

NUMERICAL METHODS IN PHYSICS

First exercise Winter Semester 2013/2014 Matlab

Roots of real-valued functions

With respect to its mathematical/numerical and physical substance, this first exercise is quite easy. The intention is, however, to give those students who are not very familiar with the chosen programming language and the LINUX-operating system the opportunity to get used to both the language and the operating system.

Method:

- **Nested Intervals - NEW**
- **Gross search using iterative improving**

as treated in chap. 5 of the lecture notes.

The file

intsch.m

referring to the method of Nested Intervals can be found on the website of this course. It is a realization of the structure chart 15 in the lecture notes as a MATLAB-function; the program was written by my colleague Peter Lichtenberger in 2002 and underwent further improvements by Martin Ratschek in October 2006:

```
function nullst=intsch(fct,anf,aend,h,gen,varargin)
%
% intsch.m calculates the roots of a function given in fct using
% the method of Nested Intervals after performing a gross search
% with the step width h.
%
% Attention: 1. fct has to take the x values as a vector and return
%            the calculated y values as a vector of the same size.
%
% INPUT-parameters: fct      name of the function to investigate
%                   anf,aend start and end of the interval for the
%                   gross search
%                   h        step size for the gross search
%                   gen      accuracy limit
%                   varargin all other parameters for the function have
%                   to be passed in an array
%                   The function fct has to take the additional
%                   parameters in an enclosed array
%                   -> fct(x,param)
```

```

%
% OUTPUT-parameters:  nullst      vector containing the calculated roots
%
%
% COMMENT: If the function fct is defined in a separate file with the name
%          "aktuell", it can be passed in the following manner:
%          intsch(@aktuell,anf,aend,h,gen);

%          In that case, the function must be defined in the file
%          aktuell.m
%          Additional parameters can be passed in the variable 'varargin'.
%          One can also use the methods of "global variables".

% AUTHOR: Peter Lichtenberger
% DATE:   3.Oktober 2002
%
% Expanded: Martin Ratschek
% Date:   10. Oktober 2006

```

Comment: When calling `intsch.m` in MATLAB, one does not need a memory allocation for the array 'nullst' where the roots are stored. For that reason, the parameter ANZMAX mentioned in the structure chart 15 of the lecture notes is not required in the MATLAB-version!

On the definition of functions:

Let us assume the function `fctest` has the form `fctest(x; a, b)` where x is the independent variable and a and b act as parameters. The function will now be defined as an external MATLAB-file, where the parameter a is defined as a global variable and b is an element, which is transferred from the calling program to the function program.

This would look like:

File containing the calling program:

=====

```

.
.
global a
a= ...;

anf=...; aend=...; h=...; gen=...;
b=...;

nullst=intsch(@fctest,anf,aend,h,gen,b);

% The vector 'nullst' contains the roots in the interval
% anf <= x <= aend .

```

File with the name `fctest.m` containing the func-definitions:

```
=====
function fct=fcttest(x,b)
```

```
    global a
```

```
    fct = Function(x) incl. parameters a und b ;
```

In the second problem of this exercise, the gross search, should be combined with an iterative root calculation as treated in chap. 5.3.3 of the lecture notes. However, for MATLAB-Users, it makes sense to use the internal MATLAB routine

`fzero.m`

instead of the Newton-Raphson-program discussed in the lecture notes. Entering `help fzero` in the command line prints informations about the input and output parameters of `fzero`. It produces the following output:

fzero.m

```
function [b,fval,exitflag,output] = fzero(FunFcnIn,x,varargin)
%FZERO Scalar nonlinear zero finding.
% X = FZERO(FUN,X0) tries to find a zero of the function FUN near X0.
% FUN accepts real scalar input X and returns a real scalar function value F
% evaluated at X. The value X returned by FZERO is near a point where FUN
% changes sign (if FUN is continuous), or NaN if the search fails.
%
% X = FZERO(FUN,X0), where X0 is a vector of length 2, assumes X0 is an
% interval where the sign of FUN(X0(1)) differs from the sign of FUN(X0(2)).
% An error occurs if this is not true. Calling FZERO with an interval
% guarantees FZERO will return a value near a point where FUN changes
% sign.
etc.
```

Preparatory tasks

- Use `intsch.m` to calculate the roots of the equation for the energy eigenvalues in the lecture notes, p.156 (German script), using `intsch.m` and verify the energy eigenvalues of the potential well.
- Using `fzero.m`, calculate the roots of the energy eigenvalue equation from the lecture notes, p.156 (German script). The required initial intervals for `fzero` are calculated using a *gross search* as described in chap. 5.3.3 of the lecture notes. Check that you obtain the correct energy eigenvalues as listed on p.157 of the lecture notes.

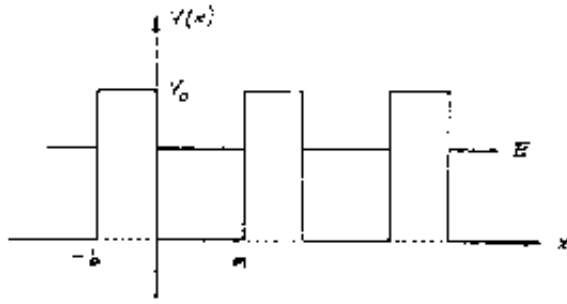


Figure 1: The Kronig-Penney-potential.

1. Task: Calculation of Kronig-Penney-energies

As mentioned before, the physical aspect (which is definitely very interesting) should remain a little in the background in favor of the 'technical-numerical' part of this exercise.

Just a few words on the theoretical aspects: an electron moves in the periodic potential of a linear chain of atoms. From quantum mechanics, the electron can only take certain (*allowed*) energy values E , which lie in fixed energy regions, the so-called **energy bands**. It can be shown (a detailed calculation can be found in numerous books about theoretical solid state physics) that one gets the edges of these bands by calculating the roots of the function:

$$\varphi(E) - 1 \quad \text{and} \quad \varphi(E) + 1 \quad (1)$$

where $\varphi(E)$ is defined as:

$$\varphi(E) = \frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh(\beta b) \sin(\alpha a) + \cosh(\beta b) \cos(\alpha a) \quad (2)$$

with

$$\alpha^2 = E \quad \text{und} \quad \beta^2 = V_0 - E \quad (3)$$

The parameters a , b and V_0 define the form of the atomic potential. In the 'Kronig-Penney-approximation', these are approximated as potential wells (see fig. 1): b and V_0 define the width and depth of a single potential and a is the spacing between two neighboring potentials. The energy E is limited to the potential interval, which means that

$$0 \leq E \leq V_0 \quad (4)$$

A note on units: we used the so-called *atomic units*. This means that the values a and b are measured in *Bohr lengths* and the potential V_0 and the energy E are given in *Rydberg*¹.

¹1 Bohr length is equal to 0.529 Angstroem, and 1 Rydberg is equal to 13.6 electron volts.

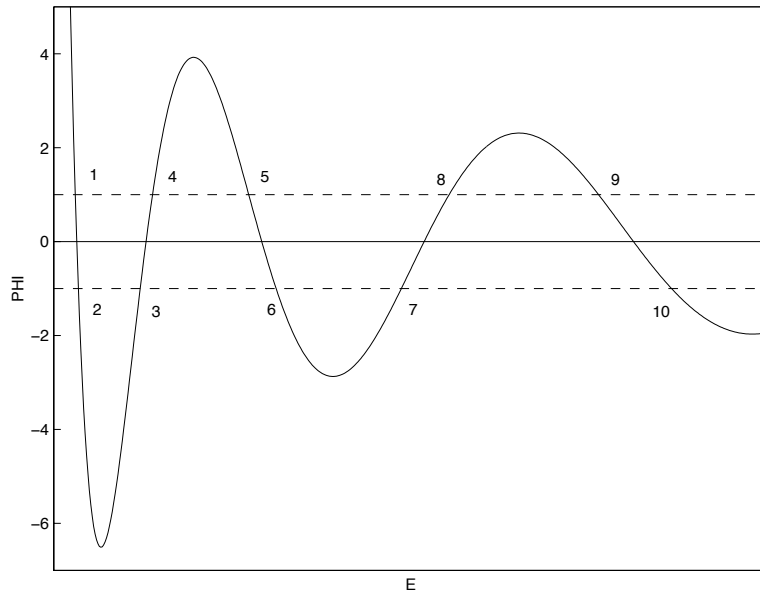


Figure 2: The Kronig-Penney-function $\varphi(E)$ and the definition of the energy bands (schematic).

Numerical solution of the problem

To solve the problem, we will use the method of *Nested Intervals*:

Calculate the roots (energies) of the function (1), with a maximum inaccuracy of 10^{-7} .

What is the physical meaning of the calculated roots? Let us take a look at fig. 2 which shows the function $\varphi(E)$. If one takes the intersections of the function with the horizontal lines at $y = +1$ and $y = -1$ as shown in the plot, one gets the following allowed areas for the energy (*bands*).

1. energy band from $E-1$ to $E-2$
2. energy band from $E-3$ to $E-4$
- .
- .
- etc.

Calculate such a table of energy values for a periodic arrangement of potential wells using the following parameters:

$$a = 6.48 \text{ Bohr} \quad b = 0.12 \text{ Bohr} \quad V_0 = 110.0 \text{ Rydberg}$$

2. Task: Calculation of the Maxwell-line of a van-der-Waals-gas

For this exercise, 2 routines are required. Both of them are already coded in MATLAB, namely the already discussed program `fzero.m` and

- a program for calculating the roots of a cubic equation:

`roots.m`

roots.m

```
function r = roots(c)
%ROOTS Find polynomial roots.
% ROOTS(C) computes the roots of the polynomial whose coefficients
% are the elements of the vector C. If C has N+1 components,
% the polynomial is C(1)*X^N + ... + C(N)*X + C(N+1).
%
```

Theoretical background

The van-der-Waals equation-of-state:

An equation-of-state of a thermodynamic system relates the state variables pressure, volume and temperature:

$$p = p(v, T)$$

A very good approximation for the equation-of-state for real gases is the van-der-Waals equation

$$p = \frac{RT}{(v-b)} - \frac{a}{v^2} \quad (5)$$

In (5), R is the general gas constant, while a and b are the so-called van-der-Waals-parameters, which can be found for many gases in numerous publications. The following figure shows three isotherms of a van-der-Waals-gas in a (p,v) -diagram.

Fig. 3 shows the most important properties of van-der-Waals-isotherms. A critical temperature T_{cr} exists. Isotherms with $T > T_{cr}$ are monotonically decreasing with increasing volume, isotherms with $T < T_{cr}$ however show distinct minima and maxima. The isotherm at the critical temperature have an inflection point with a horizontal tangent (point P in fig. 3). The coordinates of this inflection point (the so-called critical point) can be deduced from the gas equation (5). One gets:

$$T_{cr} = \frac{8a}{27Rb} \quad p_{kr} = \frac{a}{27b^2} \quad v_{kr} = 3b \quad (6)$$

For further calculations, it is convenient to write the van-der-Waals-equation (5) in reduced units:

$$\hat{p} \equiv \frac{p}{p_{kr}} \quad \hat{T} \equiv \frac{T}{T_{cr}} \quad \hat{v} \equiv \frac{v}{v_{kr}}$$

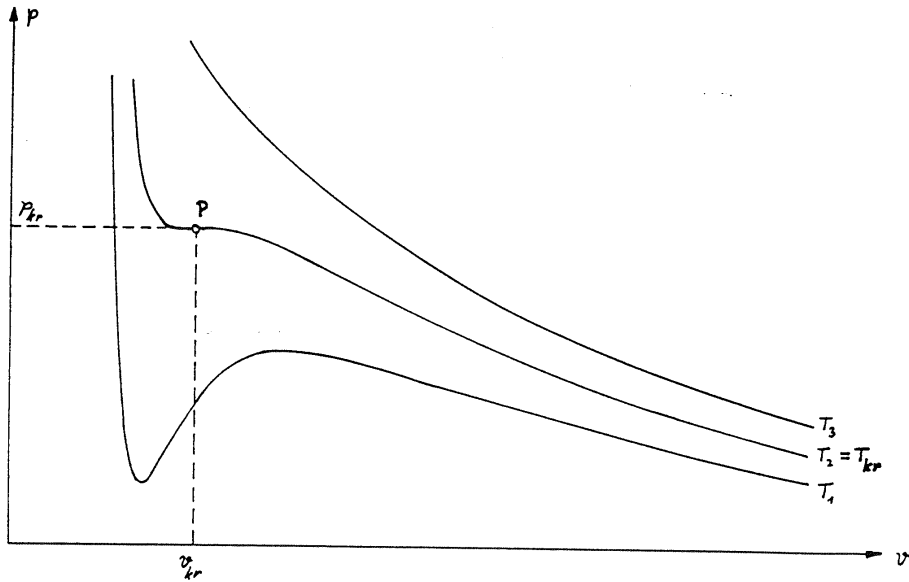


Figure 3: Isotherms of a van-der-Waals-gas: $T_1 < T_{cr}$, $T_2 = T_{cr}$, $T_3 > T_{cr}$.

One can show easily that this lead to the parameter-free equation-of-state

$$\hat{p} = \frac{8\hat{T}}{3\hat{v} - 1} - \frac{3}{\hat{v}^2} \quad (7)$$

The Maxwell-line

For further considerations, have a look at fig. 4: Consider a thermodynamic system completely in one phase (high volume, point A). Tracing the phase transition of the gas along an isotherm ($T < T_{cr}$) constantly decreasing the volume (arrow), the gas pressure increases at first. This increase of pressure should end at a certain maximum value (point B) and decrease with further compression of the gas. After reaching a minimal pressure (point C) the pressure should increase rapidly, a typical behaviour of a liquid.

Decreasing pressure when compressing a gas (B \rightarrow C) however is not seen in experiment!

In reality, the transition from the gas phase to the liquid phase happens in a slightly different way: The gas (A) is compressed until the point B_1 on the isotherm is reached. Upon further reduction of the volume, the gas starts to condense **at a constant pressure** p_o (line $B_1 \rightarrow C_1$). At the point C_1 , the condensation process is completed, a pure liquid phase exists, which reacts with high increase in pressure on further decrease of the volume. The line through \hat{p}_o parallel to the volume axis is called the Maxwell-line.

Conditions for the Maxwell-line

The pressure \hat{p}_o (reduced units) is given by the implicit equation

$$\int_{\hat{v}_{C_1}(\hat{p}_o)}^{\hat{v}_{B_1}(\hat{p}_o)} d\hat{v} \left\{ \frac{8\hat{T}}{3\hat{v} - 1} - \frac{3}{\hat{v}^2} - \hat{p}_o \right\} = 0 \quad (8)$$

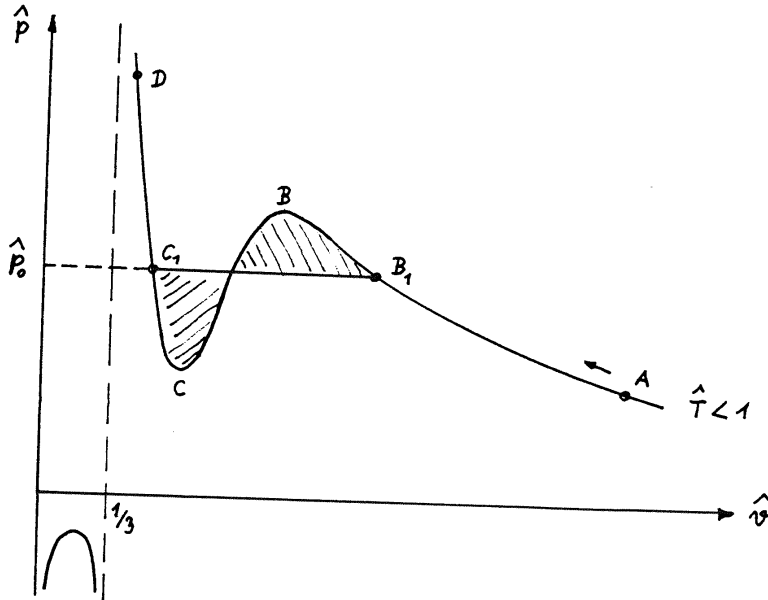


Figure 4: On the definition of the Maxwell-line.

which means that \hat{p}_o has exactly the value where the two shaded areas in fig. 4 cancel out. One has to consider that the limits of integration also depend on \hat{p}_o ! A theoretical deduction of this statement can be found in every book about thermodynamics².

Tasks

Develop a program you can use for a numerical calculation of the parameters of the Maxwell-line (\hat{p}_o , $\hat{v}_{B_1}(\hat{p}_o)$, $\hat{v}_{C_1}(\hat{p}_o)$) for every desired temperature $\hat{T} < 1$.

- In thermodynamics, the so-called locus of all points $\hat{v}_{B_1}(\hat{p}_o)$ and $\hat{v}_{C_1}(\hat{p}_o)$ for all temperatures in the interval $0 \leq \hat{T} \leq 1$ is of particular interest. In a (p,v)-diagram, this curve separates the areas with only one phase (liquid or gas) from those areas where a mixed phase can occur.

Print this limiting curve in a table which contains the numerical values of \hat{p}_o , $\hat{v}_{B_1}(\hat{p}_o)$ and $\hat{v}_{C_1}(\hat{p}_o)$ in the interval $0.20 \leq \hat{T} \leq 0.9999$ with $\Delta\hat{T} = 0.025$.

- **Furthermore, print the curve in a (p,v)-diagram.**
Comments: Range of the volume-axis: 0 to 10.

²e.g.: F. Reif, Statistik und Physik der Wärme, de Gruyter (1976) chap. 8.6, p.359.

Steps for this task

The problem can be solved as follows:

1. Fix a reduced temperature $\hat{T} < 1$.
2. Calculation of the pressure interval where the isotherm has 3 real-valued intersections with the line $p = const$. This region $\hat{p}_{min} \leq \hat{p} \leq \hat{p}_{max}$ can be found by calculating the roots of the first derivative of the gas equation (7):

$$\frac{d\hat{p}}{d\hat{v}} = -\frac{24\hat{T}}{(3\hat{v}-1)^2} + \frac{6}{\hat{v}^3} = 0$$

The resulting cubic equation for \hat{v} ,

$$4\hat{T}\hat{v}^3 - 9\hat{v}^2 + 6\hat{v} - 1 = 0 \quad (9)$$

has three real-valued roots $\hat{v}_1 < \hat{v}_2 < \hat{v}_3$. As seen in fig. 4 the extremal value belonging to \hat{v}_1 lies in the physically irrelevant region $\hat{v} < 1/3$. So one can state that

$$\hat{p}_{min} \equiv \hat{p}(\hat{v}_2) \quad \text{und} \quad \hat{p}_{max} \equiv \hat{p}(\hat{v}_3)$$

The numerical calculation of the roots of the cubic equation (9) should be done using the MATLAB-routine *roots.m*.

3. In the region $\hat{p}_{min} \leq \hat{p} \leq \hat{p}_{max}$, the isotherm always has 3 intersections with every line $\hat{p} = const$ with the corresponding volumes $\hat{v}_\alpha < \hat{v}_\beta < \hat{v}_\gamma$. Using

$$\hat{p} - \frac{8\hat{T}}{3\hat{v}-1} + \frac{3}{\hat{v}^2} = 0$$

the calculation of these \hat{v} -values again leads to a cubic equation which reads

$$3\hat{p}\hat{v}^3 - (\hat{p} + 8\hat{T}) \cdot \hat{v}^2 + 9\hat{v} - 3 = 0 \quad (10)$$

This equation can also be solved using *roots.m*.

Now \hat{p} has to be varied in the interval \hat{p}_{min} to \hat{p}_{max} until the integral condition (8) is satisfied, which means that the root of the function

$$F(\hat{p}) = \int_{\hat{v}_\alpha(\hat{p})}^{\hat{v}_\gamma(\hat{p})} d\hat{v} \left\{ \frac{8\hat{T}}{3\hat{v}-1} - \frac{3}{\hat{v}^2} - \hat{p} \right\} = 0 \quad (11)$$

has to be found. This root, which should be located using the Nested Intervals method (INTSCH.C), defines the Maxwell-pressure:

$$F(\hat{p}_o) = 0$$

Comments

- Calculate the values of the Maxwell-pressure \hat{p}_o and the corresponding volumes $\hat{v}_\alpha(\hat{p}_o)$ and $\hat{v}_\gamma(\hat{p}_o)$ for temperatures ranging from

$$0.2 \leq \hat{T} \leq 0.9999 \quad .$$

For reduced temperatures below 0.2, numerical results become unstable, since $\hat{p}_o < 10^{-6}$ and $\hat{v}_\gamma > 10^6!$

- When computing $F(\hat{p})$ according to eqn. (11), for $\hat{p} = \hat{p}_{min}$ problems can occur. To avoid this, start the *Maxwell-search* slightly below p_{min} , e.g. at

$$1.0000001 \hat{p}_{min} .$$

- For smaller values of \hat{T} , the pressure minimum becomes negative. But since for negative pressures, v_γ doesn't exist, in this case the search for the Maxwell-pressure has to start at $\hat{p} = 0!$