

- Note: If you are used to working with function prototypes¹ you can ignore this note. Else, in C-programs you have to pay attention that all the program routines are arranged in the correct logical order.

The basic structure of your least-squares program could for instance look like that:

```
#include <stdio.h>
#include <math.h>

#include "nrutil.c"

void funcs(...)
{ .
  .
  .
}

#include "gnmcode.c"

int main()
{ .
  .
  .
  return 0;
}
// -----
```

Here are the headlines of the routines MRQMIN and FUNCS:

Headline of the function MRQMIN:

```
=====
int mrqmin(double x[], double y[], double sig[], int ndata, int ma,
           double a[], double **alpha, double **covar, double beta[],
           double *chisq, double *ochisq, double *alamda)
// This function performs an iteration step of the
// Gauss-Newton-Marquardt method.
// Return values of the funktion: 0   GNM-step was successful
//                               1   GNM-step was not successful.
// Modified version from C-NUMREC, p. 685f.
```

(for the meaning of the parameters, see lecture notes (German) section 4.5.5)

¹see e.g. *c_hilfe.txt*, topic nr. 8 on the website of this course

Headline of the procedure FUNCS:

```
=====
void funcs(double x, double a[], double *ymod, double dyda[], int ma)
{
    *ymod= ...           Model function
    dyda[1]= ...
    .                   derivatives of the model function
    .                   with respect to the fit parameters
    dyda[ma]= ...
}
```

Preparatory Exercise

Test your program using the example described in the lecture notes (German) on page 128ff. Below you find the corresponding citation:

We examine a radioactive compound that consists of a mixture of J radioactive isotopes. Both types of atomic nuclei decay, starting from an initial activity A_j with a half-life T_j , according to the *law of radioactive decay*:

$$A_j(t) = A_j e^{-\ln 2 \cdot t / T_j} \quad .$$

The total activity of the source is thus

$$A(t) = \sum_{j=1}^J A_j e^{-\ln 2 \cdot t / T_j} \quad .$$

The measurement is performed as follows: During a fixed time span Δ the decays originating from the source are counted and the result is saved. Then, the count is repeated for another time span Δ , etc. That way you get a series of count values Z_k , where

$$Z_k = C \cdot \int_{t=(k-1)\Delta}^{k\Delta} dt A(t) \quad (k = 1, 2, \dots) \quad .$$

The constant C is a measure of the sensitivity of the counting apparatus.

Of course, an experiment like that is a typical counting experiment, i.e. the measured values lie on a *Poisson distribution* around their expectation value (see page 102f., German version).

By evaluating the above integral you get the model function with $2J$ parameters:

$$Z(k; A_1, \dots, A_J, T_1, \dots, T_J) = \sum_{j=1}^J \left(C \frac{A_j}{\ln 2} \right) T_j \left(e^{+\Delta \ln 2 / T_j} - 1 \right) e^{-\Delta \ln 2 \cdot k / T_j} \quad .$$

The derivatives $\partial Z / \partial A_j$ and $\partial Z / \partial T_j$ can easily be calculated from this formula. For the given example, the routine *funcs.c* which you have to write as a user of *mrqmin.c* and *mrqcof.c*, could look like the following:

```

#define DELTA 15.0    // constant of the experiment
void funcs(double x, double a[], double *z, double dzda[], int ma)
// C-VERSION
{
    int  mterm,j,ind;
    double con,fac1,fac2,fac3,fac4;
    con=DELTA*log(2.0);
    mterm=ma/2;
    *z=0.0;
    for(j=1;j<=mterm;j++) {
        ind=mterm+j;
        fac1=con/a[ind];
        fac2=exp(fac1);
        fac3=fac2-1.0;
        fac4=exp(-fac1*x);

        dzda[j]=a[ind]*fac3*fac4/log(2.0);
        *z=*z + a[j]*dzda[j];
        dzda[ind]=a[j]/log(2.0)*fac4*(fac3*(1.0+fac1*x)-fac1*fac2);
    }
}

```

Now the description of the actual example:

The count rates of a radioactive compound consisting of two components (i.e. $J = 2$) were measured. In total 40 measurements were performed, each for a time span of $\Delta = 15$ seconds.

40 data points:

1	15376.0	21	981.0
2	10903.0	22	939.0
3	7950.0	23	857.0
4	5865.0	24	790.0
5	4653.0	25	814.0
6	3721.0	26	766.0
7	3089.0	27	691.0
8	2683.0	28	681.0
9	2396.0	29	614.0
10	1992.0	30	576.0
11	1910.0	31	529.0
12	1820.0	32	488.0
13	1726.0	33	472.0
14	1600.0	34	464.0
15	1495.0	35	434.0
16	1410.0	36	380.0
17	1271.0	37	382.0
18	1197.0	38	365.0
19	1106.0	39	387.0
20	1004.0	40	296.0

These 40 data points (Poisson statistics !) can be found in the file gnmtest.txt.

```

GNM-Parameters:      guessed values:  C*A1 = 2000.0
=====              C*A2 =  500.0
                          T1 =   30.0 s
                          T2 =  200.0 s

                      rel. precision  EPS =   0.00001

```

The course of the iteration using the Gauss-Newton-Marquardt method:

t	chisq	C*A1	C*A2	T1	T2
0	196876.304	2000.000	500.000	30.000	200.000
1	1233.069	976.760	237.577	26.378	184.784
2	45.645	998.414	229.228	22.949	172.341
3	43.535	1005.360	226.315	23.159	173.250
4	43.535	1005.458	226.349	23.153	173.245
5	43.535	1005.457	226.348	23.153	173.246

Convergence was reached!

VARIANCE = 1.209 (should be between 0.764 and 1.236)

	model parameter	SD
C*A1	1005.457	10.182
C*A2	226.348	4.129
T1(s)	23.153	0.353
T2(s)	173.246	2.320

Covariance matrix:

	C*A1	C*A2	T1	T2
C*A1	1.0000	-0.0494	-0.4642	0.0811
C*A2	-0.0494	1.0000	-0.7345	-0.9370
T1	-0.4642	-0.7345	1.0000	0.6405
T2	0.0811	-0.9370	0.6405	1.0000

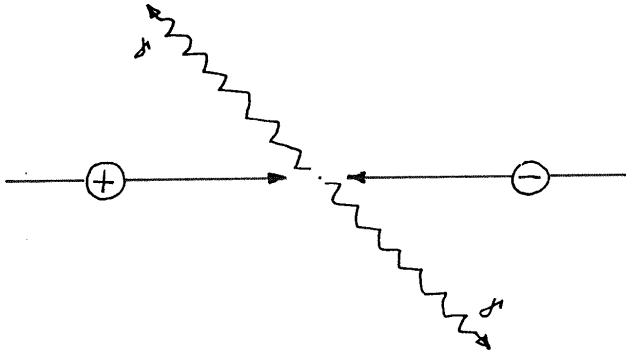


Figure 1: Schematic of a 2γ positron electron annihilation.

Task 1

Application of the least-squares method for non-linear model functions (Gauss-Newton-Marquardt-Method) to the problem of the statistical analysis of positron angular correlation spectra.

Theoretical Foundations

If you shoot *positrons* (= antiparticles of electrons) into matter, after a relatively short time span the positrons *annihilate* with the electrons in the matter (particle-antiparticle annihilation). The energy thereby released and the total momentum of every $e^+ - e^-$ pair are carried away by (usually two) annihilation photons γ (see figure 1).

Therefore the two annihilation photons contain information about the total momentum of the $e^+ - e^-$ -pair

$$\vec{p} = \vec{p}_+ + \vec{p}_- \quad .$$

As in most of the cases the momentum of the positron is much lower than the momentum of the electron, the following approximation is valid:

$$\vec{p} \approx \vec{p}_- \quad .$$

That is, the experimental analysis of annihilation radiation allows us to determine the *momentum distribution of the electrons in the specimen*.

How is it now possible to determine the momenta \vec{p} from the measured photon radiation? Suppose the annihilating $e^+ - e^-$ pair had no momentum ($\vec{p} = 0$). In that case the two annihilation photons would have to fly away in *exactly diametral* directions (conservation of momentum!). In the case $\vec{p} \neq 0$ the two photons would have to carry away a resulting momentum \vec{p} , which means that they fly away with an angle different from 180 degrees (figure 2).

The angle Θ , describing the deviation from 180 degrees, is related to \vec{p} approximately as

$$\Theta \approx \frac{|\vec{p}|}{m_0 c} \quad (1)$$

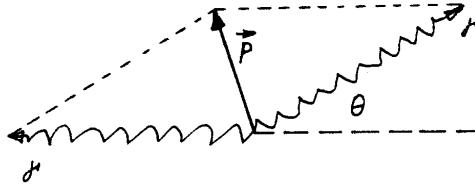


Figure 2: The direction of the two annihilation photons.

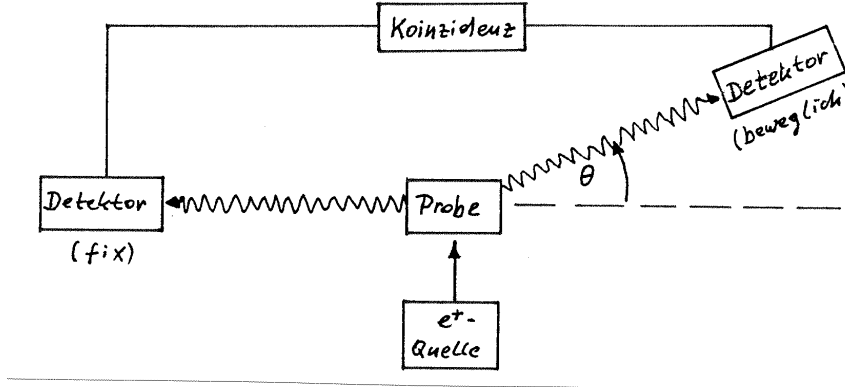


Figure 3: Principle of the angular correlation method.

(m_0 ... rest mass of electron and positron, c ... speed of light). As $|\vec{p}| \ll m_0 c$ this angle is relatively small and is usually given in milli-radians (mrad).

The angular correlation method

is based on this relation (figure 3): The positrons coming from the e^+ source penetrate the sample and annihilate there. The annihilation photons are registered using two detectors: one detector is mounted on a fixed position while the other can move to different angles Θ . The two detectors are operated *in coincidence*, i.e. only photons belonging to the same annihilation process are registered. Thus you get an angular distribution of the electron momenta $N(\Theta)$. This experimental method is called *Angular Correlation of Annihilation Radiation (ACAR) method* in the literature.

Figure 4 shows a typical ACAR spectrum of a metallic specimen. It is a Gauss-shaped distribution with a parabola put on top. It is not possible to discuss the cause for this special shape of the ACAR curves in this short problem description. Here the results:

The parabolic portion of the ACAR measurement results from the annihilation of the positrons with *nearly-free valence electrons*. As these electrons can only have a momentum between zero and the so-called Fermi momentum p_F , the parabola cuts off abruptly at the corresponding angles

$$\pm\Theta_F = \pm \frac{p_F}{m_0 c}$$

(*Fermi cut-off angle*).

The Gaussian portion of the ACAR distribution results from the annihilation of the positrons with stronger bound electrons [*core electrons* or *d-electrons* in transition metals (Ni, Pd, ...) and noble metals (Cu, Ag, Au, ...)].

The model function

The ideal model function can be written as:

$$N_{ideal}(\Theta) = \begin{cases} A \cdot (1 - \Theta^2/\Theta_F^2) + \hat{B} \cdot \exp(-\hat{C} \cdot \Theta^2) & |\Theta| \leq \Theta_F \\ \hat{B} \cdot \exp(-\hat{C} \cdot \Theta^2) & |\Theta| > \Theta_F \end{cases} \quad (2)$$

with the model parameters

A = amplitude of the parabola,

\hat{B} = amplitude of the Gaussian,

\hat{C} = width of the Gaussian distribution,

Θ_F = angle of the Fermi cutoff.

But equation (2) does not yet qualify as a model function for an experimentally obtained ACAR spectrum, because (2) describes the ideal situation, where the measuring apparatus does *not* have *any measurement uncertainty*. However, in reality the apparatus only has a *limited resolution*; therefore the *resolution function* $R(\Theta)$ has to be included in a real model:

$$N(\Theta) = \int_{y=-\infty}^{+\infty} dy \quad R(\Theta - y) \cdot N_{ideal}(y) \quad . \quad (3)$$

Most of the time the resolution function can be described quite well by a Gaussian function normalized to one, i.e. by

$$R(\Theta) = \frac{1}{\sqrt{\pi}s} \cdot \exp\left[-(\Theta/s)^2\right] \quad , \quad (4)$$

where s is the width of the resolution function: the smaller s , the better the quality of the experiment. However, this s is not a fitting parameter, but a fixed (and known) characteristic of the measuring apparatus; **please note the corresponding remarks on page 10/11 in this exercise description.**

When you plug (4) and (2) into the integral (3), you get the final (real) model function

$$N(\Theta) = \frac{1}{\sqrt{\pi}s} \left\{ A \int_{y=-\Theta_F}^{+\Theta_F} dy \left(1 - \frac{y^2}{\Theta_F^2}\right) \cdot \exp\left[-\left(\frac{\Theta - y}{s}\right)^2\right] + \hat{B} \int_{y=-\infty}^{+\infty} dy \exp\left[-\left(\frac{\Theta - y}{s}\right)^2\right] \cdot \exp(-\hat{C}y^2) \right\} + U \quad , \quad (5)$$

where a constant *background* term U was included (this term is necessary for reasons not discussed here).

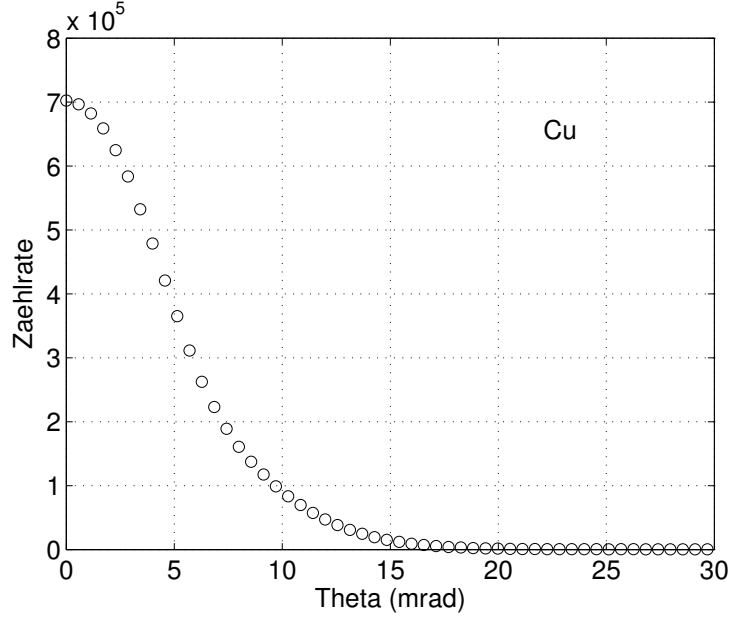


Figure 4: ACAR-spektrum of a metallic copper sample.

After the evaluation of both the integrals we finally get

$$\begin{aligned}
N(\Theta) = & A \cdot \left\{ \frac{1}{2} \left[\left(1 - \frac{\Theta^2}{\Theta_F^2} \right) - \frac{s^2}{2\Theta_F^2} \right] \cdot \left[\operatorname{erf} \left(\frac{\Theta + \Theta_F}{s} \right) - \operatorname{erf} \left(\frac{\Theta - \Theta_F}{s} \right) \right] + \right. \\
& + \frac{s}{2\sqrt{\pi}\Theta_F^2} \left[(\Theta + \Theta_F) \exp \left\langle - \left(\frac{\Theta - \Theta_F}{s} \right)^2 \right\rangle - (\Theta - \Theta_F) \exp \left\langle - \left(\frac{\Theta + \Theta_F}{s} \right)^2 \right\rangle \right] \left. \right\} + \\
& + B \cdot \exp(-C\Theta^2) + U. \tag{6}
\end{aligned}$$

Note that in equation (6) the quantities B and C were introduced. They are defined as

$$B = \frac{\hat{B}}{\sqrt{1 + \hat{C}s^2}} \quad \text{and} \quad C = \frac{\hat{C}}{1 + \hat{C}s^2} .$$

An unpleasant formula:

As the theory of the Gauss-Newton method shows (see lecture notes [German], section 4.5.3), in order to apply this method we need to evaluate the model function *and all its partial derivatives with respect to all fit parameters*.

If you look at the actual model function (6), this task is a bit cumbersome, but not particularly difficult. Bigger problems might be encountered in the calculation of the derivative of $N(\Theta)$ with respect to the parameter Θ_F . The result of this calculation is:

$$\frac{\partial N(\Theta)}{\partial \Theta_F} = A \frac{(2\Theta^2 + s^2)}{2\Theta_F^3} \left[\operatorname{erf}\left(\frac{\Theta + \Theta_F}{s}\right) - \operatorname{erf}\left(\frac{\Theta - \Theta_F}{s}\right) \right] - A \frac{s}{\sqrt{\pi}\Theta_F^3} \left[(\Theta + \Theta_F) \exp\left\{-\left(\frac{\Theta - \Theta_F}{s}\right)^2\right\} - (\Theta - \Theta_F) \exp\left\{-\left(\frac{\Theta + \Theta_F}{s}\right)^2\right\} \right]. \quad (7)$$

Equation (6) and (7) contains the so-called *error function*, which is defined as follows:

$$\operatorname{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x dz e^{-z^2}.$$

In C this function is available as *erf(x)*.

Numerical evaluation of a spectrum

This task is about approximating the measured decay rates $N_M \equiv N_{\text{measurement}}$ at the angles Θ_k , $k = 1, \dots, n$ using the model (6):

$$\chi^2 = \sum_{k=1}^n g_k [N_M(\Theta_k) - N(\Theta_k; A, \Theta_F, B, C, U)]^2 \longrightarrow \text{minimum}. \quad (8)$$

The model function contains as fit parameters the amplitude A of the parabola part and the Fermi cut-off angle Θ_F , the amplitude B of the Gaussian part and the parameter C describing the width of the Gaussian curve, and the measuring background U .

A few words about the weighting factors g_k : they are calculated automatically in the routine *mrqmin*, using the formula (4.5) in the lecture notes (German):

$$g_k = \frac{1}{\sigma_k^2}.$$

Here, σ_k is the *standard deviation of the k^{th} measured value*; as the ACAR-experiment is a typical counting experiment as described in the lecture notes (see section 4.3.3 [German]), these values obey Poisson statistics, i.e.

$$\sigma_k \approx \sqrt{N_M(\Theta_k)}.$$

Important remark: please do not confuse the standard deviations of the measured values (σ_k , $k = 1, \dots, n$) with the width of the resolution function s of the apparatus, which was introduced in equation (4). **The one has nothing to do with the other.**

Task

- Develop a program which allows you to perform a statistical least-squares analysis with the model function (6). Use the **Gauss-Newton-Marquardt** method.
- For all the analyses you perform, s is

$$s = 2.06833291 \text{ mrad.}$$

- All fit parameters have to be calculated to a relative precision of 0.000001.

An example for testing purposes

Check the correctness of your program using the following test spectrum for aluminium:

Al_Testspektrum

This spectrum contains 256 values (angle interval from 0 to about 145 mrad); it was simulated on the computer and contains no statistical uncertainties. Therefore you should obtain the result

$$\chi^2 \rightarrow 0$$

in this test.

The aim of this test is for you to check whether you have programmed the model function and its derivatives correctly. Continue only after you have made sure that your program yields the following results:

Al_Testspektrum

tmax = 100 eps = 0.100000E-05

FIXED value for the resolution function: s = 2.06833291 mrad

INITIAL VALUES for the 5 fit parameters:

a(1) = A = 0.4000000E+06

a(2) = Theta-F = 0.6900000E+01

a(3) = U = 0.1500000E+03

a(4) = B = 0.9300000E+05

a(5) = C = 0.2300000E-01

ITERATION STEPS:

	chi-sq	a1	a2	a3	a4	a5
0	0.929E+04	0.400000E+06	0.690000E+01	0.150000E+03	0.930000E+05	0.230000E-01
1	0.264E+02	0.391290E+06	0.692998E+01	0.202988E+03	0.114981E+06	0.240534E-01
2	0.639E-02	0.390010E+06	0.693100E+01	0.202997E+03	0.116290E+06	0.239983E-01
3	0.573E-02	0.389999E+06	0.693100E+01	0.202997E+03	0.116301E+06	0.239999E-01
4	0.573E-02	0.389999E+06	0.693100E+01	0.202997E+03	0.116301E+06	0.239999E-01

Results using MRQMIN and MRQCOF:

model parameters: standard deviation:

A	0.39000E+06	0.16447E+04
Theta-F	6.931	0.005
U	0.20300E+03	0.94987E+00
B	0.11630E+06	0.16728E+04
C	0.24000E-01	0.12059E-03

The variance = 0.000 should be between 0.911 and 1.089.

Please note that due to the missing statistical deviations of the input values in this test the results *standard deviation of the fit results* and *variance* have no meaning.

Two sample applications

Now apply your well-tested program to the two measured ACAR spectra

Al_Spektrum and Cu_Spektrum

of an aluminium sample and a copper sample. Both spectra contain 256 values as well and include an angle interval from 0 to about 145 mrad.

Evaluation of the fit results and their physical interpretation

1. Calculate the amplitude A and B , the Gaussian width C , the background U and the Fermi cut-off angle Θ_F with their respective standard deviations.
2. Using the variance, determine whether the model (6) is a 'good' model as discussed in the lecture notes.
3. Mainly for metallic solids the Fermi cut-off angle is a physically interesting quantity, as this angle is related to the so-called Fermi momentum p_F in (1) via²

$$p_F \approx m_0 c \cdot 10^{-3} \cdot \Theta_F \quad \Theta_F \text{ in mrad.}$$

Thus the ACAR experiment makes this *very important quantity for the physics of metals experimentally accessible*.

² $m_0 c$ in SI-units: $2.731 \cdot 10^{-22}$ kgm/s.

This quantity p_F can also be determined theoretically. According to the *Sommerfeld theory* for face centered cubic metals as Al and Cu the Fermi momentum is given by the formula³

$$p_F = \frac{\hbar}{a} \sqrt[3]{12\pi^2\gamma} \quad ,$$

where a is the lattice constant and γ is the chemical valence of each metal. The following table shows these values for the metals examined in this exercise:

	a [m]	γ
Al	$4.04 \cdot 10^{-10}$	3
Cu	$3.61 \cdot 10^{-10}$	1

Compare the experimental p_F obtained by the evaluation of the ACAR measurements with the theoretical results using the Sommerfeld theory.

- Another interesting information about electrons in a metal can be obtained by looking at the areas that are occupied by the parabola part and the Gaussian part in our model (6). The corresponding formulae can easily be derived from equation (6); here just the results are given:

$$\text{area of the parabola} = \frac{4A\Theta_F}{3} \quad ,$$

$$\text{area of the Gaussian} = \frac{B\sqrt{\pi}}{\sqrt{C}} \quad .$$

Calculate the percentage of these two area parts (with respect to the whole area) for aluminium and copper. Try to interpret these results with the help of the text "The angular correlation method" in this exercise description.

³ \hbar in SI-units = $1.05459 \cdot 10^{-34} \text{ kgm}^2/\text{s}$.

Task 2

Realtime X-ray diffraction to examine the kinematics of phospholipid phase transitions.

- The experiments that are at the basis of this exercise were performed by G. Pabst, M. Rappolt, H. Amenitsch and P. Laggner (Institut für Biophysik und Röntgenstrukturforschung, Österreichische Akademie der Wissenschaften Graz) and by S. Bernstorff (ELETTRA, Sincrotrone Trieste, Italia) at the synchrotron ELETTRA in Trieste.

I thank the project leader, Prof. P. Laggner, and UDoz. G. Pabst for the permission to use the resulting data of these experiments for this exercise.

- **Phospholipids** are the main constituents of biological membranes. In aqueous dispersion these membranes consist of lamellar phospholipid bilayers with a temperature dependent lattice constant d (see figure 5).

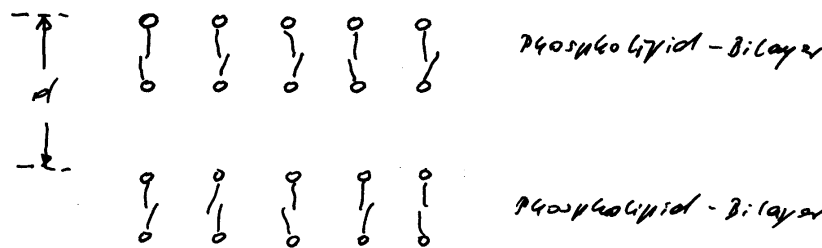


Abb. 1: Struktur von Phospholipid-Bilayer-Membranen in H_2O .

Figure 5: The structure of phospholipid bilayer membranes in H_2O .

The **experimental** determination of the lattice constant d of such bilayer structures can be done by X-ray diffraction. A typical experimental setup is shown in figure 6.

The performance of the synchrotron X-ray sources available today allows for **time-resolved** diffraction experiments, i.e. the change of structures (lattice constants) with time can be examined.

In the experiment shown in figure 6 the following steps were performed:

The sample (phospholipids in H_2O) is in a cuvette and is illuminated by an X-ray; the resulting diffraction patterns are displayed at the detector.

An infrared pulse emitted by an Erbium laser ($1.54 \mu m$) with a short duration (2 ms) and big energy (4 Joule) is shone onto the sample and leads to a temperature jump of about 15 degrees within these 2 ms.

The examined system reacts to this sudden temperature increase by an equally sudden reduction of the lattice constant of the bilayer system by about 7 percent. Then the system **relaxes** quite slowly to its original structure, i.e. d increases to its value before the "laser perturbation".

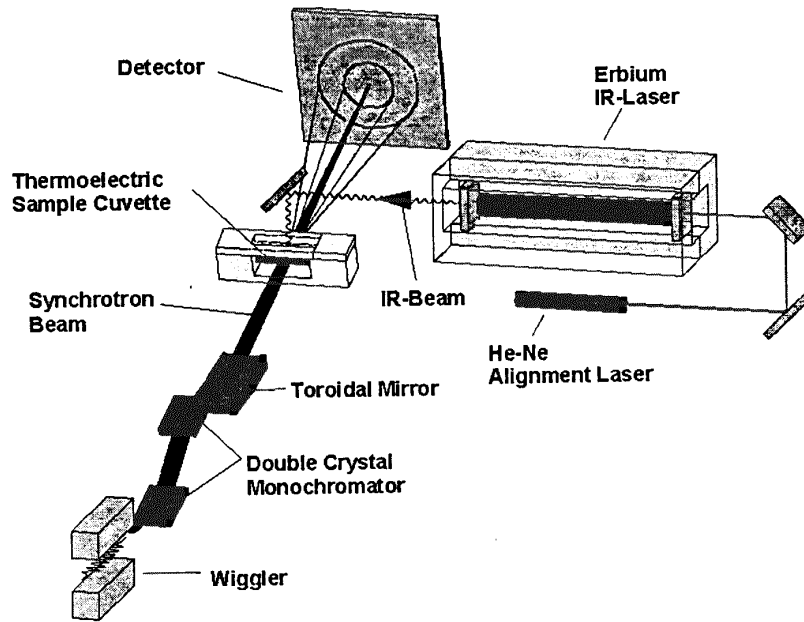


Figure 6: Schematic of the experimental setup of a temperature jump measurement using X-ray small angle diffraction (ELETTRA, Trieste, Italy).

This relaxation process can be closely observed using time-resolved X-ray diffraction. You find a typical result of a measurement like this in the data file `elettra.txt` and in figure 7.

- **Problem description:** Least-Squares-evaluation of the 245 measured data points in the file `elettra.txt` using the Gauss-Newton-Marquardt method. Please consider the following points:

1. The 245 data points are distributed around their expectation values with a (mean) **standard deviation** $\sigma = 0.069$ Angstroem.
2. Generating an appropriate **model function** is up to you! Start out by choosing the model as simple as possible and refine it until the variance condition (see lecture notes [German], section 4.3.2) is fulfilled.
3. Pay attention that your model is physically plausible (relaxation process!).
4. Think about the **physical meaning** of the fitted parameters.
5. The GNM iteration is stopped when the fitted parameters are known to a relative precision of 0.00001.
6. Generate a result file for each of your models, containing the following three columns:

t [s]	d_exp [A]	d_modell [A]

xxx	xxx	xxx
.	.	.

Plot the experimental data including the calculated model curves (e.g. using MATLAB).

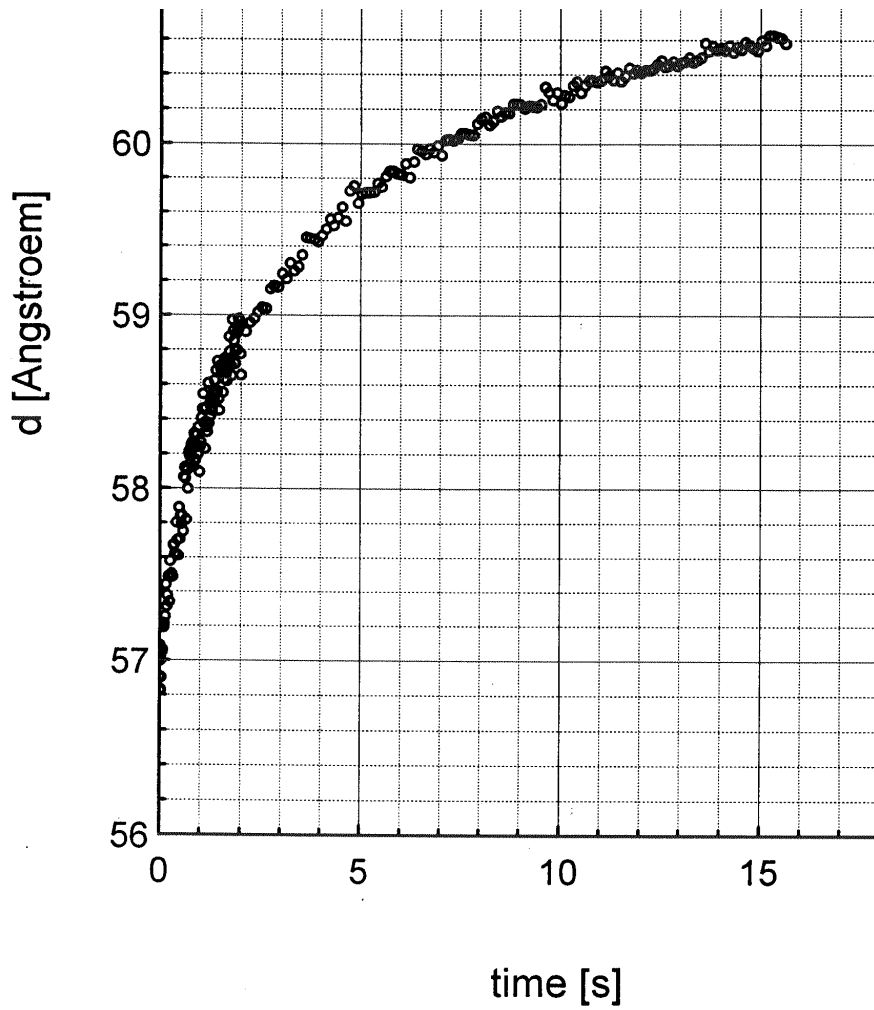


Figure 7: Dependence of the lattice constant d of the phospholipid bilayer in H_2O (in Angstrom) on the time t (in seconds), measured from the laser-induced temperature jump (G. Pabst, M. Rappolt, H. Amenitsch, S. Bernstorff und P. Laggner, 1998).