Model Interpretation in Static Light Scattering

Gudrun Rother

Max Planck Institute of Colloids and Interfaces, Am Mühlenberg Golm,
14424 Potsdam, Germany

SUMMARY: For sufficiently large species, the fit of the experimentally obtained scattering curve with theoretically calculated ones for different basic structure types (sphere, random coil, rod, wormlike chain and others) gives information about the structure type, the polydispersity, the structure density, the molecular parameters M_w and s_z, and a characteristic size parameter a_m, the definition of which depends on the used structure model type.
An iterative algorithm is offered to separate bimodal scattering curves into the curves of the components and to characterize the single ones.
The theoretical background of such procedures and a corresponding software system will be presented.
Application examples demonstrate the efficiency of the procedures.

Introduction

Static light scattering (SLS) studies, applied in the characterization of diluted polymer solutions, are able to determine the weight average of molecular mass, the z-average of radius of gyration and the second virial coefficient without knowledge of the structure type. The basis is a double extrapolation of the dates in a special Zimm plot with regard to the concentration and the scattering angle.

However the SLS may be used also to characterize larger particles as polymer latices or supramolecular structures in polymer solutions, like gel particles, aggregates or micelles. The scattering curves of such structures are more curved. This causes difficulties in the extrapolation to zero scattering angle, but on the other hand, the scattering curve contains more information on the scattering system than available by the traditional manner of data analysis.

The size, the shape, the internal structure and the polydispersity of the scatterers affect the shape of the scattering curve. An interpretation by fit with theoretical model curves, special on closer inspection of curvature of the scattering curves, should give statements to these parameters.

 CCC 1022-1360/00/$ 17.50+.50/0

Theoretical basis

The basis equation of SLS for a dilute polydisperse system of scattering particles is

$$\frac{Kc}{R(q)} = \frac{1}{M_w P_z(q)} + 2 A_2 c + \cdots$$

where K – contrast factor, R(q) – Rayleigh ratio of the scattering intensity,

A_2 – virial coefficient, c - mass concentration of the polymer,

Θ - scattering angle, $q = (4 \pi / \lambda) \sin(\Theta/2)$ - length of the scattering vector,

λ- wave length in the medium, M – molecular mass of the scattering particle.

The weight average M_w of the molecular mass is given by

$$M_w = \int_0^\infty M\, p_w(M)\, dM ,$$

where $p_w(M)$ is a normalized distribution function of M. With the scattering function or the form factor of an individual particle P(q,M) the intraparticular scattering function (z-average) of the polydisperse system is given by

$$P_z(q) = \frac{1}{M_w} \int_0^\infty P(q,M)\, M\, p_w(M)\, dM .$$

The z-average of the square of the radius of gyration is given by

$$< s^2 >_z = \frac{1}{M_w} \int_0^\infty M\, s^2\, p_w(M)\, dM .$$

Debye derived independent on shape and structure of the scattering particles the expression

$$P_z(q) = 1 - \frac{1}{3} < s^2 >_z q^2 \pm \cdots$$

With it the basis equation of classical interpretation methods follows

$$\frac{K c}{R(q)} = \frac{1}{M_w} \left(1 + \frac{1}{3} < s^2 >_z q^2 \pm \cdots\right) + 2 A_2 c + \cdots .$$

The influence of concentration is eliminated by extrapolation to zero concentration; one gets the scattering curve, which shall be interpreted

$$\lim_{c \to 0} \frac{R(q)}{K c} = M_w P_z(q) .$$

With the given equations and expressions of the form factor $P_z(q,M)$ we have all prerequisites of a more detailed scattering data analysis. However, the reversal conclusion from the experimental

scattering curve to the parameters of the scattering system is an ill-posed problem, which is ambiguously to solve, therefore.

Interpretation

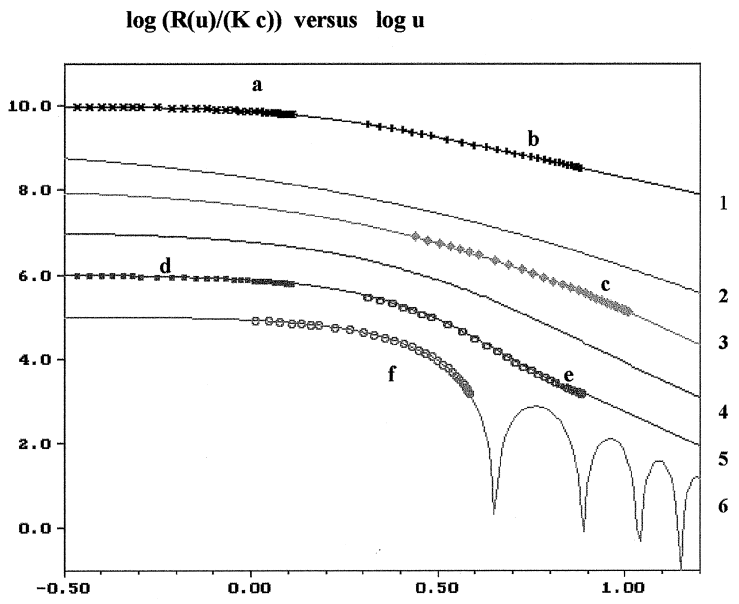
In the history, some interpretation methods have been developed, different plots of the scattering intensity as function of the scattering angle or of the length of scattering vector play an important role in this connection. The traditional interpretation methods as the double extrapolation in a Zimm plot for polymer solutions of different concentrations as well as the single scattering curve diagrams of Guinier, Zimm, Berry, Holtzer, Sloan, Kratky and so on are well-known. They all are graphs of the same dependence, but they emphasize different sections of the scattering curves. Extrapolations, specific features of the graphs, as initial or asymptotic slope, coordinates of maximum or minimum provide information about the parameters of the investigated solutions. Particularly in the case of larger particles the scattering curves have larger curvature and the extrapolation to zero scattering angle is difficult. Then such classical methods often cannot use the whole range of the experimental scattering curve and therefore, they give away information and the interpretation results are not correctly.

Scaled interpretation

The idea of the scaled or master interpretation [1,2] is to fit measured scattering curves with theoretical ones. These procedures realize the classification of scattering equivalent models and were meanwhile justified successfully by the characterization of larger particle systems and supramolecular structures [3-9].

With the given equations, expressions of the single form factor P(q,M), available from the literature, e.g.[10,11], and selected distribution functions $p_w(M)$ the requirements are given to calculate scattering curves for a lot of basis structure types, as spheres, random coils, rod like particles, wormlike chains and others by programming analytical expressions, numerical integrations or double integrations.

But the problem of the inverse conclusion from the scattering curve to the scattering system is the existence of to many free parameters: particle size, particle shape, internal structure and polydispersity of the system.



master curves,
log. distribution
1 - random coils, $\sigma = 0$
2 - spheres, $\sigma = 1.0$
3 - spheres, $\sigma = 0.7$
4 - spheres, $\sigma = 0.5$
5 - spheres, $\sigma = 0.3$
6 - spheres, $\sigma = 0$

model scattering curves:
random coils:
a,b - $\sigma = 0$, $s_m = 50$ nm (a) , 300 nm (b),

spheres
c - $\sigma = 0.7$, $r_m = 400$ nm,
d,e - $\sigma = 0.3$, $r_m = 50$ nm (d) , 300 nm (e)
f - $\sigma = 0$, $r_m = 150$ nm

Fig. 1: Position of model scattering curves (according to experimental scattering angle range: $\Theta = 30°... 150°$, refraction index $n = 1.33$, $\lambda = 633$ nm) of the corresponding master curves (logarithmic distribution, polydispersity σ, s_m – coil gyration radius, r_m - sphere radius)

The development of our simple fit procedure is based on the fact, that in the framework of Rayleigh Debye Approximation (RDA) the single particle form factors of the different structure models have commonly, that their argument is the product of the length of scattering vector q times a characteristic size parameter a. The dependence on this product is valid for polydisperse systems too:

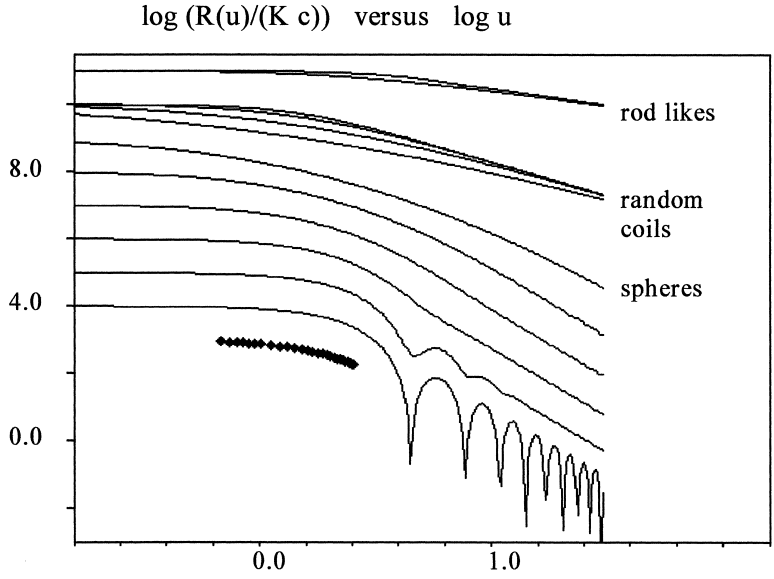
$$P_z(q,M) = P_z(u,M), \qquad u = q\ a_m\ , \qquad a_m \text{ – characteristic size parameter in } p_w(M)$$

The definition of a_m depends on the used structure type; it is for instance the sphere radius, the rod length, the radius of gyration (of coils or of star molecules) and so on.

This dependence on the product u means, that P_z scales with the characteristic parameter a_m. For a fixed polydispersity and selected structure model we have a master curve of normalized scattering intensity $P_z(u)$ versus u. The "experimental ranges" (fixed q-range, corresponding u-range) of the single scattering curves of systems with different size parameter a_m of this model covers different sections of the same master curve. In a double logarithmic plot this fact is more impressive yet; the logarithm separates multiplication to an addition:

$$\log \frac{R(q)}{K\,c} = \log M + \log P_z(u) \qquad \textit{resp.} \qquad \log u = \log q + \log a_m$$

That means, in such a double logarithmic plot (scaled plot) a change of M_w corresponds to a shift of the ordinate position and a change in the characteristic size parameter a_m corresponds to an abscissa shift of the special "experimental accessible" scattering curve along the appropriate master curve. Fig. 1 illustrates this fact.



rod likes: Schulz-Zimm distribution, polydispersity parameter $z = (M_w/M_n-1)^{-1} = 1000, 0$
random coils: logarithmic distribution, $\sigma = 3, 2, 1, 0$
spheres: logarithmic distribution, $\sigma = 1, 0.7, 0.5, 0.3, 0.1, 0$

Fig. 2: Scaled master curves: sets of different structure models ($a_m = 1\mu m$),
computer display: shift of the experimental curve (××××) to choose an appropriate structure type
(experimental q-range as in Fig. 1)

The reverse step generates a very simple fitting procedure:

(i) measurement of scattering curve of the system,

(ii) comparison of the shape of this experimental curve (scaled plot) with the shape of sets of theoretical curves of different structure type $\Rightarrow$ selection of an appropriate structure model,

(iii) choice of an appropriate master curve from a curve set of different polydispersity of the chosen structure model $\Rightarrow$ selection of polydispersity σ,

(iv) shift of measured curve along the selected master curve $\Rightarrow$ estimation of M_w, a_m.

The position of the appropriate master curve yields the molecular parameters of the system: the ordinate position gives the M_w, the characteristic size parameter a_m results from the abscissa position.

Step (ii) is verified in Fig.2, the experimental curve is given in the plot: log (R(q)/(K c)) versus log q. It is shown, that the assignment to an appropriate structure type is possible, if the experimental scattering curve corresponds to a significant q-section.

Fig. 3 shows, that the step (iii), the choice of polydispersity, is analogous possible. Here are given the scaled plot log (u^2 R(u)/(K c)) versus log u for the model master curves, and for the experimental curve log (q^2 R(q)/(K c)) versus log q.

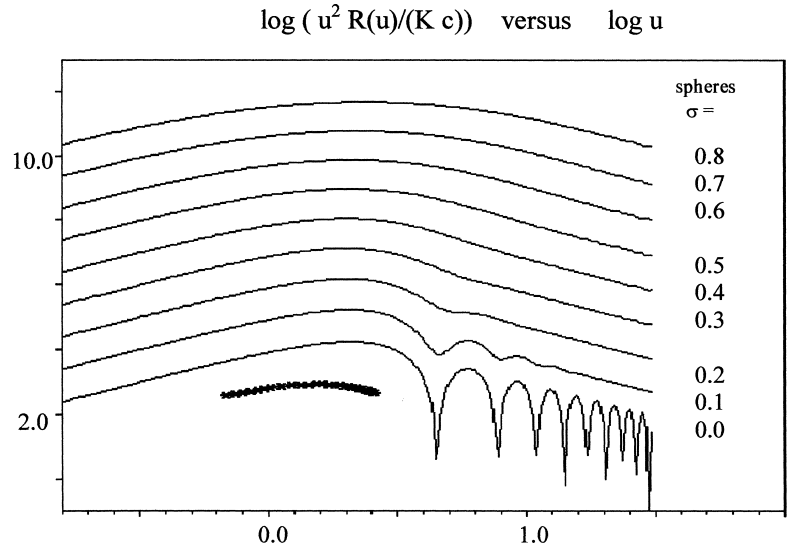


Fig. 3: Scaled master curves: set of spheres of different polydispersity σ,
computer display: shift of the experimental curve (××××) to choose an appropriate polydispersity σ
(experimental q-range as in Fig.1)

We can summarize, the scaled interpretation algorithm uses complete the measured range of the scattering curve, for larger particles (significant curved scattering curve) the interpretation yields

from the comparison of the shape information on
- structure type,
- polydispersity,

from the position of the master curve information on
- weight average of molar mass M_w,
- characteristic size parameter a_m,

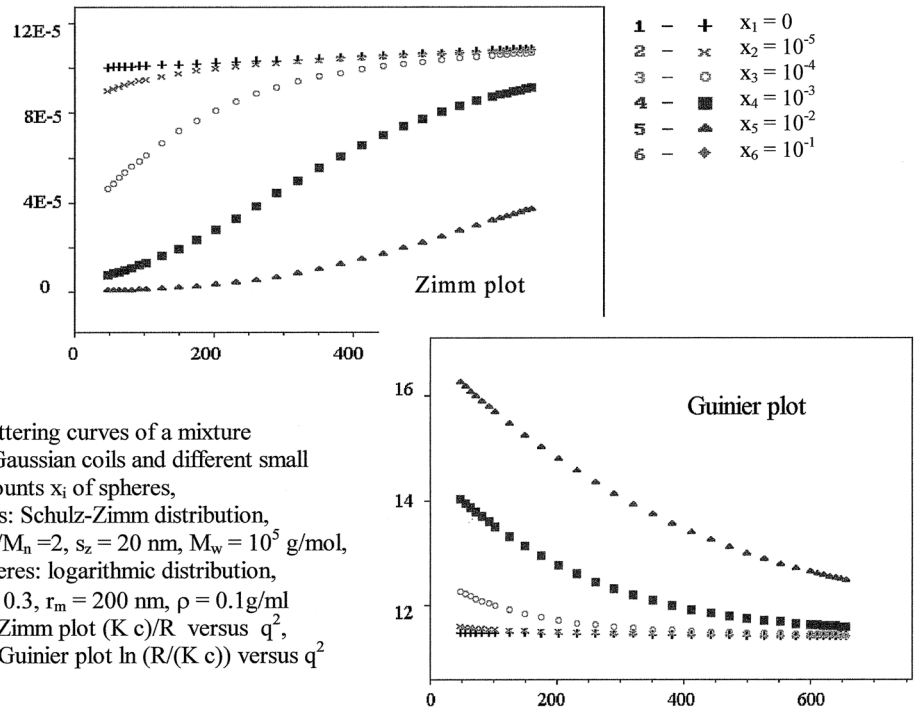
and with reflection of polydispersity will be possible:
- certain extrapolation of the scattering curve to q = 0,
- calculation of radius of gyration,
- evaluation of polymer packing density (degree of swelling respectively.).

In respect to the distribution function we restrict of monomodal systems. Commonly a special logarithmic distribution function is preferred [2,3,12].

The algorithm is extended on scaled plots of log (u^β R(u)/(K c)), this gives nothing of restrictions, but opens the possibility to work with known helpful plots as Kratky, Sloan, and others, which give special characteristic graphs for different structure types and possibly they prepare visible better the optimal fit (in Fig.3 is used exemplary such a plot with $\beta = 2$).

Bimodal systems

The investigation of native polymers by light scattering is often impeded by the presence of supramolecular structures in the polymer solutions. Already a very small amount of a particular component leads to an anomalous scattering behaviour (Fig. 4) and a misinterpretation of the experimental data. The results of a formal interpretation, for example the M_w-values obtained by a traditional Zimm plot, may be falsified by an order of magnitude. Therefore, a correct determination of the structural parameters of the molecularly dissolved polymer requires the recognition of such a particular component. A complete suppression by an appropriate preparation method is often difficult.



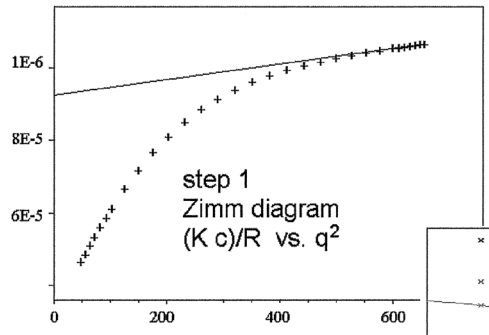
Scattering curves of a mixture
of Gaussian coils and different small
amounts x_i of spheres,
coils: Schulz-Zimm distribution,
M_w/M_n =2, s_z = 20 nm, $M_w = 10^5$ g/mol,
spheres: logarithmic distribution,
$\sigma = 0.3$, $r_m = 200$ nm, $\rho = 0.1$g/ml
(a) Zimm plot (K c)/R versus q^2,
(b) Guinier plot ln (R/(K c)) versus q^2

Fig.4: Scattering curves of bimodal model systems

However, by an iterative procedure bimodal scattering curves can be separated into the parts of the components and the supramolecular particulate component as well as the molecularly dissolved one can be characterized. The concentration influence should be eliminated before.

Fig. 5 demonstrates the algorithm of the bimodal curve separation; the investigated bimodal scattering curve is the model curve 3 of Fig. 4, what means that 10^{-2} mass percents of the particulate component are involved.

The assumption, that the scattering intensity is additively, gives the idea of curve separation.
The requirements are, that the components dominate different sections of the scattering curve. We suggest an iterative procedure of separation. The first step (i = 1) starts with interpretation of either the wide- or the small-angle range and yields a start model by traditional or scaled algorithms.



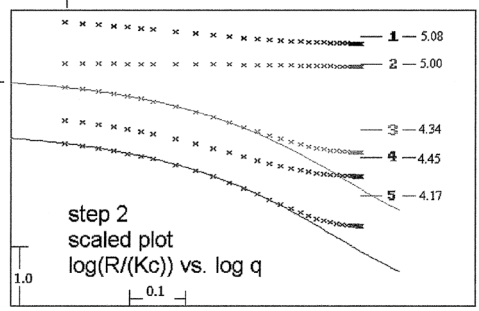
step 1: classical interpretation of the original curve (wide-angle range, polynomial fit = solid line)

⇒ (model curve)$_1$

⇓

[(difference curve)$_2$] =

[original curve] - b_1[(model curve)$_1$]



step 2:

1 – original curve, 2 – model$_1$,

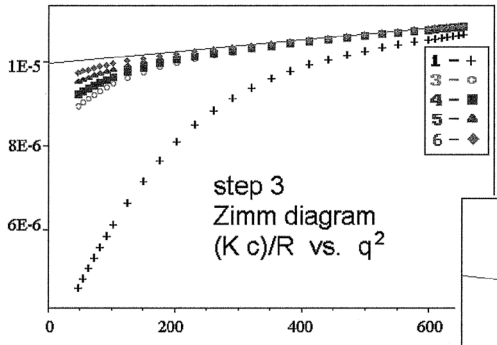
3,4,5 – difference curves

(b_1 = 0.9, 0.85, 0.95),

scaled interpretation (emphasized the low angle range) of selected difference curves

⇒ selection of curve 5 (b_1 = 0.95)

⇒ (model curve)$_2$ ⇒ [(difference curve)$_3$] = [original curve] - b_2[(model curve)$_2$]

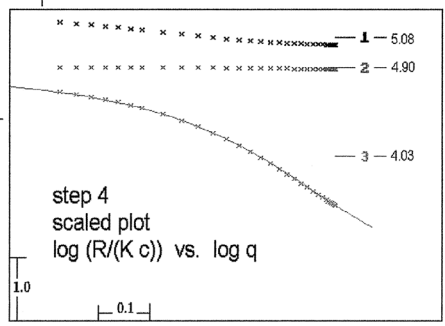


step 3:

1 – original curve, 3,4,5,6 - difference curves (b_2 =0.92, 0.95, 0.98, 1.0), classical interpretation

⇒ (model curve)$_3$ (select. b_2 = 1.0)

⇒ difference curve …



step 4:

1 – original curve, 2 – model$_3$,

3 – difference curve (b_3 = 1.0)

scaled interpretation of difference curve ⇒ (model curve)$_4$

… ⇒ end of iteration: step i (b_{i-1} = 1)

⇓

resulting interpretation model: original curve = (model)$_{i-1}$ + (model)$_i$

⇒ parameters of the components (x_c - mass fraction of the component):

model (classical interpreted) : $M_w = x_c (M_w)_c$, s_z

model (scaled interpreted) : $M_w = x_c (M_w)_c$, structure type, polydispersity, a_m , s_z

Fig. 5: Bimodal curve separation, pattern of the iterative procedure

Evaluation of the corresponding function (model curve)$_i$ and difference forming give the basis of the next step, i – number of iteration:

$$[\text{ (difference curve)}_{i+1}\text{ }] = [\text{ original curve }] - b_i\ [(\text{ model curve})_i\text{ }],$$

The factors b_i can be chosen, its value controls the amount of the component and affects the form of the resulting difference curve, the criterion of choice is "an useful one" in the sense of scattering equivalent. We start with $b_i < 1$ because the separated model curve contains the second component yet, at the end of iteration the b_i approximate $b_i \Rightarrow 1$. Now we interpret the difference function, but have in view the other range of the curve as emphasized in the first step. This procedure will be continued up to a satisfied splitting, and then we obtained the parameters of the components. In Fig. 6 the results of the bimodal curve separation are shown. Table 1 gives the interpretation parameters.

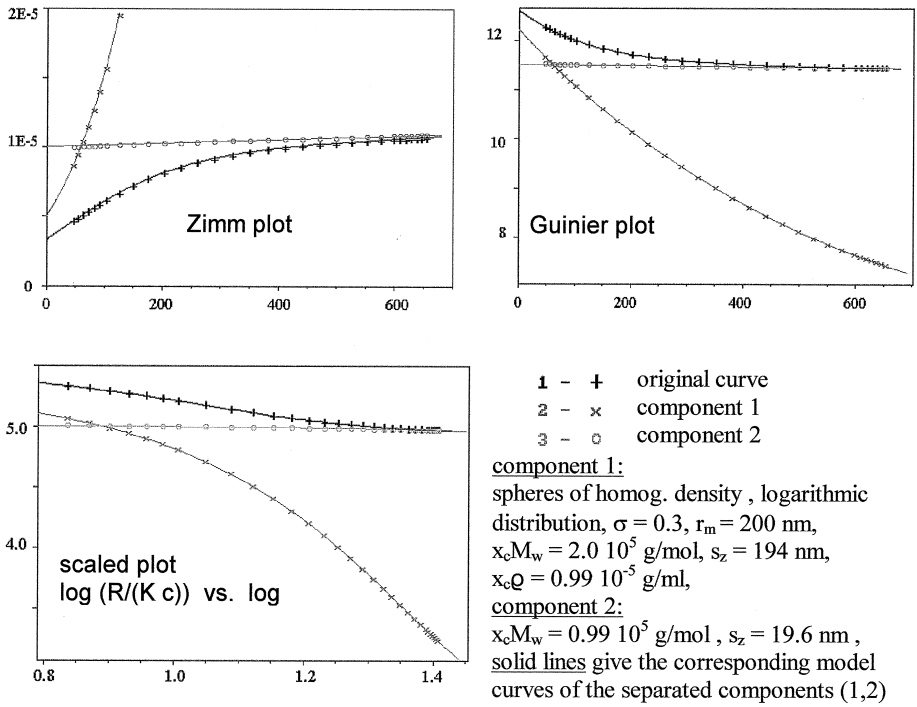


Fig.6: Bimodal curve separation – results

Table 1: Bimodal curve separation – results of the iteration

wide-angle range Zimm diagram, polynomial fit				iteration step number I			low angle range scaled plot, model interpretation spheres - logarithmic distribution			
x_c M_w [g/mol]		s_z [nm]		$b_{(i-1)}$	i	$b_{(i-1)}$	x_c M_w [g/mol]		r_m [nm]	σ
1.08 10^5		26.5			1					
					2	0.9	1.89 10^5		189	0.3
						0.95	1.96 10^5		200	0.3
0.99 10^5		19.6		**1.0**	3					
					4	**1.0**	2.0 10^5		200	0.3
coils, Schulz-Zimm distribution				**original bimodal model**			spheres, logarithmic distribution of r_m			
x_c	1.0	s_z	20				x_c	10^{-4}	r_m	200
M_w	1.0 10^5	M_w/M_n	2				M_w	2.02 10^9	s_z	194	0.3

The given procedure cannot determine quantitatively correct the M_w of the components, because the SLS can evaluate the product of $(x\ M_w)_c$ only and x_c, the mass fractions of the components, are unknown. However, if the scattering curve of one of the components is known and with it the molecular mass too, the quantitative estimation of contents is feasible. Estimation of the particle density by scaled method offers to speculate concerning the mass amount.

Of course the algorithm of curve separation is a scattering equivalent splitting, but the practical employment shows the efficiency of the procedure, Fig. 9 gives an application example.

Software System

We prepared a program system realizing the here given variety of interpretation methods, special the scaled or master interpretation, evaluation of theoretical scattering curves and the procedure of bimodal curve separation. This software works on personal computers.

The program system contains many help texts, which concerns the physical and mathematical connections, restrictions and conditions respectively. It operates in dialog with the user; he disposes of the next step and of the efficiency of the results. Fig. 7 gives an overview about this system.

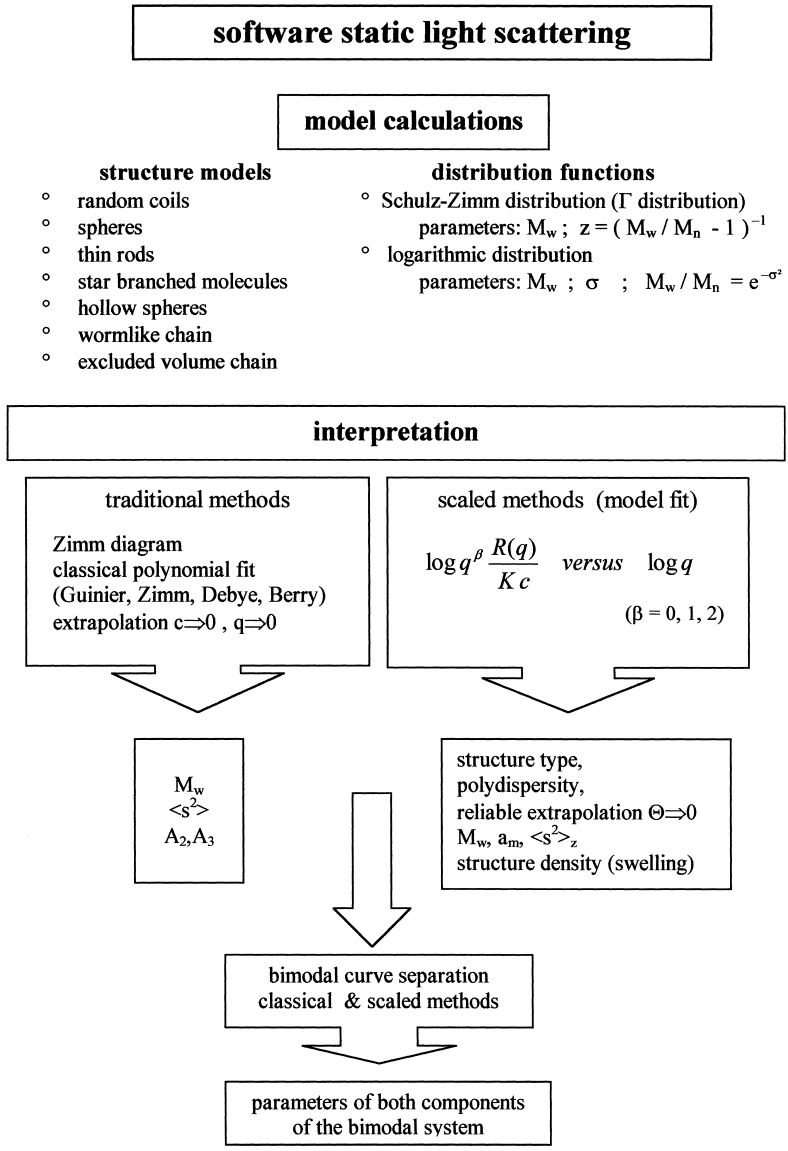


Fig. 7: Overview about our software system of static light scattering

The input of various data pattern and the combination of different scattering curves are possible.
The classical double Zimm extrapolation is involved.
To investigate single scattering curves you can select between the variety of traditional interpretation algorithms of polynomial curve fit in different plots (Zimm, Guinier, Berry, Debye) and our scaled interpretation methods of scattering equivalent model fit, which give more resulting parameters in the case of larger particles. The variety of resulting parameters is also given in the block diagram of Fig. 7.
The impressive simplicity of the procedures fascinates, for instance the fit immediately by curve shifting on the display.
A great number of varying graphs are offered, including the known plots from literature, the model fit curves can be drawn in the traditional plots as well as in the scaled ones.
Moreover the curve separation is programmed in a comfortable and efficient manner yielding results of the parameters of both components in bimodal scattering systems.

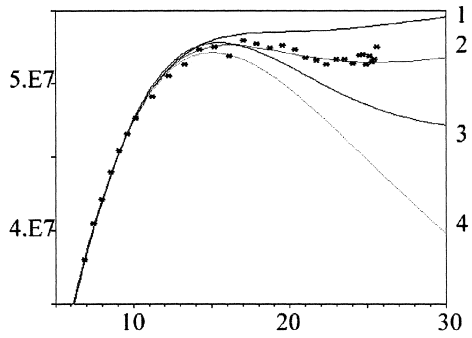
Application examples

(i) Micelles of a special surfactant, interpretation with the model of worm like chains

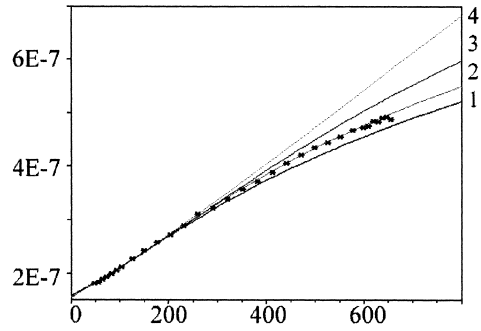
We use the particle form factor for wormlike chain model developed by Koyama[13]. Dependent on the structural parameter $L_{red} = L_c/L_p$, where L_c is the contour length of the chain and L_p the persistence length, the resulting particle form factor describes the scattering behaviour from Gaussian coils to rigid rods. The stiffness is managed by the parameter $1/L_{red}$.

Compared with other structure models, for instance spheres or coils, the number of model parameters increases by one, and consequently, the problems of unambiguity of interpretation increase. The effects of changes in L_{red} and polydispersity overlap.

Fig. 8 shows an experimental scattering curve of micelles of a special surfactant[7] together with three model curves for wormlike chains of the same polydispersity σ (logarithmic distribution of L_{red}), nearly the same molecular parameters M_w, s_z, but different stiffness. Moreover, a model curve of random coils has been added.



(a) Holtzer plot :
(q R(q)) / (K c) versus q



(b) Zimm plot :
(K c) / R(q) versus q^2

interpretation model	σ	M_w [g/mol]	s_z [nm]	L_c [nm]	L_p [nm]	L_{red}
1 wormlike chains	0.2	$6.49\ 10^6$	103	354	708	0.5
2 wormlike chains	0.2	$6.48\ 10^6$	102	379	291	1.3
3 wormlike chains	0.2	$6.36\ 10^6$	98	416	139	3.0
4 random coils	0.3	$6.45\ 10^6$	101			

wormlike chain: L_c – contour length, L_p – persistence length, $L_{red} = L_c / L_p$,
σ - polydispersity (logarithmic distribution of L_{red}) ;
random coil: σ - polydispersity (logarithmic distribution of s_m, radius of gyration)

Fig. 8: Micelles of a special surfactant, interpretation of scattering curves

The different plots are: the Holtzer plot, which is commonly used for wormlike structures, and the Zimm plot, where all curves coincide in the initial range controlled by M_w and $\langle s^2 \rangle_z$.
The advantages of the scaled interpretation to get more information, and to manage the stiffness are clear to see in both Holtzer and Zimm plot.

(ii) Bimodal interpretation

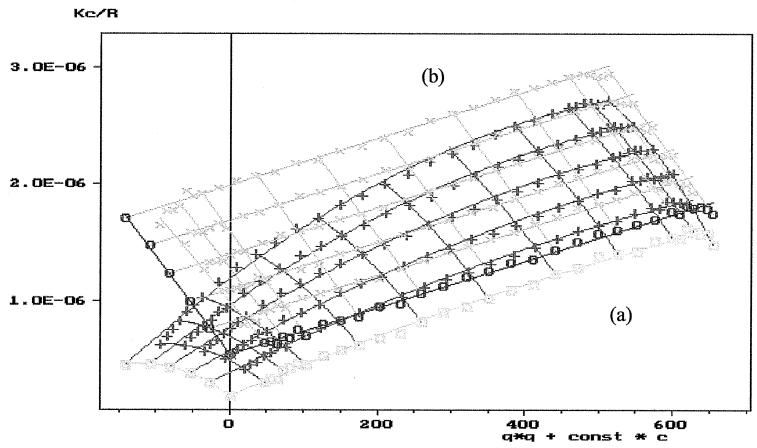


Fig. 9: Zimm plot: copolymer PDADMAC / acryl amide,
(a) - original one, (b) - after correction by theoretical curve separation

To demonstrate the efficiency of our procedure of curve separation we will regard the Zimm curves of five concentrations of a copolymer (diallyl dimethyl ammonium chloride / acryl amide 54% / 46%), filtered by a 5μm membrane[14]. Fig. 9 (a) gives the Zimm diagram. The shape of the scattering curves, special their curvature, indicates the presence of a supramolecular component. Application of the created iterative algorithm of curve separation gives a corrected Zimm diagram (Fig.9 (b)), which yields reliable results.

To test the quality of our results we separated preparative the supramolecular component, we filtered the solutions sharp yet (by 0.45 μm membrane). After correction of concentration change we get a better Zimm diagram too. Fig. 10 illustrates the comparison of the two diagrams, the theoretical and preparative selected ones. The results certify the efficiency of the used curve separation method.

Table 2 compares by means of this example of a "disturbed" measured Zimm diagram the results of a formal interpretation of the original dates and the results after theoretical and preparative correction respectively. The extrapolation to $c \Rightarrow 0$ is realized by a first order

polynomial, the extrapolation to $q \Rightarrow 0$ by first or second order polynomials of the basis of the whole range or the wide-angle range of the corresponding scattering curves respectively.

We notice, the results without correction are wrong in all cases, special in the case of using the wide-angle range only the M_w value is falsified too by a factor of about 1.5. This confirms the necessity of the curve correction.

Table 2: Comparison of the results of the different interpretation algorithm

interpretation of the Zimm diagram of Fig. 9	M_w [g/Mol]	s_z [nm]	A_2 [Mol L g^{-2}]
formal evaluation:			
first order polyn. (whole range) $q \Rightarrow 0$	$3.02\ 10^6$	138	$1.97\ 10^{-7}$
second order polyn. (whole range) $q \Rightarrow 0$	$3.47\ 10^6$	161	$0.91\ 10^{-7}$
first order polyn. (wide-angle range) $q \Rightarrow 0$	$2.81\ 10^6$	133	$3.23\ 10^{-7}$
corrected evaluation:			
theoretical correction, first order polyn. (whole range) $q \Rightarrow 0$	$1.91\ 10^6$	111	$6.1\ 10^{-7}$
preparative correction, first order polyn. (whole range) $q \Rightarrow 0$	$2.06\ 10^6$	115	$6.5\ 10^{-7}$

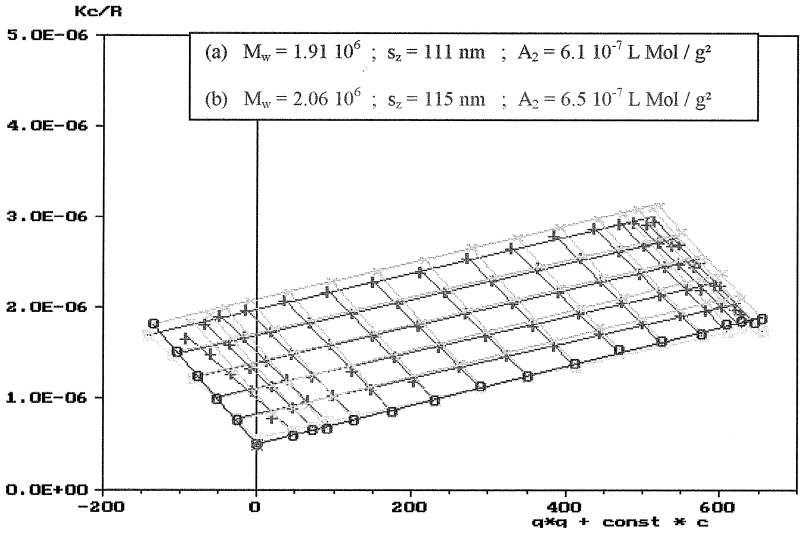


Fig. 10: Zimm plot: copolymer PDADMAC / acryl amide,
(a) - after correction by theoretical curve separation,
(b) - preparative correction (sharp filtration, 0.45 µm)

Conclusion

The method of scaled interpretation with theoretical models was introduced. The advantages of this algorithm are the use of the whole scattering curve, the simple fitting procedure, the careful extrapolation to zero scattering angle, additionally in the case of larger scattering particles to get information to structure type, polydispersity, characteristic size parameter, M_w, $\langle s^2 \rangle_z$ and the degree of swelling. Moreover an iterative procedure of theoretical curve separation was offered.

The efficiency of the developed program system has been shown by application examples.

References

1. H. Dautzenberg, G. Rother, *J. Polymer Sci. , Part B, Polym. Phys.*, **26,** 353 (1988)
2. H. Dautzenberg, G. Rother, *Makromol. Chemie, Macromol. Symp.* **61**, 94 (1992)
3. H. Dautzenberg, G. Rother, *J. Appl. Polym. Sci. , Appl. Polym. Symp.* **48**, 351 (1991)
4. H. Dautzenberg, J. Kötz, B. Philipp, G. Rother, A. Schellenberger, J. Mansfeld, *Biotechnology and Bioengineering*, **38**, 1012 (1991)
5. H. Dautzenberg, G. Rother, J. Hartmann, *ACS Symp. Ser.* **548**, 210 ((1994)
6. G. Berth, H. Dautzenberg, G. Rother, *Carbohydrate Polym.* **25**, 177 (1994)
7. H. v.Berlepsch, H. Dautzenberg, G. Rother, J. Jaeger, *Langmuir* **12,** 3613 (1996)
8. G. Berth, H. Dautzenberg, B.E. Christensen, G. Rother, *Biopolymers*, **39**,70ß (1996)
9. G. Berth, H. Dautzenberg, B.E. Christensen, S.E. Harding, G. Rother, O. Smidsrod, *Macromolecules* **29**, 3491 (1996)
10. M. Kerker, The Scattering of Light and other Electromagnetic Radiation, Academic Press, New York (1991)
11. P. Kratochvil, Classical Light Scattering from Polymer Solutions, Polymer Science Library 5 (ed. A.D. Jenkins), Elsevier (1987)
12. H. Dautzenberg, this issue, (2000)
13. R. Koyama, *J. Phys. Soc. Jpn.*, **34**, 1029 (1973)
14. F. Brand, H. Dautzenberg, W. Jaeger, M. Hahn, *Angew. Makrom. Chem.* **248**, 41 (1997)