Analytic Expression for Non-linear Ion Extraction Fields Which Yield Ideal Spatial Focusing in Time-of-flight Mass Spectrometry

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Abstract

One of the factors limiting the achievable mass resolution in time-of-flight mass spectrometers is the non-zero extent of the ion spatial distribution along the dimension parallel to the extraction axis. The effects of this spatial distribution are normally minimized by placing the detector at the position along the flight path where the temporal spread of an isomass ion packet is minimized. This position is known as the space-focus plane. In this paper, an analytic expression is obtained for the non-linear field in the extraction region which would yield theoretically perfect ion packet focusing at the space-focus plane. The mathematical techniques required are those commonly used in the solution of calculus of variations problems.

I. Introduction

A common embodiment of a time-of-flight (TOF) mass spectrometer as originally conceived by Wiley and McLaren [1] is schematically illustrated in Figure 1. It consists of an extraction region containing the initial distribution of ions to be accelerated, a second acceleration region external to the first, and a field-free drift region. The extraction and acceleration fields are created by applying appropriate voltages, as a step-function in time, to parallel wire grids which define the regions. The potential field distributions in these two regions are thus linear, generating uniform electric fields. Spatial focusing occurs due to the fact that ions further away from the exit grid of the extraction region gain more energy during the extraction process than those initially close to the exit. As the packet of ions travels through the drift region, the trailing ions eventually will overtake the lower energy leading edge, generating a packet of minimal temporal spread at a position known as the space-focus plane. The voltage applied to the acceleration region external to the extraction region can be used to tune the position of the space-focus plane, as well as affect the quality of the achieved minimum temporal spread.

The space focusing achievable using the above described linear extraction field is not ideal, i.e. the packet width at the space-focus plane is non-zero. However, it is clear that in principle, a non-linear potential distribution for the extraction region could be determined which would cause the space focus to be perfect. In this case, the potential of region II would remain linear, and the computed non-linear potential distribution in the extraction region would cause all ions of the same mass to arrive at the space-focus plane at identical times regardless of their relative starting position. Previous attempts to obtain the form of this ideal extraction potential field distribution have been approximate, e.g. representing the ideal field as a series of short segments of uniform electric field, and adjusting the magnitudes to obtain minimum packet width at the desired space-focus plane [2].

In this paper, an analytic expression is obtained for the non-linear potential which generates perfect spatial focusing. The mathematics required is that commonly used in calculus of variations problems, and the analytic closed-form solution obtained for the potential can be quickly verified to yield isochronous trajectories for all ions originating in the extraction region. The relatively simple form of this so-called “isochronous potential” allows it to be easily used for theoretical analyses of TOF systems, as well as for evaluating approximate physically realizable non-linear potentials.

II. Integral equation for the extraction potential

The equation that determines the behavior of the non-linear isochronous potential is derived by calculating the time of flight for an ion to travel from an arbitrary position in the extraction region to the space focus plane as defined in Figure 1. The first step in the derivation is to use the property of conservation of energy to determine an expression for flight times between two points under the effects of an arbitrary potential distribution. Restricting to one-dimensional motion along the x-axis, the energy of an ion with initial position and velocity x_0 and v_0 is given by

$$\frac{1}{2}mv^2(x) + q\Phi(x) = \frac{1}{2}mv_0^2 + q\Phi(x_0) \tag{1}$$

where $\Phi(x)$ is the scalar potential and q is the ion charge. Solving for $v(x)$, and integrating the instantaneous velocity yields the general expression for the elapsed time of flight between points x_0 and x

$$\Delta t = \int_{t_0}^{t} dt' = \left(\frac{m}{2q}\right)^{\frac{1}{2}} \int_{x_0}^{x} \frac{\mathrm{d}x'}{\left(\Phi(x_0) + mv_0^2/2q - \Phi(x')\right)^{1/2}}. \tag{2}$$

Equation (2) can be used to evaluate the elapsed time of flight for an ion in each of the three regions depicted in Figure 1. For region I, the initial velocity is zero, and the non-linear potential distribution is given by $U(x)$, where $U(0) = 0$. This yields

$$t_I = \left(\frac{m}{2q}\right)^{\frac{1}{2}} \int_{x_0}^{0} \frac{\mathrm{d}x'}{(U(x_0) - U(x'))^{1/2}}. \tag{3}$$

The elapsed times in regions II and III are exactly integrable. In region II, the potential drop is linear from $x = 0$ to $x = d$ and of magnitude $\Delta\phi$, giving

$$t_{II} = \left(\frac{m}{2q}\right)^{\frac{1}{2}}\left(\frac{2d}{\Delta\phi}\right)\left[(U(x_0) + \Delta\phi)^{1/2} - (U(x_0))^{1/2}\right]. \tag{4}$$

Region III is field-free, and has an elapsed time of flight given by

$$t_{III} = \frac{D}{\left(\frac{2q}{m}(U(x_0) + \Delta\phi)\right)^{1/2}}. \tag{5}$$

Defining the “mass normalized” time

$$\tilde{t} = \left(\frac{2q}{m}\right)^{1/2} t \quad , \tag{6}$$

the total normalized time of flight from position x_0 in the extraction region to the space focus plane is given by the sum of the times in the three regions

$$\tilde{T}(x_0) = \int_{x_0}^{0}\left(\frac{\mathrm{dx}'}{(U(x_0) - U(x'))^{1/2}}\right) + \frac{\left[(U(x_0) + \Delta\phi)^{1/2} - (U(x_0))^{1/2}\right]}{(\Delta\phi/(2\mathrm{d}))} \tag{7}$$

$$+ \frac{D}{(U(x_0) + \Delta\phi)^{1/2}}.$$

Equation (7) is the integral equation that defines the function $U(x)$. A concise statement of the problem of finding the isochronous potential required to give ideal space focusing is the following: Find the function $U(x)$ such that the computed time-of-flight $\tilde{T}(x_0)$ is independent of x_0, i.e.

$$\frac{\partial}{\partial x_0}\left(\tilde{T}(x_0)\right) = 0. \tag{8}$$

III. Solution of the integral equation

III.1 Rewrite using dimensionless variables

To further simplify the notation, scaled variables are defined:

$$\bar{x} \;=\; (x/d) \qquad\qquad \bar{D} \;=\; (D/d)$$

$$\bar{U}(x) \;=\; U(x)/\Delta\phi \tag{9}$$

$$\bar{T} \;=\; \Delta\phi^{1/2}\,\tilde{T}/d\,,$$

yielding a normalized integral equation

$$\bar{T} \;=\; \int_{\bar{x}}^{0} \frac{d\overline{x'}}{\left(\bar{U}(\bar{x}) - \bar{U}(\overline{x'})\right)^{1/2}} + 2\left[\left(1+\bar{U}(\bar{x})\right)^{1/2} - \left(\bar{U}(\bar{x})\right)^{1/2}\right] + \frac{\bar{D}}{\left(1+\bar{U}(\bar{x})\right)^{1/2}}\,. \tag{10}$$

It is further to be noted that the normalized time-of-flight $\bar{T}$ is required to be independent of $\bar{x}$, which implies that $\bar{T}$ can be evaluated using the right side of Equation (10) at the coordinate $\bar{x} \;=\; 0$, which yields $\bar{T} \;=\; (2+\bar{D})$. With this boundary condition, the simplified scaled integral equation for $\bar{U}(\bar{x})$ has the form

$$0 \;=\; \int_{\bar{x}}^{0} \frac{d\overline{x'}}{\left(\bar{U}(\bar{x}) - \bar{U}(\overline{x'})\right)^{1/2}} + 2\left[\left(1+\bar{U}(\bar{x})\right)^{1/2} - \left(\bar{U}(\bar{x})\right)^{1/2} - 1\right] \tag{11}$$

$$+\,\bar{D}\left[\frac{1}{\left(1+\bar{U}(\bar{x})\right)^{1/2}} - 1\right]\,.$$

III.2 Transform to differential equation using Laplace transforms and Convolution theorem

Problems of this sort can be solved by inverting the usual approach and treating $\bar{U}(\bar{x})$ as the independent variable, and $\bar{x}$ as the dependent variable. Defining the independent variable

$$\xi \equiv \bar{U}(\bar{x}) \tag{12}$$

and the variable of integration

$$\eta \equiv \bar{U}(\overline{x'}) \tag{13}$$

implies that the integration volume in Equation (11) is transformed by the relation

$$d\eta = \left| \frac{d\bar{U}(\bar{x}')}{d\bar{x}'} \right| d\bar{x}' . \tag{14}$$

The integral equation then takes the form

$$0 = \int_0^{\xi} \frac{F(\eta)}{(\xi - \eta)^{1/2}} d\eta + 2\left[(1+\xi)^{1/2} - \xi^{1/2} - 1 \right] + \bar{D}\left[\frac{1}{(1+\xi)^{1/2}} - 1 \right] \tag{15}$$

where

$$F(\eta) = \left| \frac{d\bar{U}(\bar{x}')}{d\bar{x}'} \right|^{-1} \tag{16}$$

is merely the Jacobian factor of the variable transformation.

In order to isolate the complicated behavior of the integral term in Equation (15), the entire expression is Laplace transformed, and the convolution theorem of Laplace transforms [3] employed. This theorem states that for

$$g(\xi) = \int_0^{\xi} f_1(\eta)\; f_2(\xi - \eta)\; d\eta \tag{17}$$

it can be shown that

$$\boldsymbol{L}[\, g(\xi)\,] = \boldsymbol{L}[\, f_1(\xi)\,] \quad \boldsymbol{L}[\, f_2(\xi)\,] \tag{18}$$

where $\boldsymbol{L}[f]$ denotes the Laplace transform of the function f. Under the Laplace transform, the integral Equation (15) becomes

$$0 = \boldsymbol{L}\left[\frac{1}{\xi^{1/2}} \right] \boldsymbol{L}[F(\xi)] + \boldsymbol{L}\left[2\left((1+\xi)^{1/2} - \xi^{1/2} - 1 \right) \right] + \boldsymbol{L}\left[\bar{D}\left(\frac{1}{(1+\xi)^{1/2}} - 1 \right) \right] . \tag{19}$$

Using the result [4] that

$$\boldsymbol{L}\left[\frac{1}{\xi^{1/2}} \right] = \sqrt{\frac{\pi}{s}} , \tag{20}$$

the complicated Jacobian factor can be isolated

$$\boldsymbol{L}[F(\xi)] = 2\sqrt{\frac{s}{\pi}}\; \boldsymbol{L}\left[1 + \xi^{1/2} - (1+\xi)^{1/2} \right] + \sqrt{\frac{s}{\pi}}\; \boldsymbol{L}\left[\bar{D}\left(1 - \frac{1}{(1+\xi)^{1/2}} \right) \right] . \tag{21}$$

Taking the inverse Laplace transform of the equation yields an expression for the Jacobian factor in terms of calculable functions

$$F(\xi) = 2\boldsymbol{L}^{-1}\left[\sqrt{\frac{s}{\pi}}\ \boldsymbol{L}\left[1+\xi^{1/2}-(1+\xi)^{1/2}\right]\right]+\boldsymbol{L}^{-1}\left[\sqrt{\frac{s}{\pi}}\ \boldsymbol{L}\left[\bar{D}\left(1-\frac{1}{(1+\xi)^{1/2}}\right)\right]\right]. \quad (22)$$

Recalling that $F(\xi)$ is merely the first derivative of the desired extraction potential as defined in Equation (16), and referring to the Appendix for the above Laplace and inverse Laplace transforms, a simple differential equation for the extraction potential can be determined

$$\left|\frac{\partial\bar{U}}{\partial\bar{x}}\right|^{-1} = 1 - \frac{2}{\pi}\operatorname{atan}\left(\bar{U}^{1/2}\right) + \frac{\bar{D}}{\pi}\frac{\bar{U}^{1/2}}{(1+\bar{U})}. \quad (23)$$

III.3 Solution of the differential equation and the non-linear extraction potential

The scalar potential function for the ideal extraction field can be easily determined from the differential equation (23). Changing the interpretation of the $\bar{x}$ variable to reference the magnitude of the distance behind the extraction grid rather than the (negative) coordinate along the x-axis, the variables $\bar{x}$ and $\bar{U}$ can be separated and integrated directly

$$\int_0^{\bar{x}} d\bar{x} = \int_0^{\bar{U}}\left[1 - \frac{2}{\pi}\operatorname{atan}\left(\bar{U}^{1/2}\right) + \frac{\bar{D}}{\pi}\frac{\bar{U}^{1/2}}{(1+\bar{U})}\right] d\bar{U}. \quad (24)$$

These integrals are well known [5], and yield a simple closed form expression for the ideal extraction field potential

$$\bar{x} = \frac{2(\bar{D}+1)}{\pi}\left(\bar{U}^{1/2} - \operatorname{atan}\left(\bar{U}^{1/2}\right)\right) + \bar{U}\left(1-\frac{2}{\pi}\operatorname{atan}\left(\bar{U}^{1/2}\right)\right). \quad (25)$$

This is our desired result of a simple closed form expression for the extraction field potential which will generate ions with zero temporal spread at the space focus plane.

IV. Solution verification

To verify that this expression for the extraction field potential generates a perfect spatial focus, a numerical simulation is performed. Choosing the geometrical ratio $\bar{D}$ to be 10 (i.e. the ratio of the field-free drift distance is 10 times the length of the post-extraction acceleration distance), the normalized potential $\bar{U}$ is determined by incrementing from the starting value of zero, computing $\bar{x}$ using equation (25), again incrementing $\bar{U}$, computing $\bar{x}$, and iterating until the potential is known over the entire length of the extraction region. The potential computed in this manner and the associated electric fields are plotted in Figures 2a and 2b respectively.

Next, individual ion trajectories are numerically calculated through the extraction and acceleration potentials, and their positions as a function of time determined. Assuming an initially uniform spatial distribution of ions in the extraction region, Figure 3 shows a series of "snapshots in time" of the ion packet as it approaches the specified space focus plane at $\bar{D} = 10$. Note the apparent zero width of the packet as it passes through the space focus plane, unambiguously verifying the validity of equation (25) as the expression for the ideal non-linear extraction field.

V. Conclusions

It has been demonstrated that an analytic closed-form solution exists for the ideal non-linear extraction fields required to give perfect spatial focusing in TOF applications. This result can be useful for designing improved non-linear extraction fields of the sort described in reference [2], as well as for studying the potential benefits to the resolution of TOF instruments via enhanced spatial focusing.

Appendix

In this section the Laplace and inverse Laplace transformations occurring on the right-hand side of Equation (22) are explicitly evaluated. These transforms as written can not be found in the standard Laplace transform tables, but using certain mathematical identities can be rewritten in known forms. The expression to evaluate has two terms

$$J_1 = 2\boldsymbol{L}^{-1}\left[\sqrt{\frac{s}{\pi}}\ \boldsymbol{L}\left[1 + \xi^{1/2} - (1+\xi)^{1/2}\right]\right] \tag{A1}$$

$$J_2 = \boldsymbol{L}^{-1}\left[\sqrt{\frac{s}{\pi}}\ \boldsymbol{L}\left[\bar{D}\left(1 - \frac{1}{(1+\xi)^{1/2}}\right)\right]\right]. \tag{A2}$$

The Laplace transform in Equation (A1) can be computed by using the identity [4]

$$s\boldsymbol{L}[f(\xi)] - f(0+) = \boldsymbol{L}[f'(\xi)] \tag{A3}$$

in the form

$$\boldsymbol{L}[f(\xi)] = \frac{1}{s}\ (\boldsymbol{L}[f'(\xi)] + f(0+)). \tag{A4}$$

Then J_1 becomes

$$J_1 = \boldsymbol{L}^{-1}\left[\sqrt{\frac{1}{\pi s}}\;\boldsymbol{L}\left[\frac{1}{\xi^{1/2}} - \frac{1}{(1+\xi)^{1/2}}\right]\right] \tag{A5}$$

which has Laplace transforms which exist in the standard tables, yielding

$$J_1 = \boldsymbol{L}^{-1}\left[\frac{1}{s}\left(1 - e^{S}\ \mathrm{erfc}(\sqrt{s}\,)\right)\right] = 1 - \boldsymbol{L}^{-1}\left[\frac{1}{s}\ e^{S}\ \mathrm{erfc}(\sqrt{s}\,)\right]. \tag{A6}$$

To evaluate this last expression, use the identity [3]

$$\frac{1}{s}\boldsymbol{L}\,[f(\xi)] = \boldsymbol{L}\left[\int_0^{\xi} f(y)\ dy\right] \tag{A7}$$

in the form

$$\boldsymbol{L}^{-1}\left[\frac{1}{s}\ \boldsymbol{L}\,[f(\xi)]\right] = \int_0^{\xi} f(y)\ dy\,. \tag{A8}$$

Thus J_1 can be put in the form

$$J_1 = 1 - \int_0^{\xi} \frac{1}{\pi y^{1/2}\,(1+y)}\ dy \tag{A9}$$

which immediately yields

$$J_1 = 1 - \frac{2}{\pi}\mathrm{atan}\left(\xi^{1/2}\right). \tag{A10}$$

The Laplace transforms and inverse transforms required in the evaluation of J_2 are in standard tables of Laplace transforms [4]. Looking up the inner transform in Equation (A2) yields

$$J_2 = \boldsymbol{L}^{-1}\left[\overline{D}\left(\frac{1}{\sqrt{\pi s}} - e^{s}\ \mathrm{erfc}\,(\sqrt{s})\right)\right] \tag{A11}$$

which further gives

$$J_2 = \frac{\overline{D}}{\pi}\ \frac{\xi^{1/2}}{(1+\xi)}\,. \tag{A12}$$

Equations (A10) and (A12) are the final expressions needed in the main text.

References

[1] W.C. Wiley and I.H. McLaren, Rev. Sci. Instrum., 26 (1955) 1150.

[2] B.D. Gardner, J.F. Holland, and V.B. Artaev, Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, Illinois, May 29-June 3, 1994.

[3] J. Mathews and R. Walker, “Mathematical Methods of Physics,” W. A. Benjamin, Inc., Menlo Park, CA, 1970.

[4] “Handbook of Mathematical Functions,” M. Abramowitz and I. Stegun, Eds., U.S. Government Printing Office, Washington, D.C., 1972.

[5] I. Gradshteyn and I. Ryzhik, “Table of Integrals, Series, and Products,” Academic Press, New York, NY, 1965.

Figure Captions

Fig. 1. Schematic illustration of a Wiley-McLaren style TOF mass spectrometer consisting of an extraction region, acceleration region, and drift region. The x-axis is orthogonal to the wire grids, and directed from the extraction region to the drift region.

Fig. 2a. The calculated isochronous potential which gives perfect ion spatial focusing. The normalized drift distance to the space focus plane, $\bar{D}$, is chosen to be 10. The potential is in units of $\Delta\phi$, the potential drop across the acceleration region.

Fig 2b. The calculated isochronous E-field which gives perfect ion spatial focusing. The normalized drift distance to the space focus plane, $\bar{D}$, is chosen to be 10. The E-field is in units of $\Delta\phi / d$, the uniform E-field across the acceleration region.

Fig. 3. Equally spaced time snap-shots of an isomass ion pulse as it approaches the space focus plane at $\bar{D} = 10$, for extraction fields corresponding to the isochronous fields plotted in Figure 2. The plots are normalized to have equal area under each snapshot, except for the plot at the space focus plane, which has zero width.

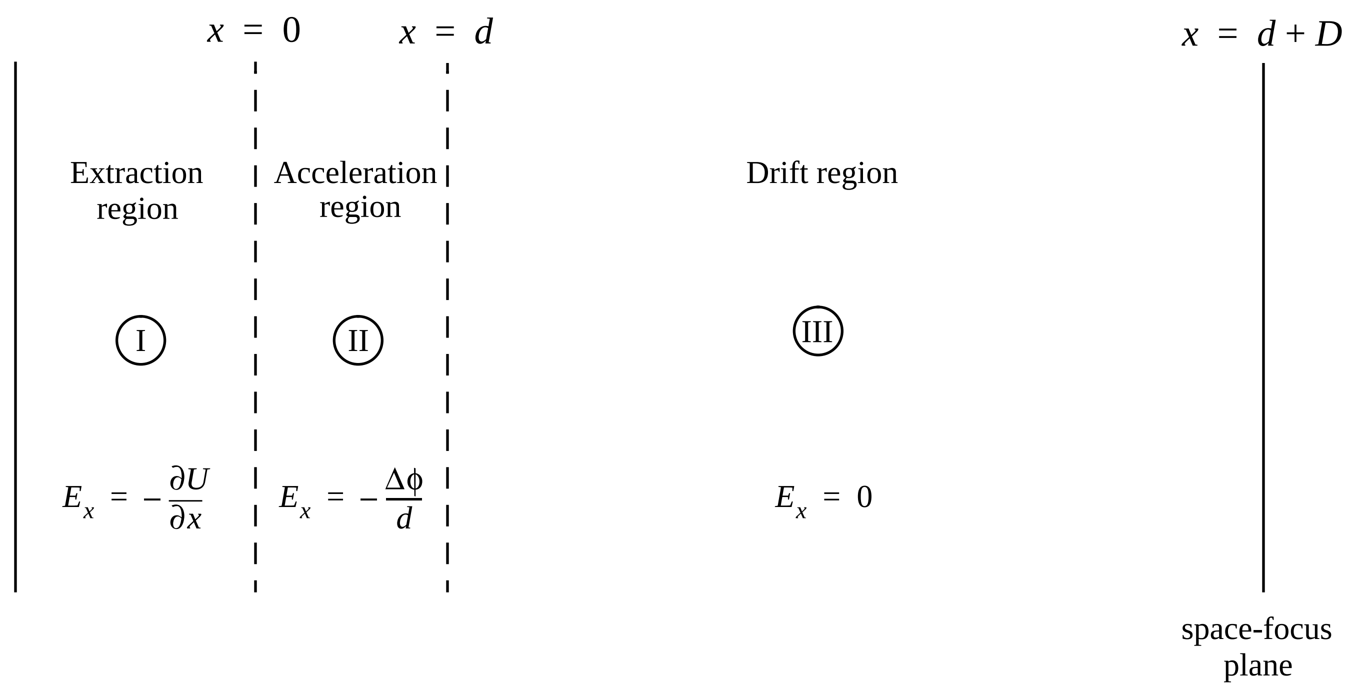
x = 0
x = d
x = d + D
Extraction region
Acceleration region
Drift region
I
II
III
E_x = −∂U/∂x
E_x = −Δϕ/d
E_x = 0
space-focus plane

Figure 1

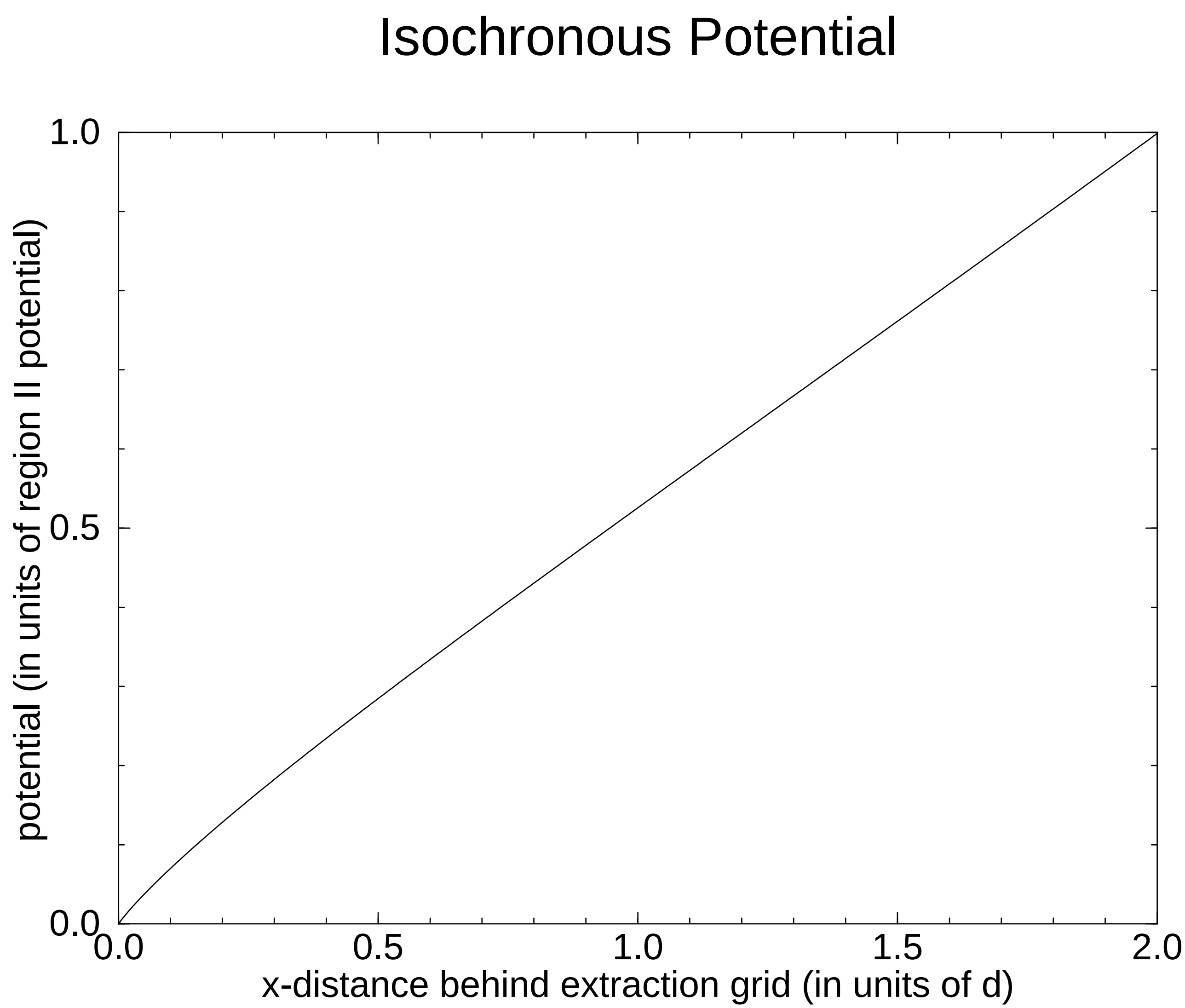
Isochronous Potential
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
potential (in units of region II potential)
x-distance behind extraction grid (in units of d)

Figure 2a

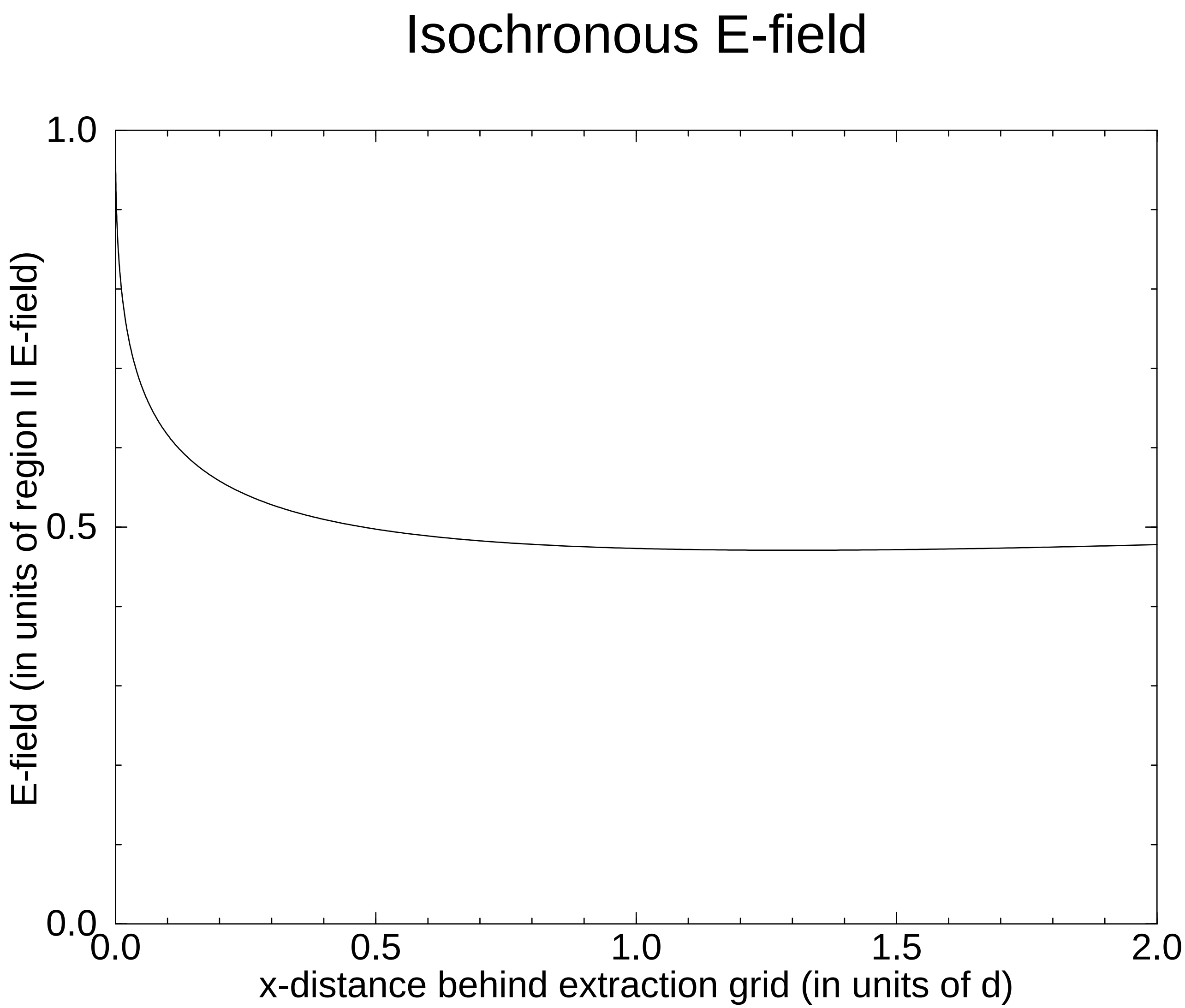
Isochronous E-field
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
E-field (in units of region II E-field)
x-distance behind extraction grid (in units of d)

Figure 2b

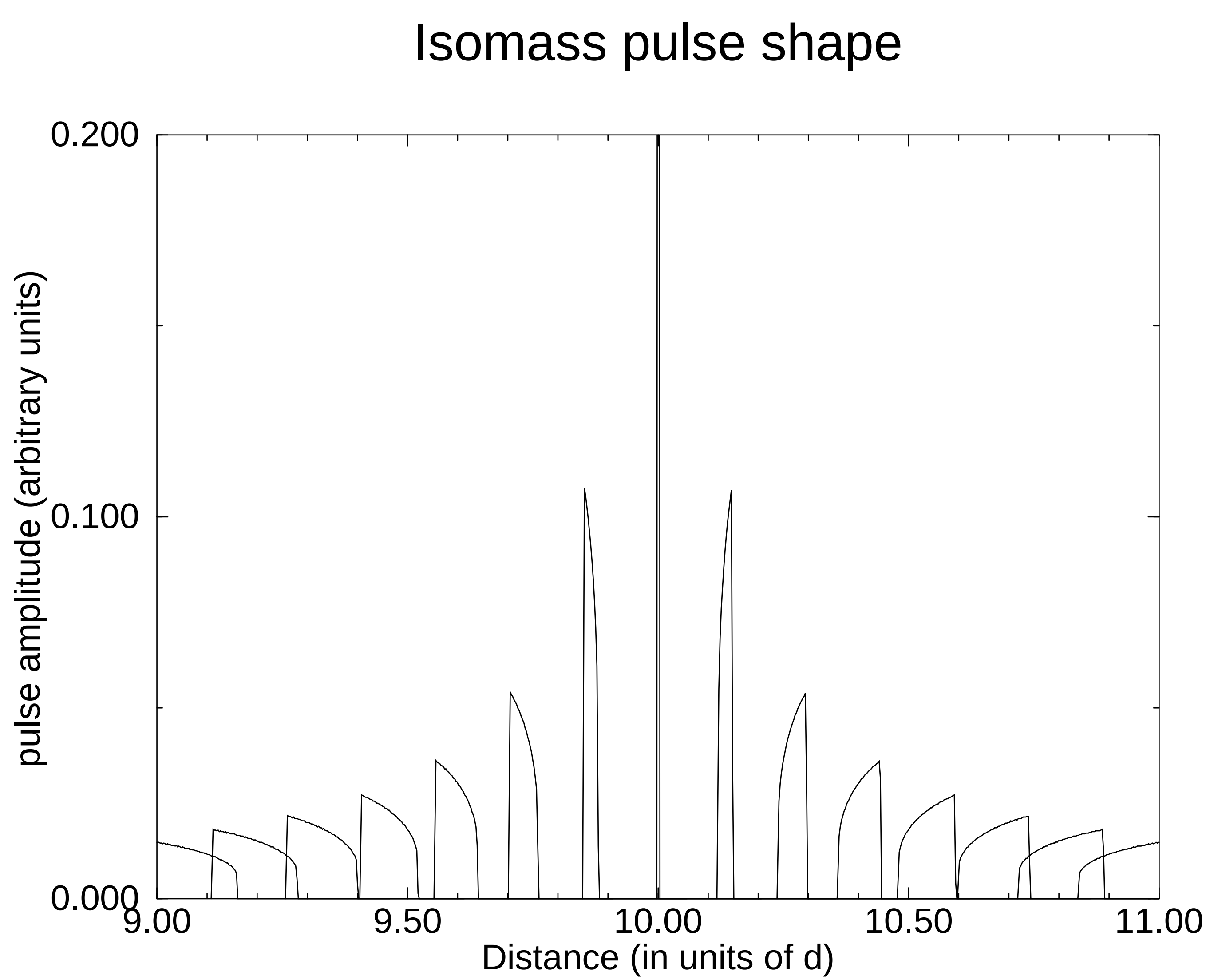
Isomass pulse shape
0.200
0.100
0.000
pulse amplitude (arbitrary units)
9.00
9.50
10.00
10.50
11.00
Distance (in units of d)

Figure 3