

# Some aspects of the use of small-angle spectrodissymmetry in granulometry

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Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

The spectral dependence of small-angle dissymmetry  $Z$  in polydispersions containing spherical particles with lognormal distribution was theoretically studied. It has been found for instance for polystyrene latices that this dependence may be used for determining the distribution parameters in systems with particle size 120—1400 nm on the basis of measurements of  $Z(10^\circ/5^\circ)$  at two wavelengths of radiation.

Теоретически изучалась спектральная зависимость низкоугловой диссимметрии  $Z$  в полидисперсиях шаровидных частиц с логнормальным распределением. Показалось, что например в полистироловых латексах приведенные зависимости можно использовать для определения распределяющих параметров в системах с размером частиц 120—1400 нм на основании измерения  $Z(10^\circ/5^\circ)$  при двух волновых длинах излучения.

In the theory of light scattering the coefficient of dissymmetry  $Z$  is defined as the ratio of the light fluxes  $\Phi$  scattered in two angles of observation  $\Theta$

$$Z = \Phi(\Theta_1)/\Phi(\Theta_2) \quad (I)$$

In harmony with the exact Lorenz—Mie theory [1],  $Z$  is a function of the relative index of refraction  $m$  as well as of the parameter of size  $\alpha = 2\pi r/\lambda$  ( $r$  is the radius of particle and  $\lambda$  is the wavelength of radiation in system). The relationship  $Z(45^\circ/135^\circ) = f(\alpha)$ , e.g. for polystyrene latex [2] exhibits monotonous character up to  $\alpha = 2$  and thus may be used for determining the size of particles in the system on the basis of comparison of the theoretical and experimental values of  $Z$ . Thereby Hodgkinson [3] has shown that the angular distribution of scattered light in the sector 0—90° gives the possibility of unambiguous determination of particle size up to  $\alpha = 14$ , e.g. for  $Z(10^\circ/5^\circ)$ .

As it has appeared [4] that the spectral dependence of dissymmetry  $Z(45^\circ/135^\circ)$  or  $Z(45^\circ/90^\circ)$  can be used for distribution analysis of polydispersions, the topic of this paper is characterization of model polystyrene polydispersions on the basis of the spectral dependence of small-angle dissymmetry  $Z(10^\circ/5^\circ)$ .

## Theoretical

The theoretical coefficient of dissymmetry [1] for nonpolarized primary ray may be expressed by the following equation

$$Z_n(\Theta_1/\Theta_2) = \frac{\int_0^x [i_1(m, \alpha, \Theta_1) + i_2(m, \alpha, \Theta_1)] f(\alpha) d(\alpha)}{\int_0^x [i_1(m, \alpha, \Theta_2) + i_2(m, \alpha, \Theta_2)] f(\alpha) d(\alpha)} \quad (2)$$

where  $i_1, i_2$  are the Mie intensity functions. The distribution of particle sizes of the polydispersion was expressed by means of the lognormal distribution of negative order [4] (NOLD) in the form

$$f(\alpha) = \left( \frac{K}{\pi} \right)^{1/2} \alpha^{-1} \exp \left( -K \log^2 \frac{\alpha}{\alpha_M} \right) \quad (3)$$

where  $\alpha_M = 2\pi r_M/\lambda$  and  $K$  are medial size and width parameter, respectively ( $r_M$  is the medial radius of particle).

The Mie intensity functions  $i_1, i_2$  for vertically and horizontally polarized primary ray [1] are to be expressed as follows

$$i_1(m, \alpha, \Theta) = \left| \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n) \right|^2 \quad (4)$$

$$i_2(m, \alpha, \Theta) = \left| \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n) \right|^2 \quad (5)$$

where the angular coefficients  $\pi_n$  and  $\tau_n$  may be expressed by the Legendre polynomials and coefficients  $a_n, b_n$  by the Bessel functions. The number of terms in these summations [5] was determined from the relation

$$n_{\max} = 1.84 \alpha^{0.904} + 4$$

The integrals in eqn (2) were solved numerically for the step  $\Delta\alpha = 0.05$  by using a computer Siemens 4004. A program in language Fortran IV was applied and all calculations were performed within twofold precision. The calculations were checked in the way described in previous paper [4].

## Results and discussion

The spectral dependence of dissymmetry  $Z(10^\circ/5^\circ)$  is represented in Fig. 1a for  $r_M = 400$  nm and different width parameters. Analogous course is characteristic of the interval  $r_M = 100$ — $700$  nm. In this case, the theoretical relationships  $Z_n(10^\circ/5^\circ) = f(\lambda_0)$  are fairly distinguishable for a given  $r_M$  and different values of  $K$ . But if  $r_M > 700$  nm, they overlap one another and an oscillating course appears (Fig. 1b).

In consistence with the course of the relationship  $Z_n(10^\circ/5^\circ) = f(\alpha)$  it was found that the value of  $Z_n(10^\circ/5^\circ)$  decreased with increasing value of  $r_M$  and that the increase in polydispersity had equal influence. According to the course [4] of nonsymmetrical NOLD, the fraction of larger particles increases with polydispersity of system and thus the dissymmetry decreases.

It results from Fig. 1a and analogous relationships valid for  $r_M$  in the range 100—700 nm that the spectral dependence of dissymmetry monotonously increases because  $\alpha$  decreases with increasing wavelength according to definition and thus the dissymmetry of polydispersion increases. At medians  $r_M < 100$  nm the values of  $Z_n(10^\circ/5^\circ)$  approximate the value  $Z = 1$  and the influence of  $r_M$  and  $K$  on the course of the investigated relationships decreases. At  $r_M < 60$  nm the influence of the distribution parameters of NOLD is so small that the theoretical relationships  $Z_n(10^\circ/5^\circ) = f(\lambda_0)$  practically coalesce.

Now we shall pay attention to the possibility of determining the distribution parameters of polydispersion on the basis of comparison of the experimental with the theoretical values of the investigated dissymmetry. It results from the examined spectral relationships of dissymmetry that this method cannot lead to an unambiguous solution because several pairs of parameters  $r_M$  and  $K$  always correspond to the value of dissymmetry of polydisperse system at a certain wavelength of radiation. This fact is obvious in Fig. 2 where the relationship  $Z_n = f(r_M, K)$  is represented for the wavelength of 436 nm. Therefore the determination of distribution parameters of polydispersion necessitates to compare at minimum two experimental values of dissymmetry (measured at two wavelengths of radiation) with the theoretical values of dissymmetry. Thus we obtain for each wavelength a few pairs  $r_M—K$  among which the pair searched for is equal for all wavelengths chosen. In other words, the required distribution parameters are to be found as intersection of the plots  $r_M = f(K)$  constructed by using the read pairs median—width parameter from the plot  $Z = f(r_M, K)$  (Fig. 2) for two wavelengths.

As already stated, in the range of medians  $r_M = 60$ — $700$  nm the relationship  $Z_n = f(\lambda_0)$  exhibits monotonous course and there is a possibility of determining the distribution parameters of polydispersion by the above method. Owing to the oscillating course of  $Z_n = f(\lambda_0)$  at  $r_M > 700$  nm a comparison of the experi-

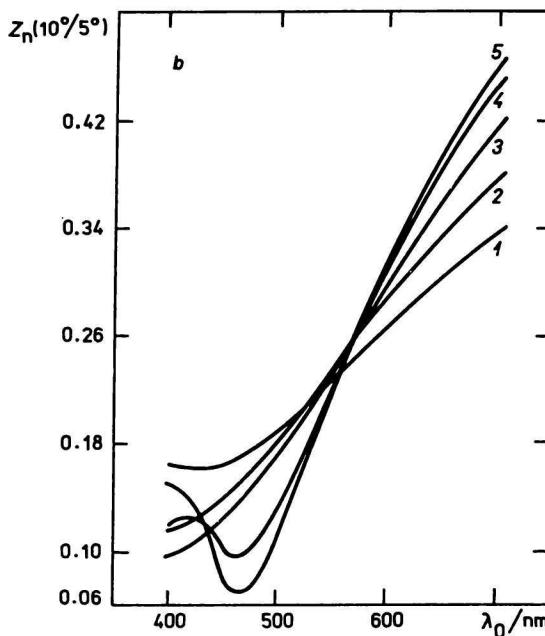
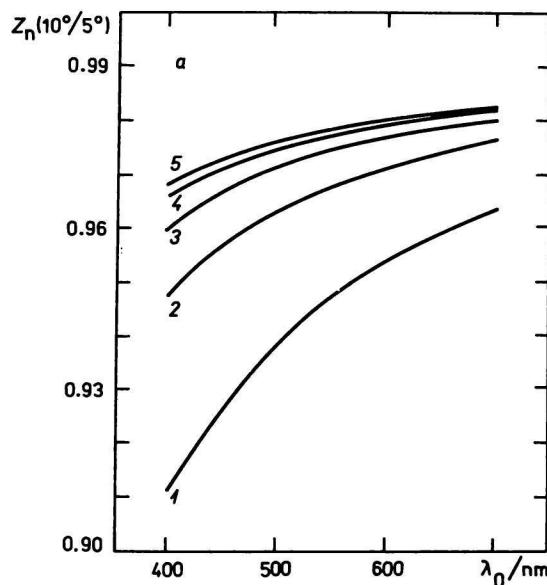


Fig. 1. Influence of polydispersity on the spectral dependence of the coefficient of dissymmetry  $Z_n(10^\circ/5^\circ)$  in the system with  $m = 1.20$ , NOL distribution,  $K = 1, 5, 2, 10, 3, 20, 4, 50, 5, 100$ .  $r_M/\text{nm}$ :  
a) 400, b) 900.

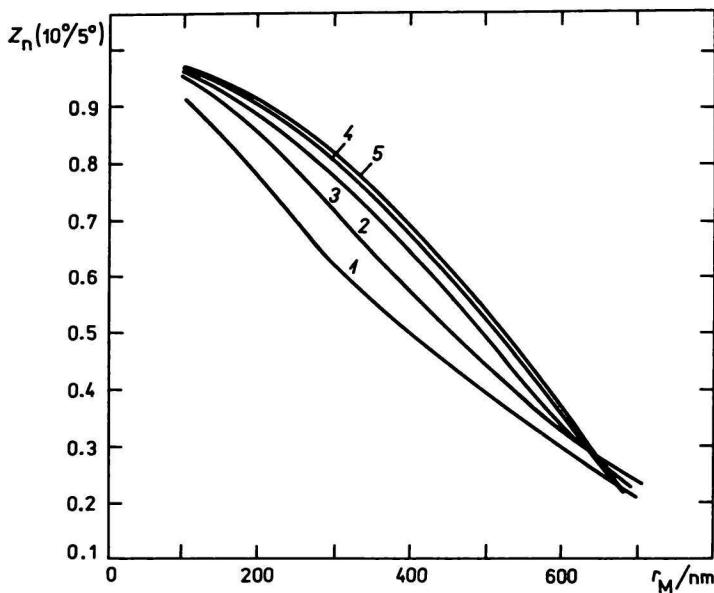


Fig. 2. Variation of dissymmetry  $Z_n(10^\circ/5^\circ)$  with medial radius  $r_M$  for various degrees of polydispersity;  $\lambda_0 = 436$  nm.

$K = 1, 5, 2, 10, 3, 20, 4, 50, 5, 100$ .

mental dependence of dissymmetry on wavelength with the theoretical "spectrum" of  $Z_n = f(\lambda_0)$  in a wide range of wavelengths appears as a convenient method of determination of distribution parameters.

As for classical dissymmetry, the oscillating character and the overlap of relationships  $Z_n(45^\circ/135^\circ) = f(\lambda_0)$  manifest themselves as early as at  $r_M = 100$  nm owing to which only the application of a wide range of wavelengths comes into consideration for granulometric purposes.

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