

NUMERICAL METHODS IN PHYSICS

First exercise Winter Semester 2013/2014 C

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**

as treated in chap. 5 of the lecture notes.

The routine

`intsch.c`

which is required for this exercise, can be found in the lecture notes (structure chart 15) and on the website of this course.

Usage of the routine INTSCH **new version**:

```
#include <stdio.h>
#include <math.h>
#include "nrutil.c"      //utility programs for dynamical storage
                        //taken from Numerical Recipes C
                        //on the website of this course.

double funcname(double x)
// Calculates the function values of 'F(x)'.
// Its name, which was chosen freely, has to be passed
// as the first parameter when calling intsch.
{
double f;

f= ... F(x) ...;

return f;
}

void intsch(double (*fct)(double),double anf, double aend, double h,
           double gen, int anzmax, double nullst[], int *anz)

/*
This program performs a gross search in the interval [anf,aend]
```

using the step width h . In case of a sign change of the function 'fct', Nested Intervals are performed, until the root of the function is known with the required accuracy 'gen'. All roots are being stored in the one-dim array 'nullst'. This array and the number of found roots ('anz') are returned to the program calling the routine. In case of an overrun of the array 'nullst', meaning that 'anz>anzmax', an error message is returned. For a detailed description, see chap. 5.5 in the lecture notes.

ATTENTION: It has proved to be virtually, that, when using INTSCH, it is convenient to choose the name of the function which roots are required from the program calling the routine. This is possible with the present version of INTSCH. As one can see, the first parameter of INTSCH reads

double (*fct)(double) : this means that inside INTSCH, everytime the function is being accessed, the wildcard fct is replaced by the actual name of the function defined in the program calling INTSCH, which has the form

```
&actual_name.
```

Naturally, a (double)-function with that particular name and which depends on one (double)-argument has to exist.

```
*/
... (*fct)(x) ...
}

int main()
{
// main program:   reading parameters,
//                size of the array 'nullst':
  int anzmax=100, ...;
  double *nullst;  // Def. one-dim array.

  nullst=dvector(1,anzmax);
  //Allocating the array 'nullst' using the
  //NRUTIL-routine 'dvector'.

//                calling INTSCH:

  intsch(&funcname,anf,aend,hgrob,gen,anzmax,nullst,&anz);

//          Here, the actual name of the function,
//          which roots are to be calculated, is required.

//                Returning the roots.

return (0)
}
```

Preparatory tasks

Calculate the roots of the equation for the energy eigenvalues in the lecture notes, p.156 (German script), and verify the energy eigenvalues of the potential well.

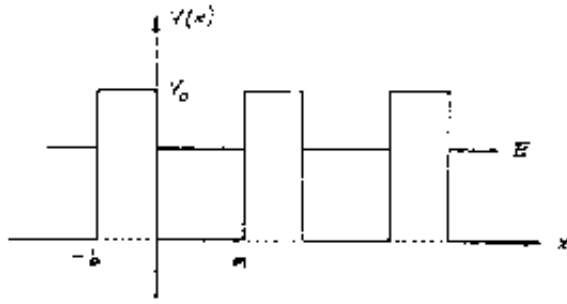


Figure 1: The Kronig-Penney-potential.

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.

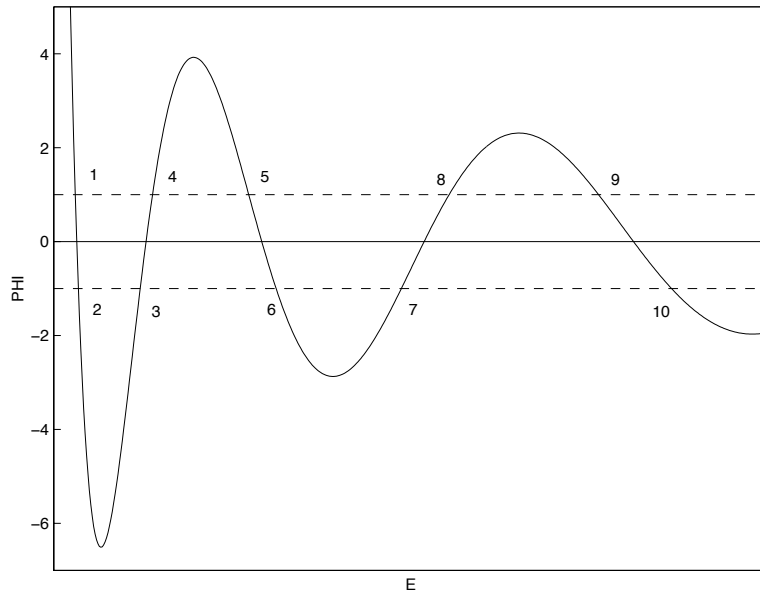


Figure 2: The Kronig-Penney-function $\varphi(E)$ and the definition of the energy bands (schematic).

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

The second program required for this exercise origins from *Numerical Recipes C*, p.184². It deals with the

real-valued solutions of a cubic equation with real-valued coefficients:

The equation

$$c_1x^3 + c_2x^2 + c_3x + c_4 = 0$$

resp.

$$x^3 + \frac{c_2}{c_1}x^2 + \frac{c_3}{c_1}x + \frac{c_4}{c_1} = 0$$

can be treated in the following manner:

For the cubic equation

$$x^3 + a_1x^2 + a_2x + a_3 = 0$$

with real-valued coefficients a_1 , a_2 and a_3 , the first step is to calculate

$$Q = \frac{a_1^2 - 3a_2}{9} \quad \text{und} \quad R = \frac{2a_1^3 - 9a_1a_2 + 27a_3}{54}$$

Next, one checks if $Q^3 - R^2 \geq 0$. If this holds, the equation has 3 real-valued roots. Those can be calculated using

$$\Theta = \arccos\left(\frac{R}{\sqrt{Q^3}}\right)$$

The roots read as

$$\begin{aligned}x_1 &= -2\sqrt{Q} \cos\left(\frac{\Theta}{3}\right) - \frac{a_1}{3} \\x_2 &= -2\sqrt{Q} \cos\left(\frac{\Theta + 2\pi}{3}\right) - \frac{a_1}{3} \\x_3 &= -2\sqrt{Q} \cos\left(\frac{\Theta + 4\pi}{3}\right) - \frac{a_1}{3}\end{aligned}$$

The required program KUBGL.C looks like this:

```
double min(double a,double b,double c)
{
    double wert;
    if(a<b && a<c) wert=a;
    if(b<a && b<c) wert=b;
    if(c<a && c<b) wert=c;
    return wert;
}
```

²The following equations can already be found in a work by Francois Viète named *De emendatione*, chap. VI (1615).

```

double max(double a,double b,double c)
{
    double wert;
    if(a>b && a>c) wert=a;
    if(b>a && b>c) wert=b;
    if(c>a && c>b) wert=c;
    return wert;
}

int kubgl(double c1, double c2, double c3, double c4, double *x1, double *x2,
          double *x3)

// PROGRAM FOR THE CALCULATION OF 3 REAL-VALUED ROOT OF A
// CUBIC EQUATION.

// INPUT-parameters:  c1  c2  c3  c4 : coefficients defining the equation
// OUTPUT-parameters: x1  x2  x3      : real-valued roots
//                    problem          : .false. = 3 real-valued roots
//                    : .true. = 1 real-valued,
//                    2 complex-conj. roots

{
    int problem;
    double a1,a2,a3,q,r,z1,z2,y1,y2,y3,theta;
    problem=0;

    a1=c2/c1;
    a2=c3/c1;
    a3=c4/c1;

    q=(a1*a1-3.e0*a2)/9.e0;
    r=(2.e0*pow(a1,3)-9.e0*a1*a2+27.e0*a3)/54.e0;

    if(pow(q,3)-r*r < 0.e0) {
        printf("IN KUBGL: EIN NULLSTELLENPAAR KONJ.-KOMPLEX\n");
        problem=1;
    }
    else {
        theta=acos(r/sqrt(pow(q,3)));
        z1=-2.e0*sqrt(q);
        z2=-a1/3.e0;

        y1=z1*cos(theta/3.e0)+z2;
        y2=z1*cos((theta+2.e0*M_PI)/3.e0)+z2;
        y3=z1*cos((theta+4.e0*M_PI)/3.e0)+z2;

        *x1=min(y1,y2,y3);
        *x3=max(y1,y2,y3);
        if(y1>*x1 && y1<*x3) *x2=y1;
        else if(y2>*x1 && y2<*x3) *x2=y2;
    }
}

```

```

    else *x2=y3;
  }
  return problem;
}

```

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.

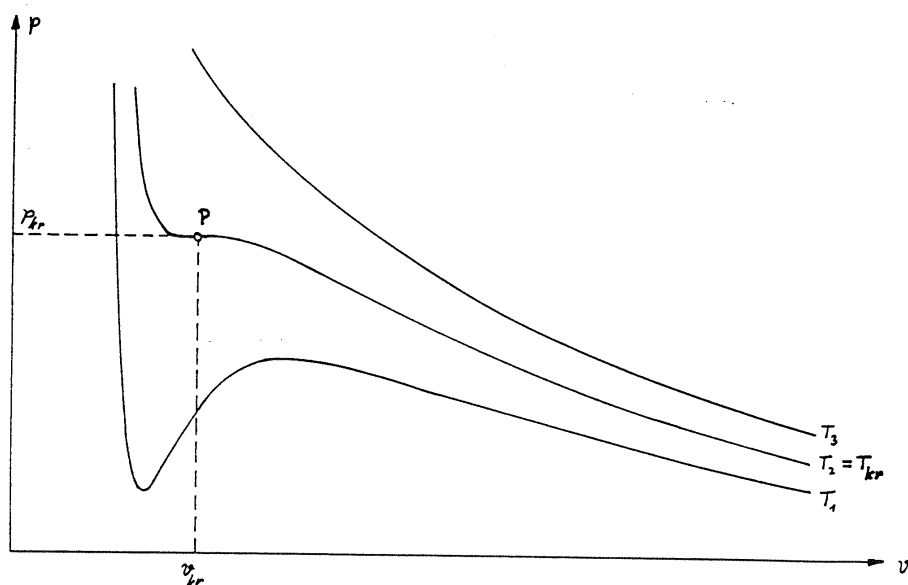


Figure 3: Isotherms of a van-der-Waals-gas: $T_1 < T_{cr}$, $T_2 = T_{cr}$, $T_3 > T_{cr}$.

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:

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

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.

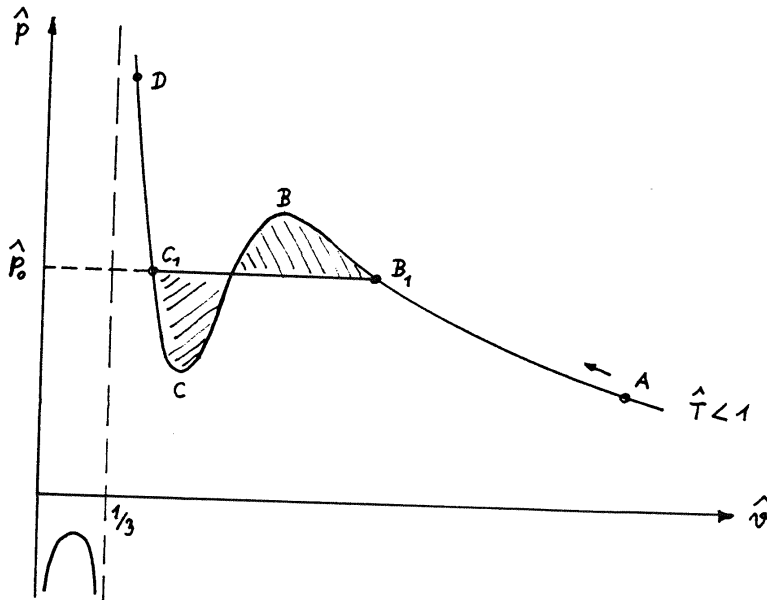


Figure 4: On the definition of the Maxwell-line.

Conditions for the Maxwell-line

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

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

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 thermodynamics³.

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.

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

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

³e.g.: F. Reif, Statistik und Physik der Wärme, de Gruyter (1976) chap. 8.6, p.359.

The numerical calculation of the roots of the cubic equation (9) could of course be done using INTSCH.C. But it is recommended to use the routine KUBGL.C.

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 KUBGL.C.

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 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 $\hat{p} = 0$!

General comments on creating plots using C

There are numerous possibilities to create plots and diagrams using C/C++. Here it should be noted, that a very effective and easy method is to store

data in a file and read the content of that file in MATLAB, where plots can be done easily. An alternative method would be to use *gnuplot* (<http://www.gnuplot.info>) instead of MATLAB.

There are a few (some rudimentary) interfaces for directly accessing gnuplot from C (e.g. `gnuplot_i`). Of course, such tools can be used as well, we however do not recommend them, since using such systems normally require an unreasonable amount of time to get used to them and we cannot guarantee any trouble-free function of such piping-systems.