APD 100

ANISOTROP PARTICLE DETECTOR
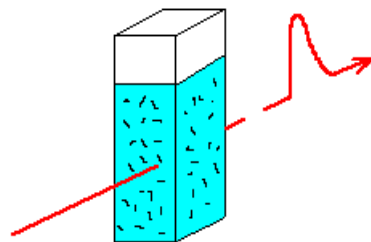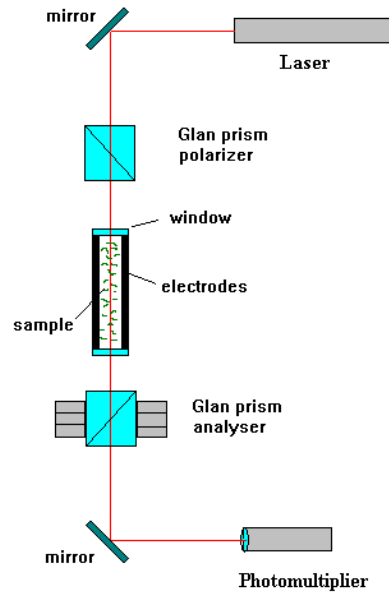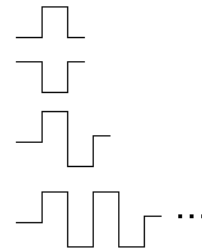
Photometersystem APD 100

Photometer

Rotational diffusion coefficient
axial ratio
Particel size distribution
Kerr-constant
Dipoles charakter
optical retardation
sign of birefringence
difference between the refractive indices

mirror

Laser

Glan prism
polarizer

window

electrodes

sample

Glan prism
analyser

mirror

Photomultiplier

High voltage pulser

singel pulse positiv
single puls negativ

reversed puls

square wave

...

General

Many substances transform an incident light beam into two perpendicular polarized beams wich are propagated at different velocities in the medium. This property is called birefringence. The two transmitted orthogonal vibrations are then out of phase by an optical retardation δ, and the birefringent medium shows different refractive indices with respect to the two beams. The birefringence of the medium is defined as the difference between the refractive indices of the two beams, $\Delta n = n_x - n_y$. Normaly particles in solution don't show birefringence. If the particles undergo oriential order, it's possible to detect the double refraction. A simple and rapid method is the orientation by an electric field. A Laser light beam, linearly polarized by a Glan prism, falls on a measuring cell containing two electrodes to which an electric field is applied. The resulting anisotropic light beam leaving the cell passes through a second Glan prism, and a photomultiplier detect the change of light intensity.

Cell design

The rotary diffusion coefficient depends on the temperatur. In the new cell design a fluid bath can be connected directly to the cell. The sample is between two electrodes wich are mounted in teflon. Selected glases without birefringence are used for the cell windows. Standard glases can't be used because the birefringencs is to strong. It's also possible to use the cell as a flow-through cell.
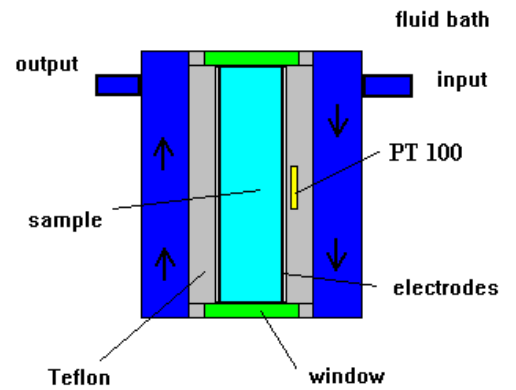
Increase of birefringence

When an electric field is applied to a solution the birefringence increase until they reach a value wich corresponds to a steady-state orientation of the particles. On the other hand, when the electric field is suddenly removed, oriented particles return to the random orientation state and the birefringence fall asymptotically to zero. The rise and decay of the electro-optical parameters are characteristic of the particles and can be used for calculating their molecular dimensions.
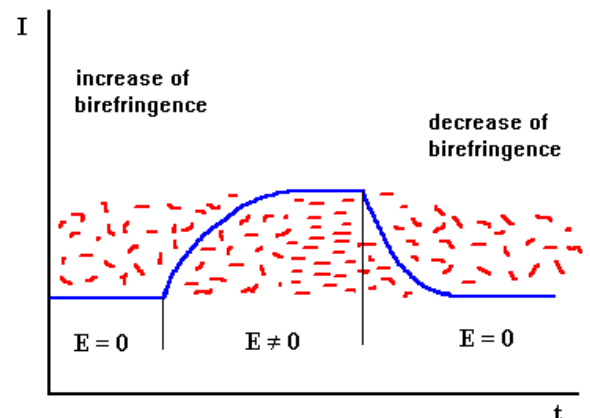
Measurments

Kerr- constant

Normaly particles in solution don't show birefringence. The application of electric fields may induce electric birefringence. The electric birefringence effect was first observed in 1875 by Kerr who established the proportionality of the birefringence to the square of the field strength- the Kerr low.

$$B := \frac{\Delta n}{\lambda \cdot E^2}$$

E: electric field
Δn: n_x - n_y
λ : wave-length
B: Kerr constant

Rotational diffusion coefficient

When the electric field is removed, oriented particles return to the random orientation state and the birefringence fall asymtotically to zero. The decay of the birefringence is characteristic for the particles. A monodisperse solution is described by a single decay curve. For polydisperse solutions the variation of the birefringence takes the simple form:

$$\Delta n(t) := \sum_i \left(\Delta n_0\right)_i \cdot e^{-6 \cdot D_i \cdot t}$$

$\Delta n(t)$ is the birefringence at time t after removal of the field, Δn_O the birefringence of the steady-state and D_i the rotational diffusion coefficient from the ith species.
The rotational diffusion coefficient is related to the molecular parameters by the following equations:

$$D_R := \frac{3 \cdot k \cdot T}{16 \cdot \pi \cdot \eta \cdot a^3} \cdot \left(\ln\left(\frac{2 \cdot a}{b}\right) - 1 \right)$$

Ellipsoid

$$D_R := \frac{3 \cdot k \cdot T}{8 \cdot \pi \cdot \eta \cdot a^3} \cdot \left(\ln\left(\frac{2 \cdot a}{b}\right) - 0.8 \right)$$
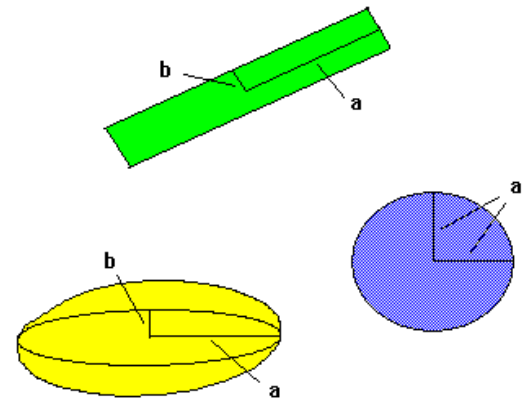
Zylinder

$$D_R := \frac{k \cdot T}{8 \cdot \pi \cdot \eta \cdot a^3}$$

Kugel

Measurments

Axial ratio

When the rotational diffusion coefficient is known, the length of the particle can be calculated from the axial ratio a/b. E. g. for surfactant micelles the length of the monomer is given, and it's possible to calculate the length of the rod.

Particle size distribution

To calculate the particle size distribution two high voltage pulses must be applied. First a low voltage pulse (birefringence is proportional to the square of the field strength -Kerr low) and second a high voltage pulse for the steady state orientation of the particles. Determination of the two discrete experimental diffusion coeffizients, provides sufficient information to generate the characteristic parameters of two parameter distribution function for the spread of particle sizes. The most commonly used distribution is the log-normal.
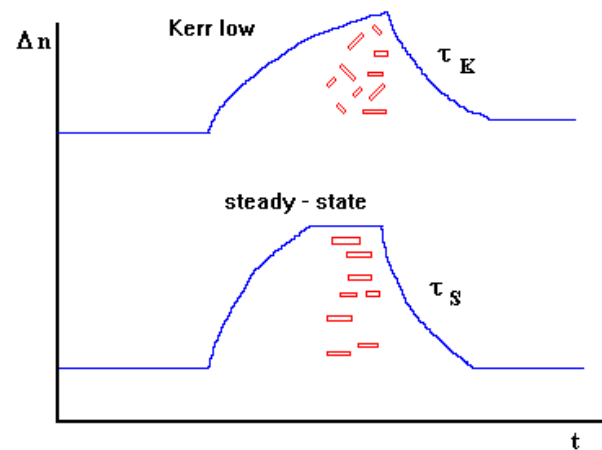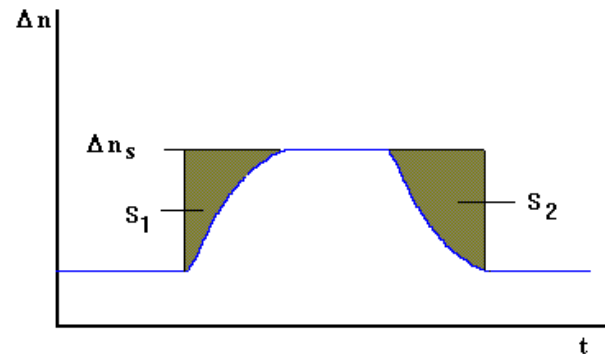
Log-normal

$$f(l) := \frac{1}{\sigma \cdot l \cdot \sqrt{2 \cdot \pi}} \cdot e^{-\frac{\ln\left(\frac{l}{m}\right)^2}{2 \cdot \sigma^2}}$$
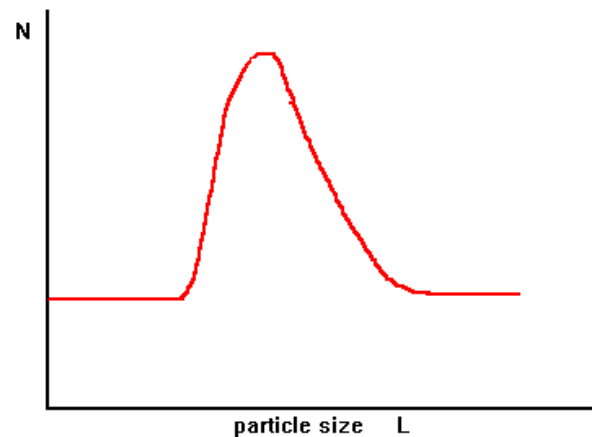
Measurments

Induced Dipoles

Cunductive substances must be studied with short pulses, but it's necessary to reach the steady state. If the areas S1 and S2 are equal the birefringence depends only on induced moments.

Dipoles charakter

The use of reversing pulses is a rapid method for studying the character of dipoles. When the steady state value of the birefringens has been reached, a reverse pulse of the same voltage is applied. The change has no influence by an induced moment. A pure permanent moment , like water, shows a minimum for the birefringence signal.
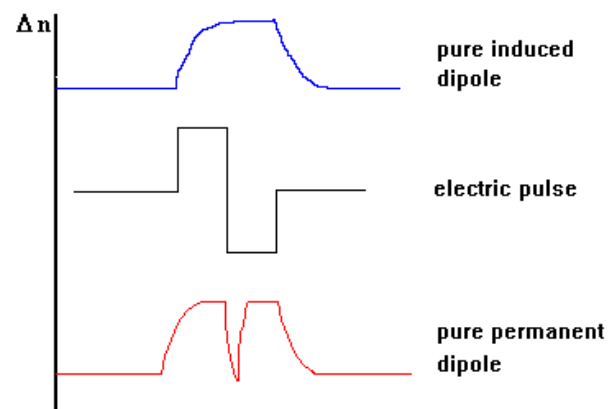
Sign of the birefringence

The presence of a quarter-wave device between the sample and the analyser will give the possibility of making the distinction between positive and negative birefringence, and will also increase the sensitivity of the measurment. If the quarter-wave device has it's slow axis at $3\pi/4$ with respect to the field, this vibration will undergo an additional retardation of $\pi/2$. If the analyser is turned through an angle α from the crossed position towards the polarizer, the sign of the birefringence can be deteced.