0^2}V cos(\Omega t))\ x = 0$$

$$\frac{\partial^2 y}{\partial t^2} - (\frac{2e}{mr_0^2}U + \frac{2e}{mr_0^2}V cos(\Omega t))\ y = 0$$

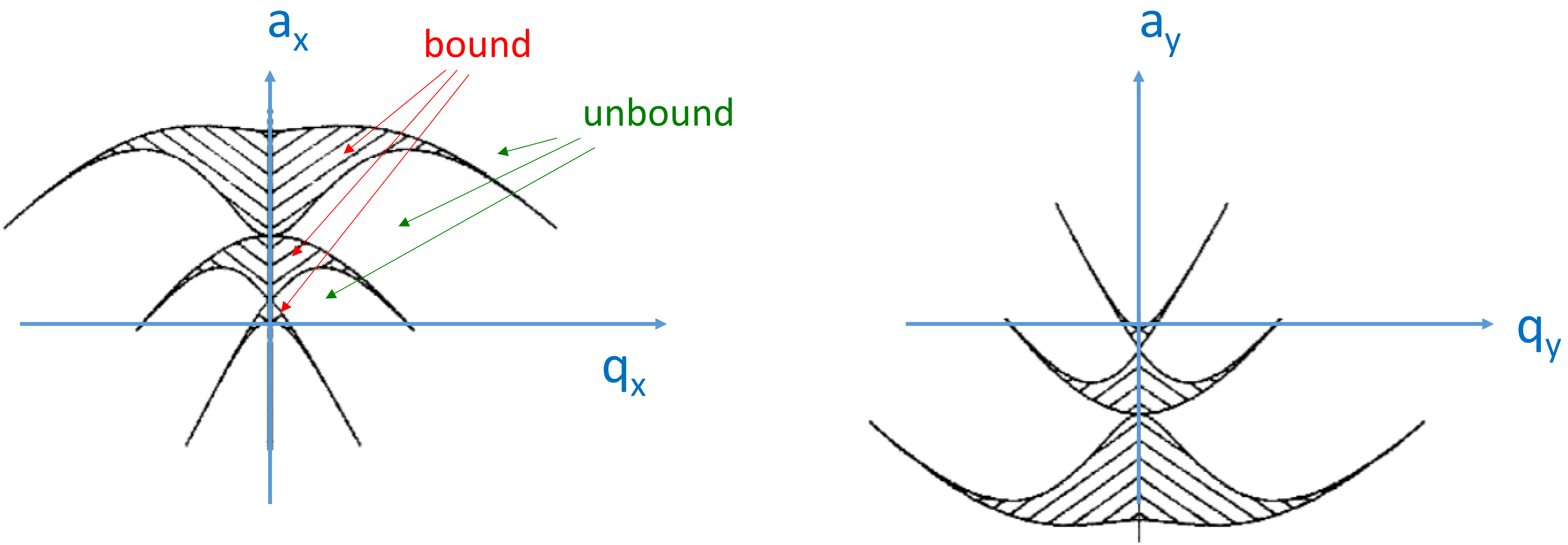
$\xi = \Omega t/2$ $\qquad u$ = x or y

# The Mathieu Equation

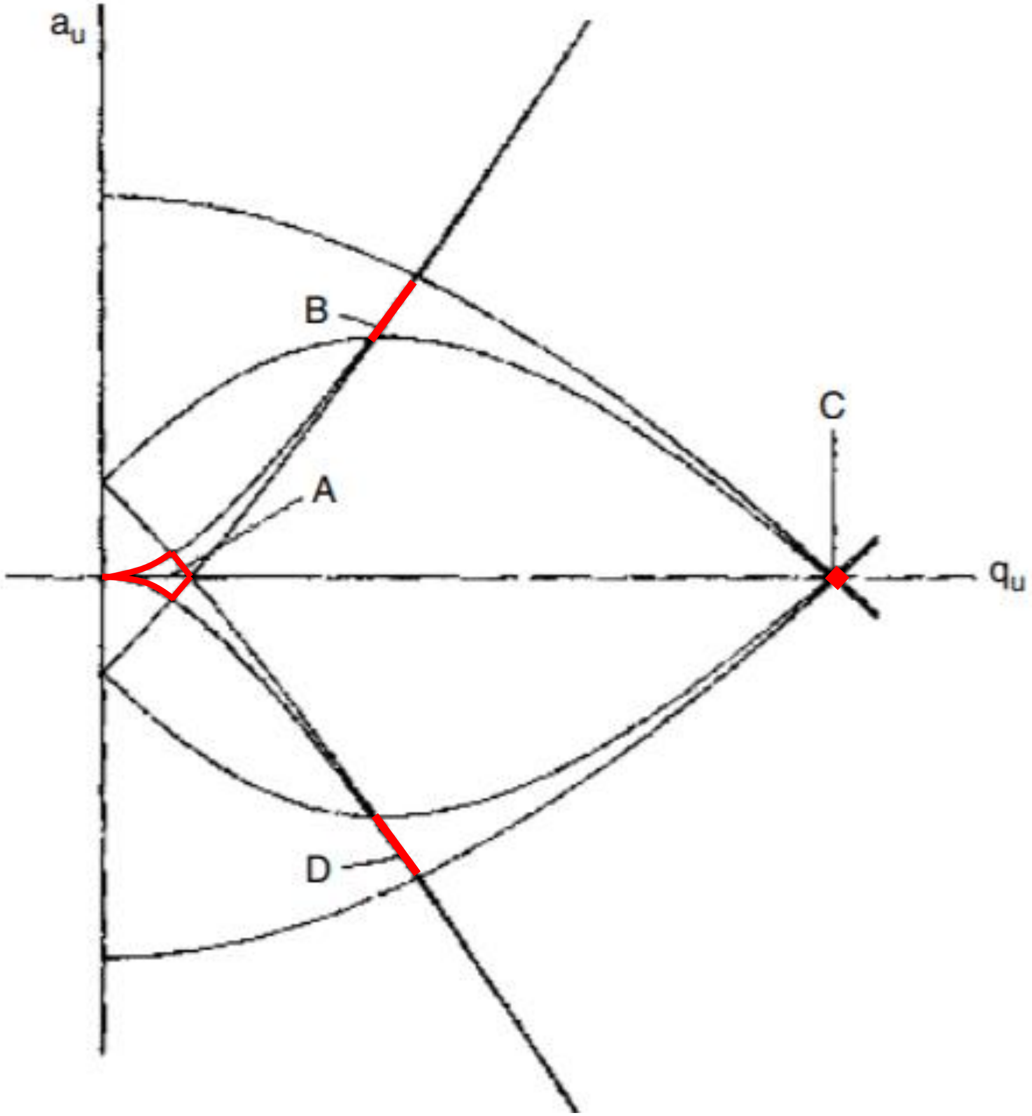
$$\frac{d^2 u}{d\xi^2} + (a_u + 2q_u cos 2\xi)u = 0$$

$$a_x = \frac{8eU}{mr_0^2\Omega^2} \qquad q_x = \frac{4eV}{mr_0^2\Omega^2}$$

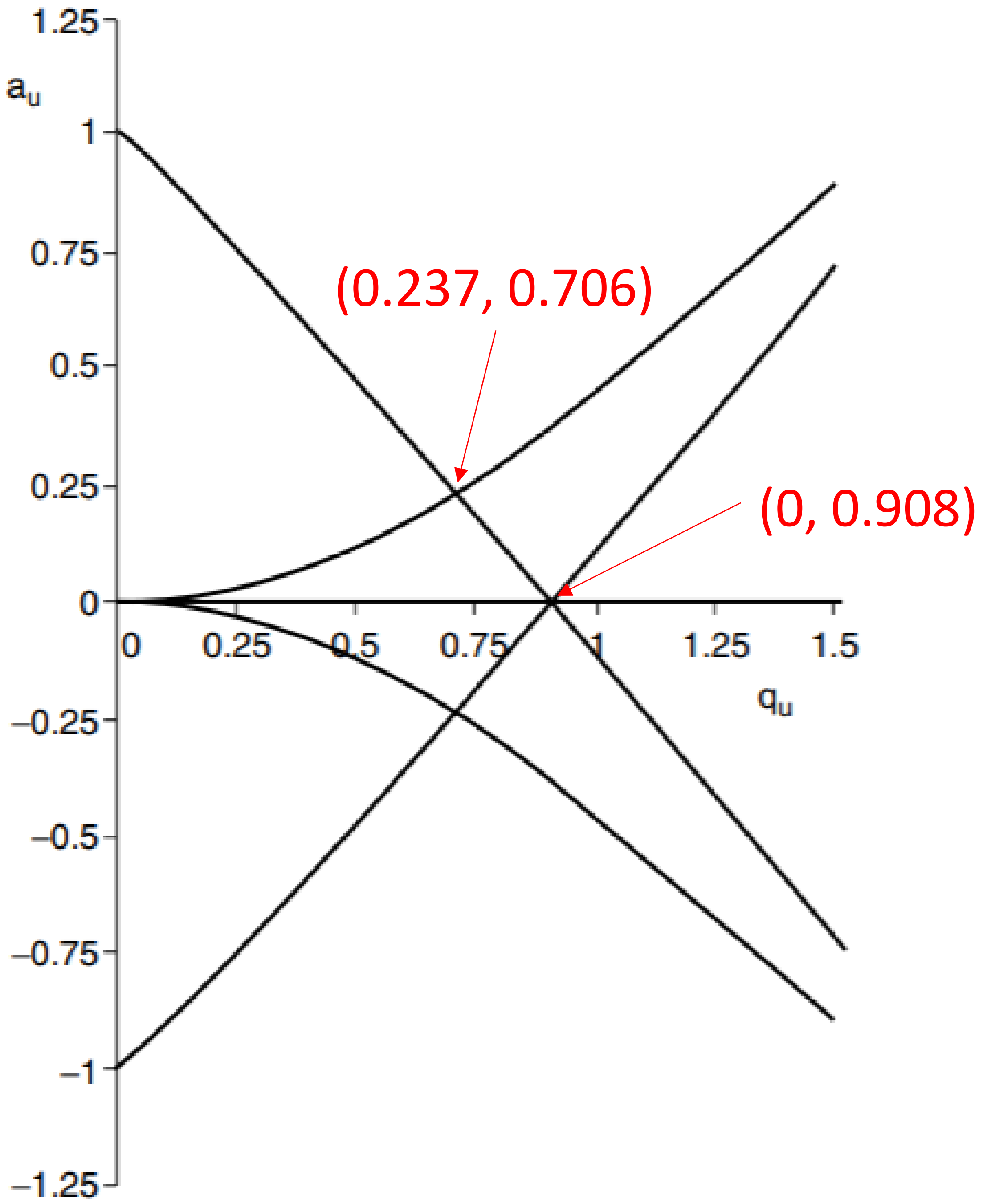
$$a_y = \frac{-8eU}{mr_0^2\Omega^2} \qquad q_y = \frac{-4eV}{mr_0^2\Omega^2}$$



a_x
bound
unbound
q_x
a_y
q_y



$a_u$
B
A
C
$q_u$
D




$$a_u = \frac{8eU}{mr_0^2\Omega^2}$$

$$q_u = \frac{4eV}{mr_0^2\Omega^2}$$

$$a_x = \frac{8eU}{mr_0^2\Omega^2} \qquad q_x = \frac{4eV}{mr_0^2\Omega^2} \quad \Rightarrow \quad U = \frac{mr_0^2\Omega^2}{8e}a_x \qquad V = \frac{mr_0^2\Omega^2}{4e}q_x$$

For a given $r_0$ and $\Omega$: e.g., $r_0$ = 4 mm and $\Omega$ = 1MHz

$$V = \frac{1000g/mol \times 10^{-3}kg/g \times (0.004m)^2(2\pi \times 1 \times 10^6 rad/s)^2}{6.02 \times 10^{23}\ 1/mol \times 4 \times 1.6 \times 10^{-19}C} \times 0.706 = 1157.4\ V\ (V_{0\text{-}p})$$

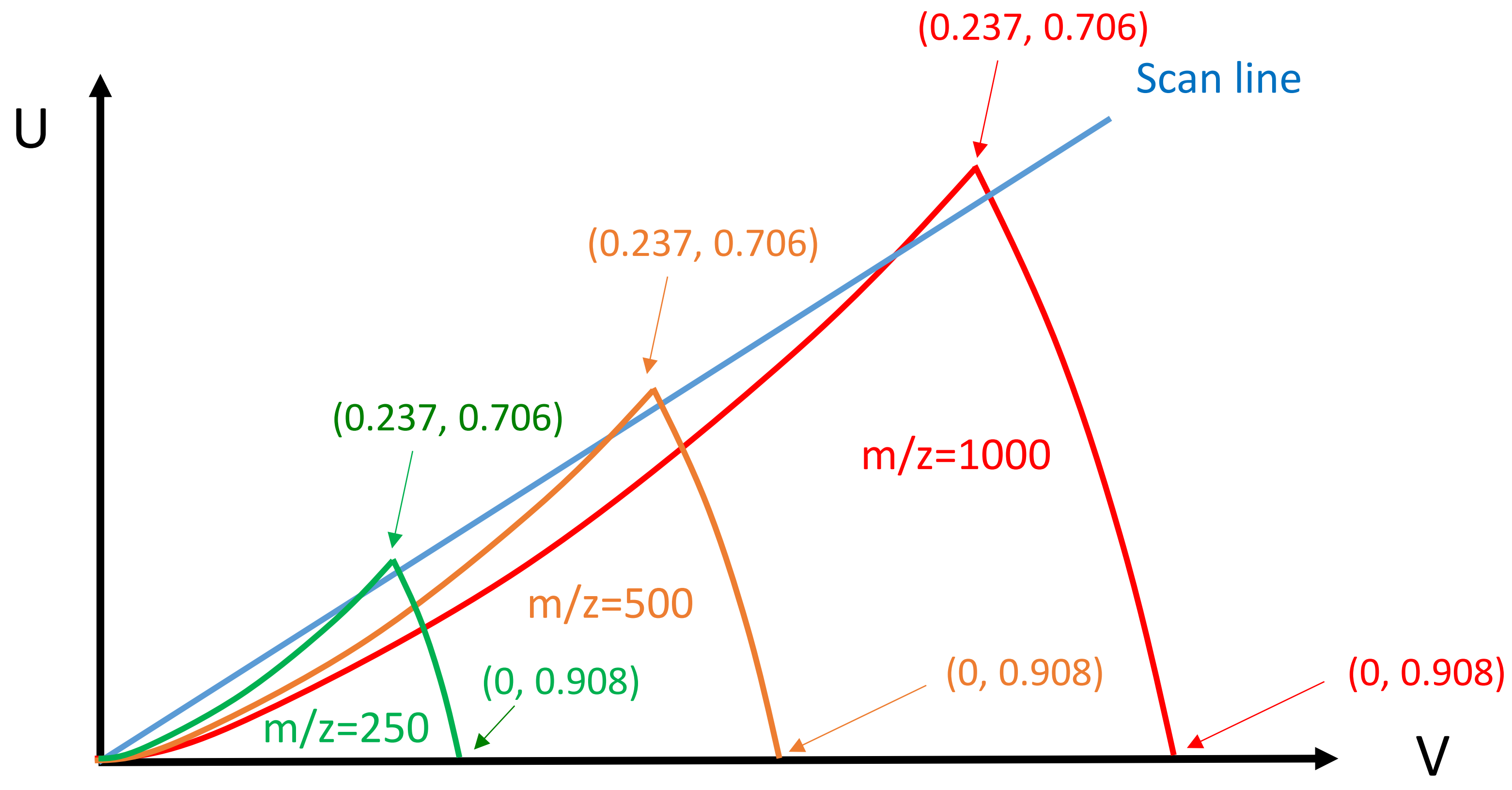
Mass upper limit: available voltage

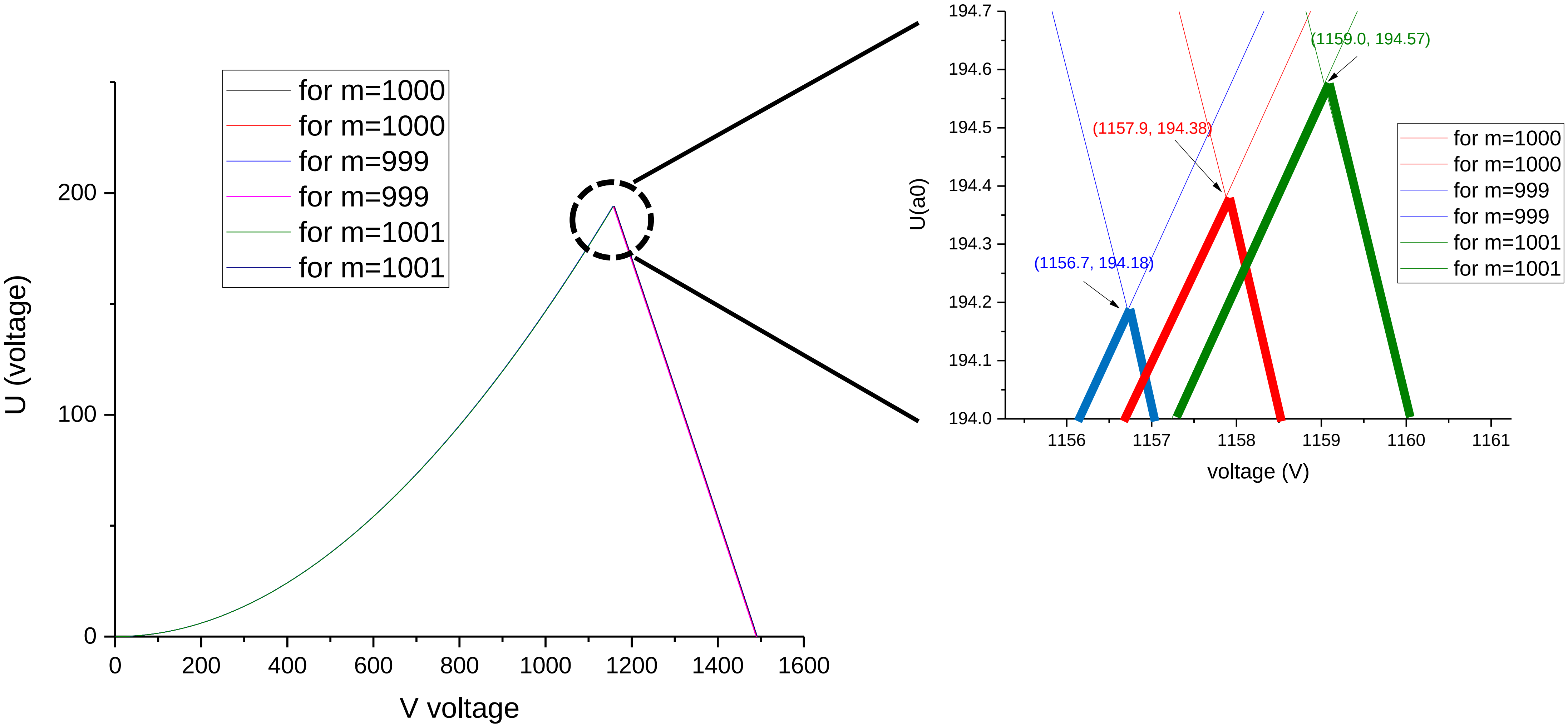
$$U = \frac{1000g/mol \times 10^{-3}kg/g \times (0.004m)^2(2\pi \times 1 \times 10^6 rad/s)^2}{6.02 \times 10^{23}\ 1/mol \times 8 \times 1.6 \times 10^{-19}C} \times 0.237 = 194.2\ V\ (DC)$$

At Q=0.706, r=6 mm, 800KHz
V=1666 for 1000 amu
V=4998 for 3000 amu

At Q=0.706, r=6 mm, 700KHz
V=1275 fro 1000 amu
V=3826 for 3000 amu

At Q=0.2, r=6 mm, 800KHz
V=471 for 1000 amu
V=1415 for 3000 amu




for m=1000
for m=1000
for m=999
for m=999
for m=1001
for m=1001
U (voltage)
V voltage
0
100
200
0
200
400
600
800
1000
1200
1400
1600
(1159.0, 194.57)
(1157.9, 194.38)
(1156.7, 194.18)
U(a0)
194.0
194.1
194.2
194.3
194.4
194.5
194.6
194.7
1156
1157
1158
1159
1160
1161
voltage (V)
for m=1000
for m=1000
for m=999
for m=999
for m=1001
for m=1001

At apex:

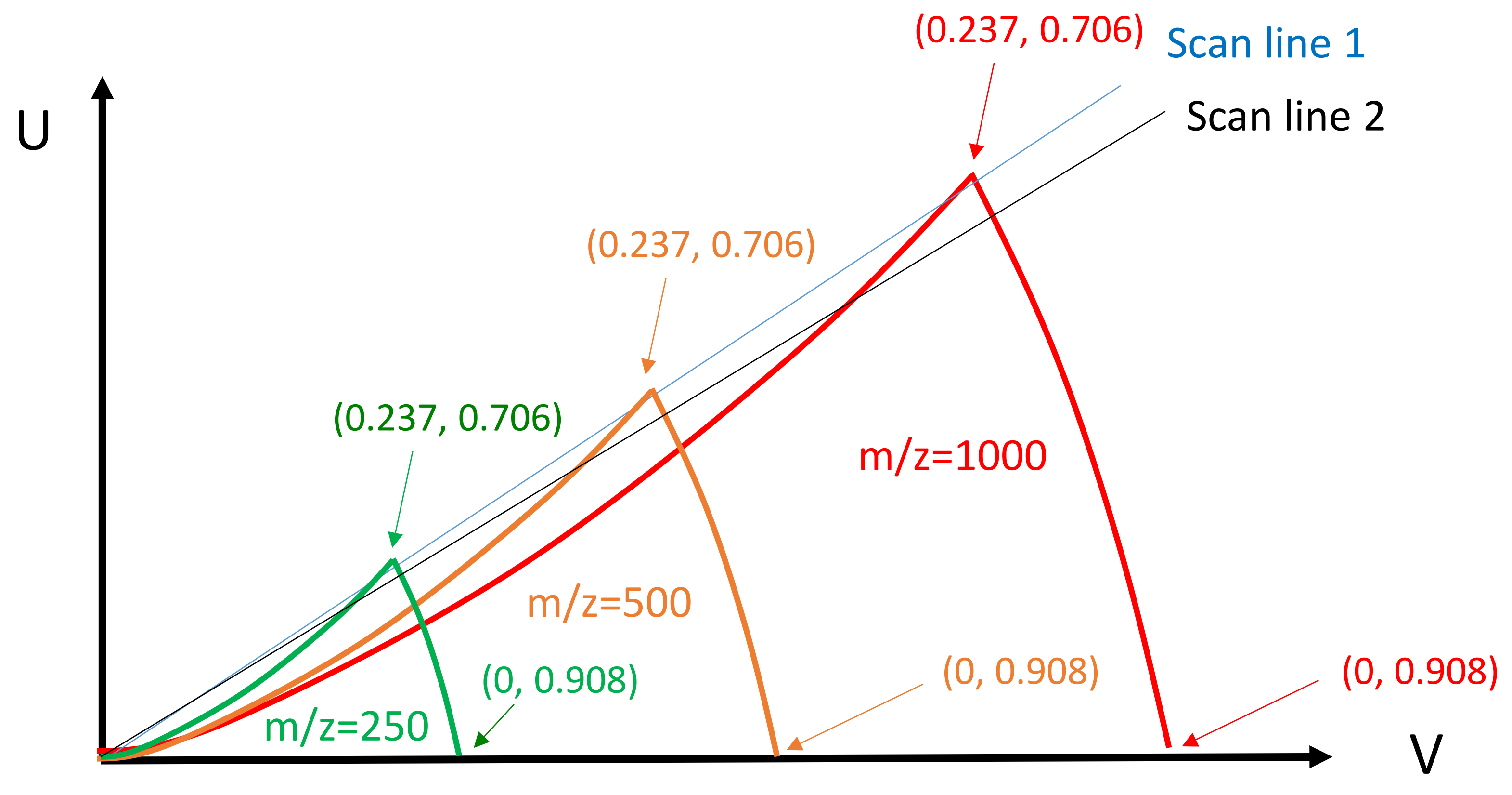
$$\Delta U = \frac{m_1 r_0^2 \Omega^2}{8e} a_x - \frac{m_2 r_0^2 \Omega^2}{8e} a_x = \Delta m \ \frac{r_0^2 \Omega^2}{8e} a_x = \frac{1\times10^{-3}}{6.02\times10^{23}} \times \frac{0.004^2(2\pi\times10^6)^2}{8\times1.6\times10^{-19}} 0.237 = 0.19\ \mathrm{V}$$

$$\Delta V = \frac{m_1 r_0^2 \Omega^2}{4e} q_x - \frac{m_2 r_0^2 \Omega^2}{4e} q_x = \Delta m \ \frac{r_0^2 \Omega^2}{4e} q_x = \frac{1\times10^{-3}}{6.02\times10^{23}} \times \frac{0.004^2(2\pi\times10^6)^2}{4\times1.6\times10^{-19}} 0.706 = 1.13\ \mathrm{V}$$

$\Delta U$, $\Delta V$ are  m independent

For $m/\Delta m > 1000$

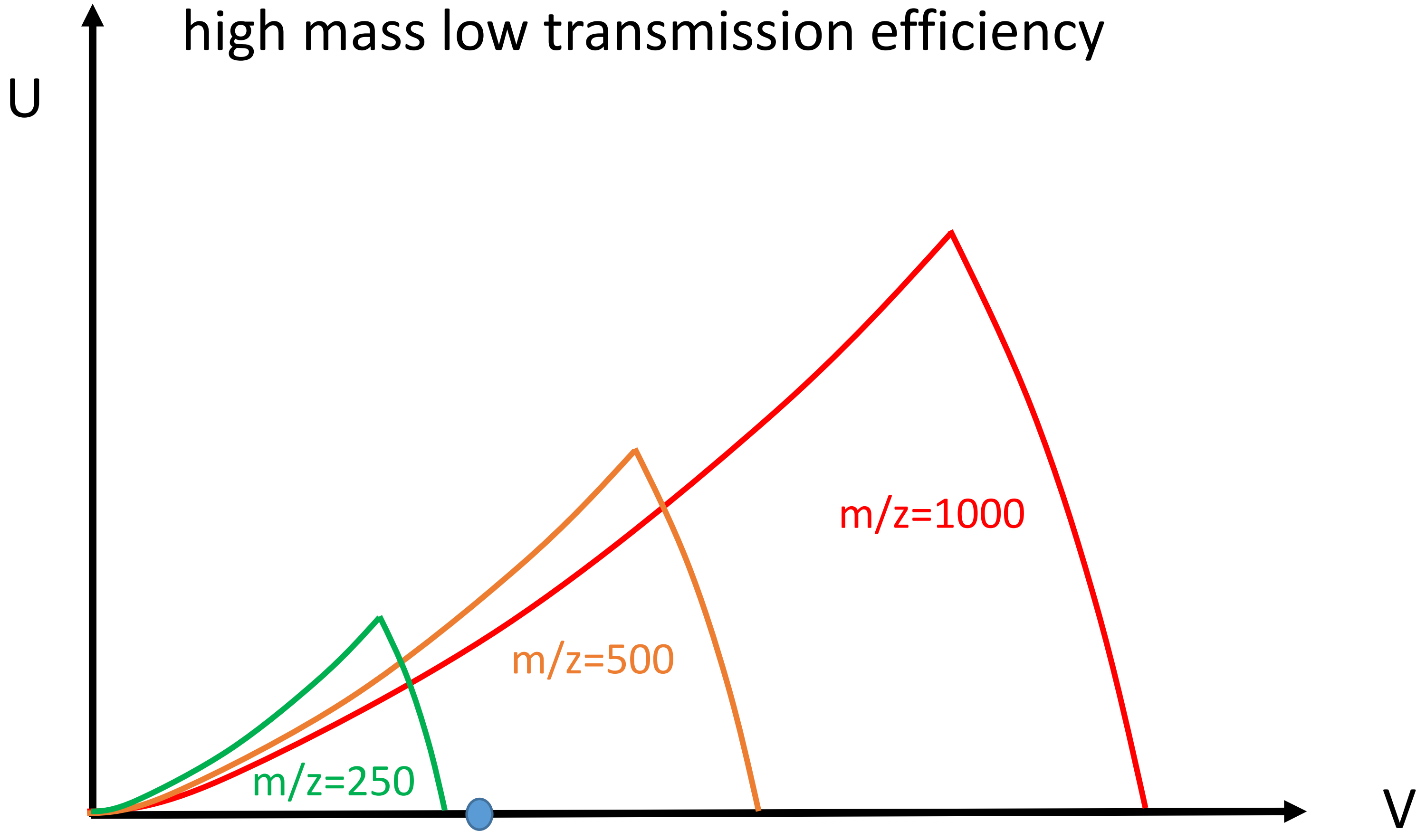
- $\Delta\Omega/\Omega < 1/2000$
- $\Delta r_0/r_0 < 1/2000$



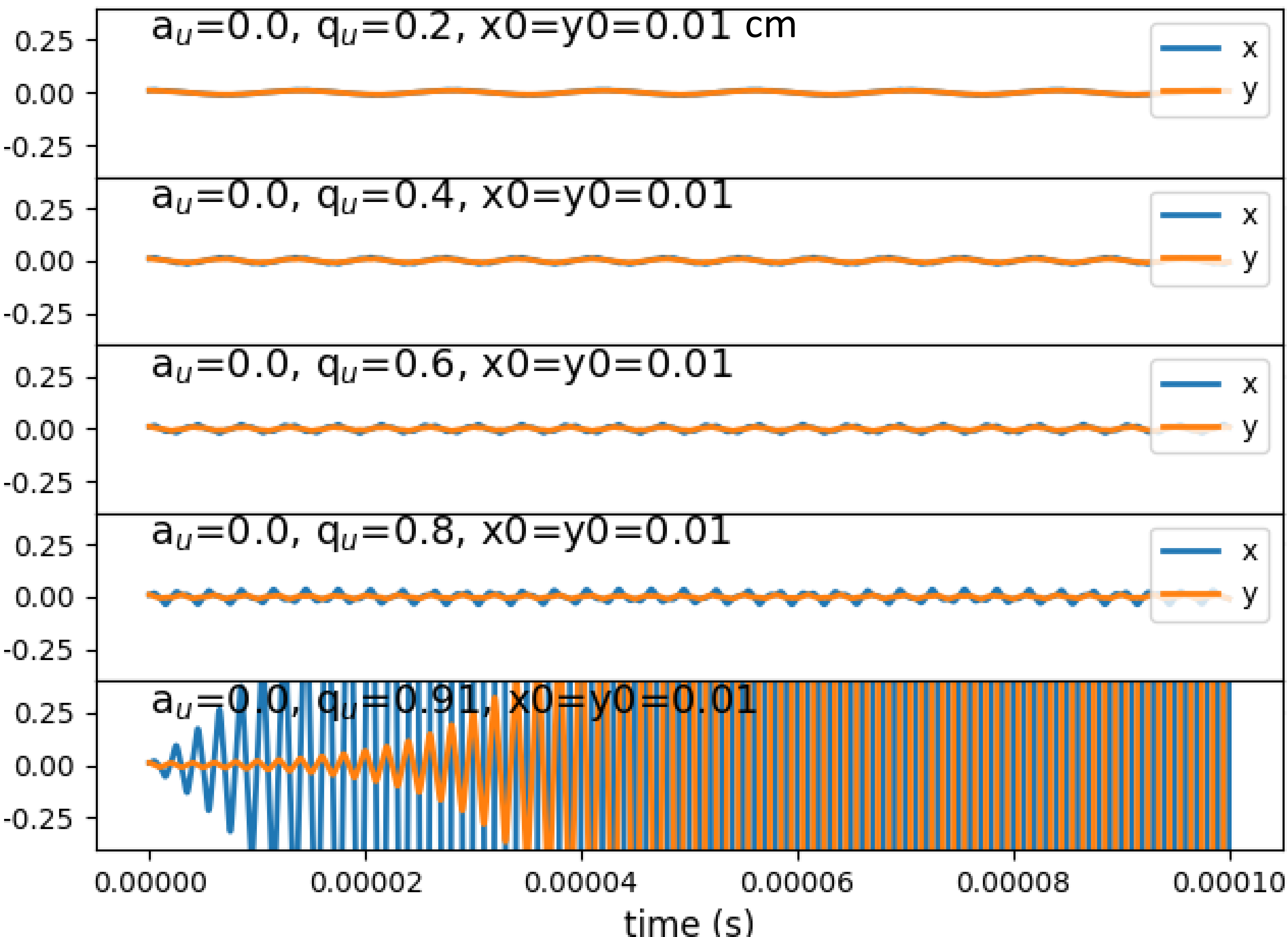

Scan line 1: $U/V = 0.5x(0.237/0.706) = 0.1678$, best resolution, small signal

Scan line 2: $U/V < 0.5x(0.237/0.706) = 0.1678$, low resolution, large signal

**Ion guide**: turn off DC voltage (U=0), $a_x$=0
low mass cutoff
high mass low transmission efficiency



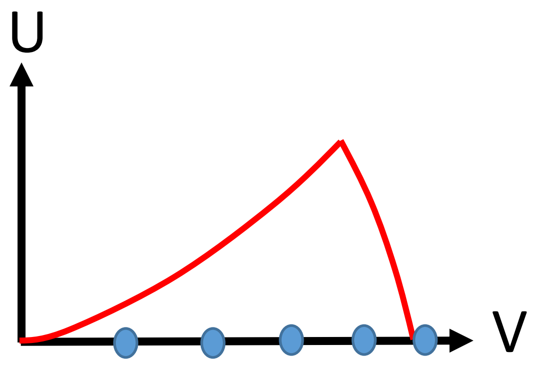
# Trajectory

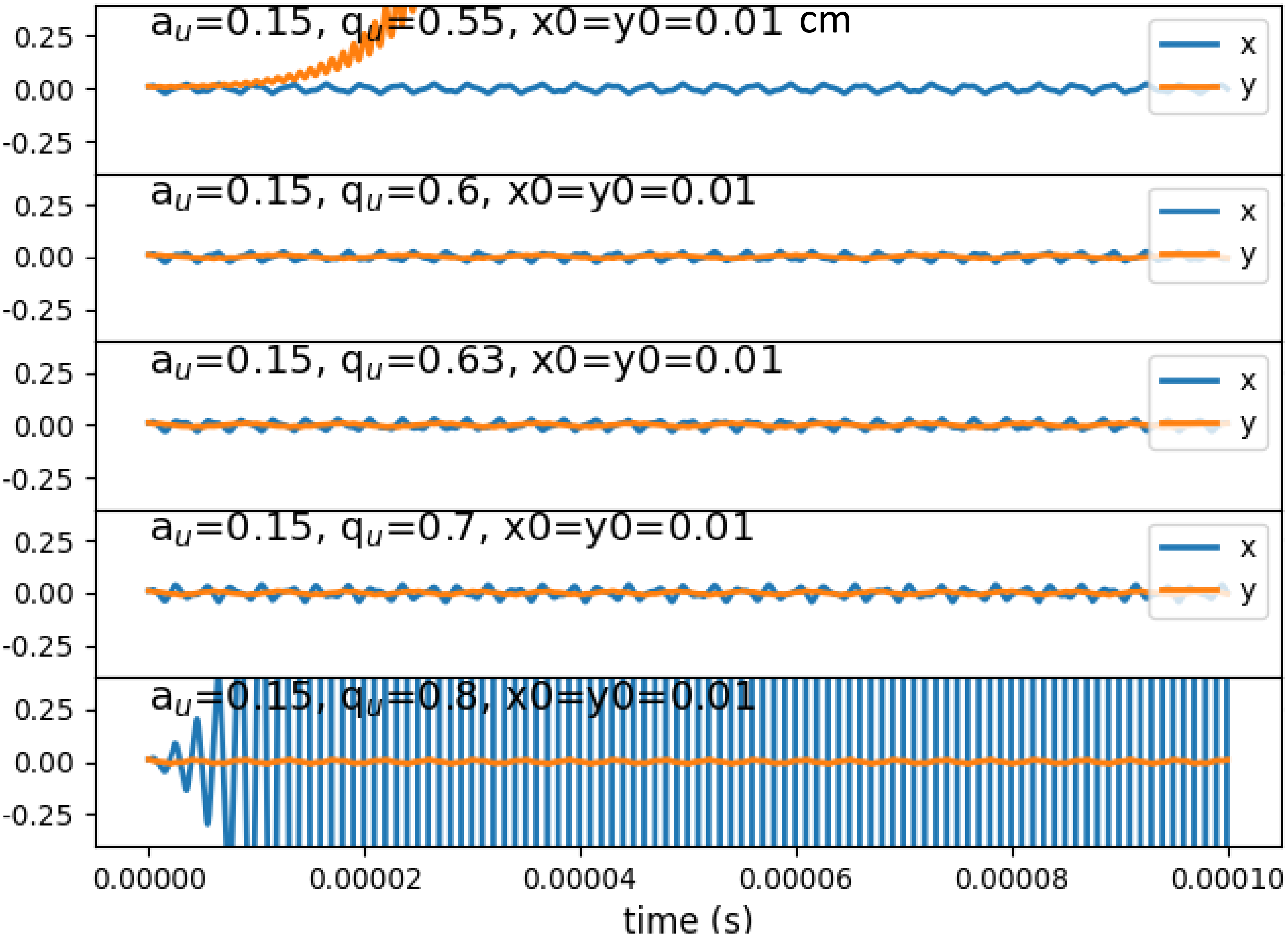



Initial velocity

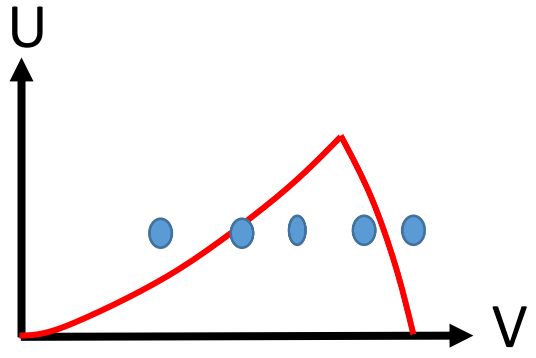
Vx=Vy=0

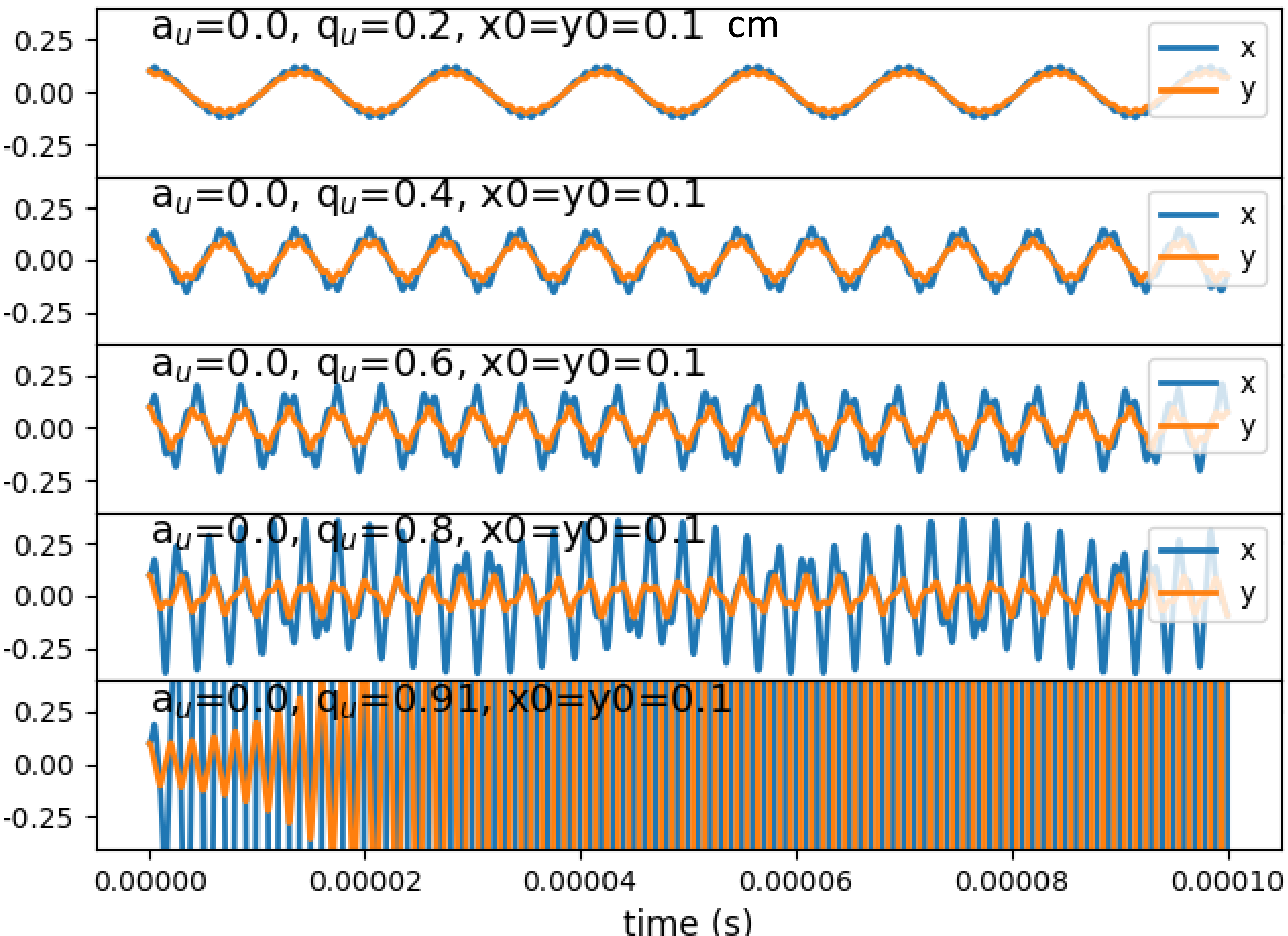
Phase=0



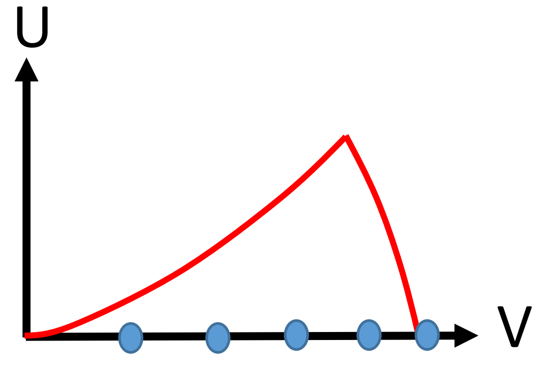


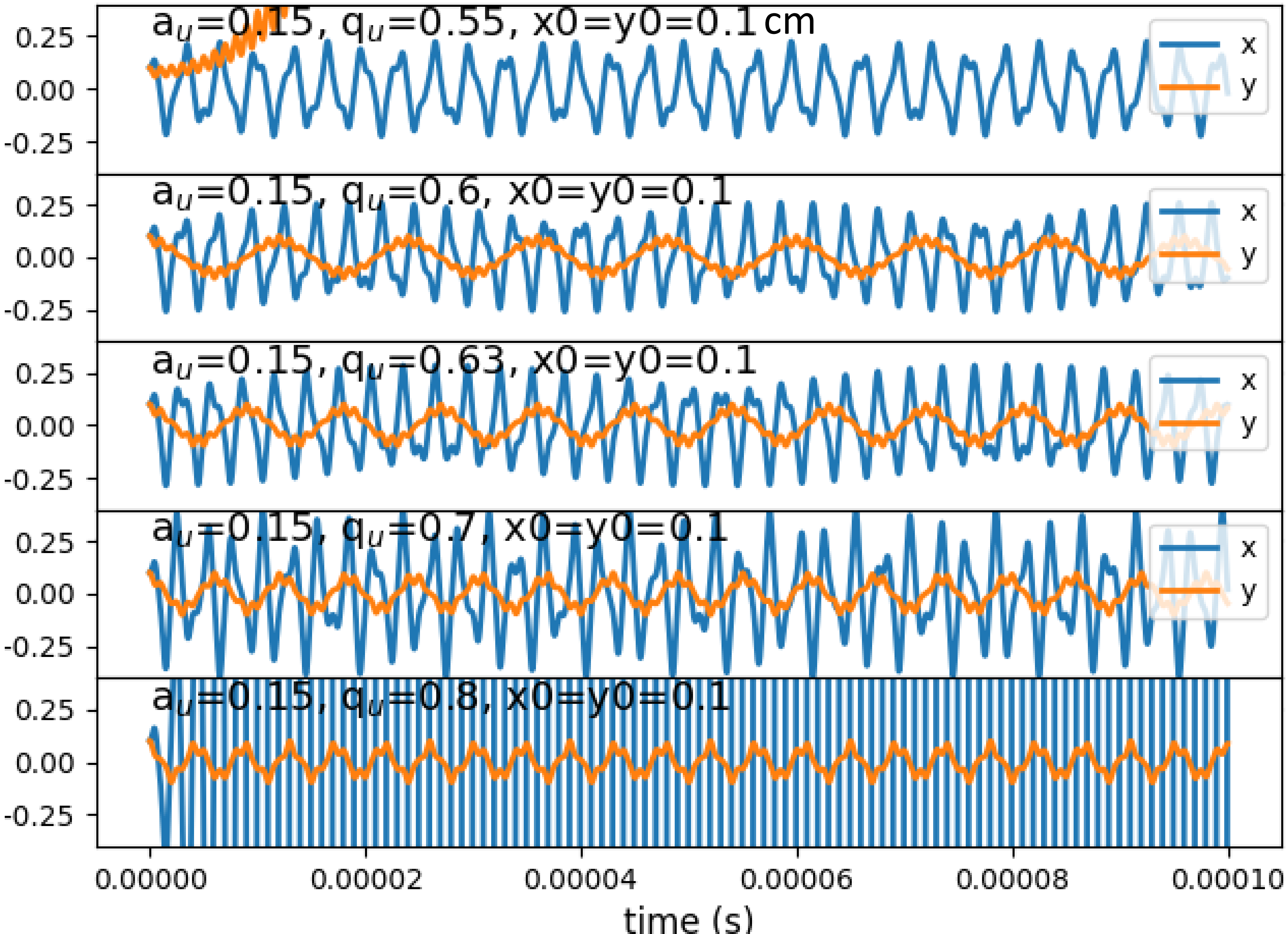

Initial velocity
Vx=Vy=0
Phase=0



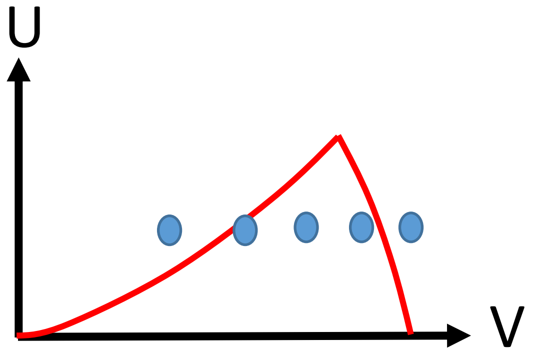


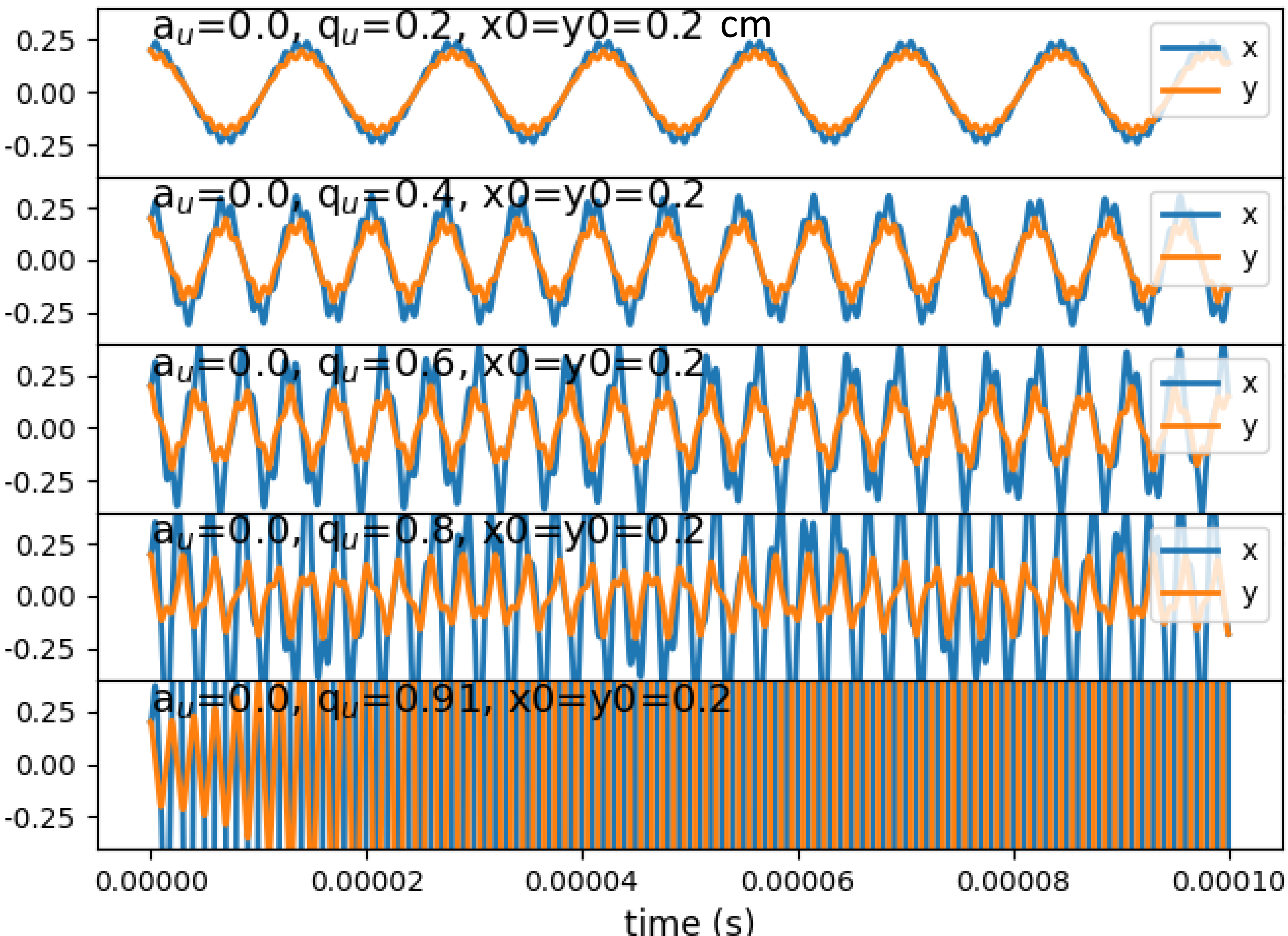

Initial velocity
Vx=Vy=0
Phase=0






Initial velocity
Vx=Vy=0
Phase=0






Initial velocity
Vx=Vy=0
Phase=0