

# Influence of polydispersity on Mie scattering from colloid dispersions

J. VAVRA

*Department of Physical Chemistry, Slovak Technical University,  
880 37 Bratislava*

Received 6 May 1975

The influence of polydispersity and size of particles on the course of both the angular dependence of the Mie intensity functions and the polarization ratio in the systems with  $m = 1.10$  was studied theoretically. It was shown that the combination of the results of the intensity and polarization measurements can be used for characterization of the mentioned dispersions. The possibility of using both the minimum intensity methods and the polarization ratio for particle size determination is discussed from the point of view of the results obtained.

Теоретически было исследовано влияние полидисперсности и размера частиц на угловую зависимость функций интенсивности по Мию и фактора деполаризации систем с  $m = 1,10$ . Было показано, что взаимное сочетание результатов измерений поляризации и интенсивности можно использовать для характеристики этих дисперсий. На основе полученных результатов обсуждается возможность использования метода минимальной интенсивности и деполаризации для определения размера частиц.

It is known that light scattering methods can provide valuable information on mono- and polydisperse systems of spherical particles [1, 2]. Thus *e.g.* Kerker *et al.* [3] proposed the measurement of polarization ratio in the region of angles  $30-135^\circ$  for determination of distribution parameters in systems with narrow particle size distribution. Shifrin [4] showed the possibility of determining the particle size distribution by means of the low angle light scattering.

This paper deals with the influence of polydispersity and the size of particles on both the course of angular dependence of the Mie intensity functions and the polarization ratio in colloid dispersions with the relative refractive index  $m = 1.10$ .

## *Scattering from polydisperse system*

According to the Mie theory, for the vertical ( $V_u$ ) and horizontal ( $H_u$ ) components of the intensity of the light scattered by a polydisperse system of spherical particles at non-polarized primary beam one can write [2]

$$V_u = \frac{N \lambda^2}{4\pi^2} \int_0^\infty i_1(\alpha, m, \Theta) f(\alpha) d\alpha = \frac{N \lambda^2}{4\pi^2} i_1^*, \quad (1)$$

$$H_u = \frac{N \lambda^2}{4\pi^2} \int_0^\infty i_2(\alpha, m, \Theta) f(\alpha) d\alpha = \frac{N \lambda^2}{4\pi^2} i_2^*, \quad (2)$$

where  $N$  is the number of particles in a volume unit,  $\lambda$  the wave length of the light used,  $i_1, i_2$  are the Mie intensity functions,  $\alpha$  is the size parameter ( $\alpha = \pi D/\lambda$ ,  $D$  is the particle diameter),  $\Theta$  is the observation angle and  $f(\alpha)$  is the function describing the particle size distribution. According to eqns (1) and (2) it is possible to express the polarization ratio as  $\rho(\Theta) = H_u(\Theta)/V_u(\Theta)$ .

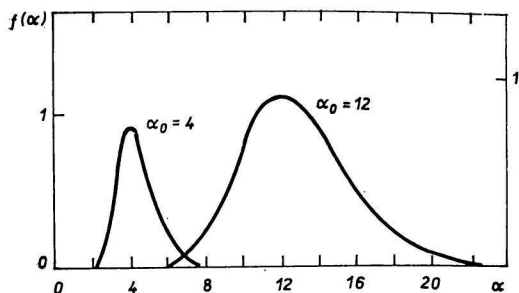


Fig. 1. "Polydispersity" ( $K = 10$  for  $\alpha_0 = 4$  and  $\alpha_0 = 12$ ) of Evva's distribution.

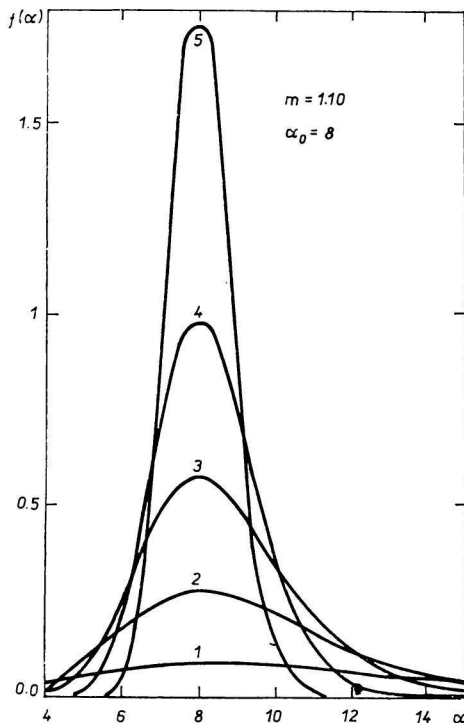


Fig. 2. The significance of the width parameter  $K$  of Evva's distribution.

1.  $K = 2.5$ ; 2.  $K = 5$ ; 3.  $K = 10$ ;  
4.  $K = 20$ ; 5.  $K = 50$ .

The assumed particle size distribution can be described by various distribution functions. For many systems the lognormal distribution function turned out satisfactory [2] and in the present study it was used in the *Evva's* [5] rearrangement

$$f(\alpha) = C \exp[-K(\ln \alpha/\alpha_0)^2], \quad (3)$$

where  $K$  and  $\alpha_0$  are the width and the modal parameters, respectively; for  $\alpha = \alpha_0$  it holds  $f(\alpha) = C$ . It is to be noted (Fig. 1) that with increasing  $\alpha_0$  the distribution becomes wider in spite of a constant  $K$ . The significance of the width parameter  $K$  for  $\alpha_0 = 8$  is shown in Fig. 2.

### Results and discussion

Integrals in eqns (1) and (2) were solved numerically (the programme in Fortran IV for a computer CDC 3300) with an interval  $\alpha = 0.5$  while the values of the intensity functions were calculated by means of tables [6–8]. The correctness of calculations was checked by means of the published angular dependence of  $\rho(\Theta)$  [3]. Fig. 3 shows

the fundamental correctness of the numerical solution, the deviations being obviously due to the application of slightly different distribution functions. Fig. 4 shows the influence of different degree of polydispersity  $K$  and size parameter  $\alpha_0$  on the course of curves  $i_1^*(\theta)$ ,  $i_2^*(\theta)$ , and  $\varrho(\theta)$ .

For  $\alpha_0 = 4$  and a low degree of polydispersity the curves  $i_1^*(\theta)$  show typical minima and maxima which become flattened with an increasing width of distribution. At a medium polydispersity of the system a parallel monotonous course of curves can be seen in the whole region of angles studied. For highly polydisperse systems

Fig. 3. The control of calculations.  
— published [3] curve (ZOLD distribution);  
○ calculated values.

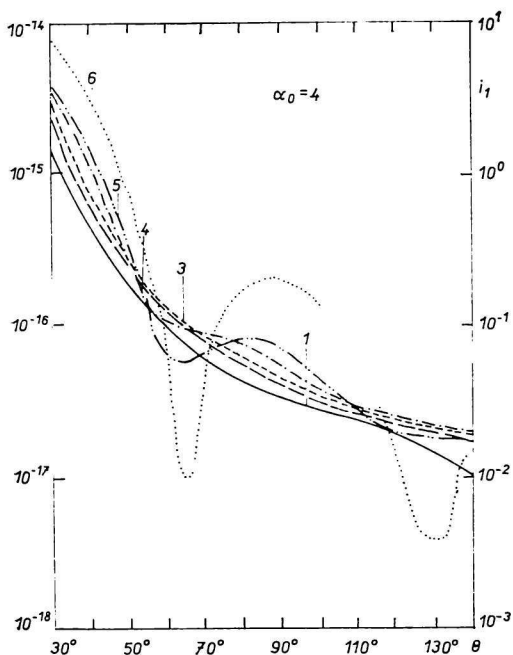
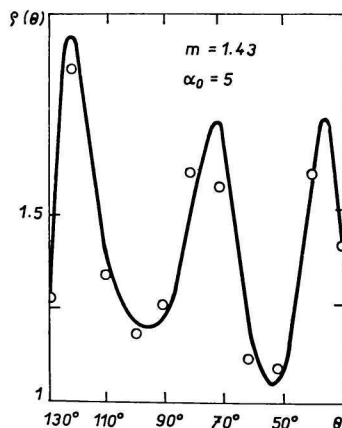


Fig. 4a

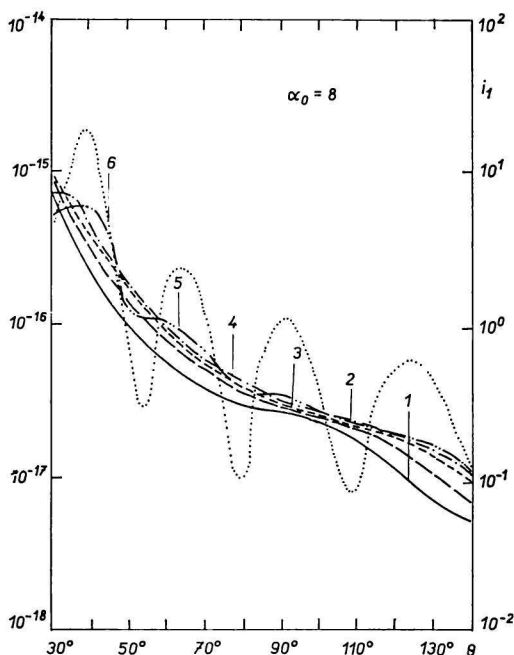


Fig. 4b

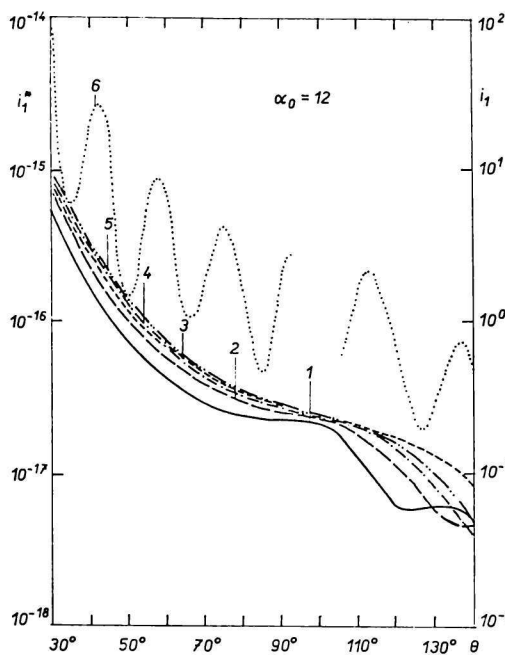


Fig. 4c

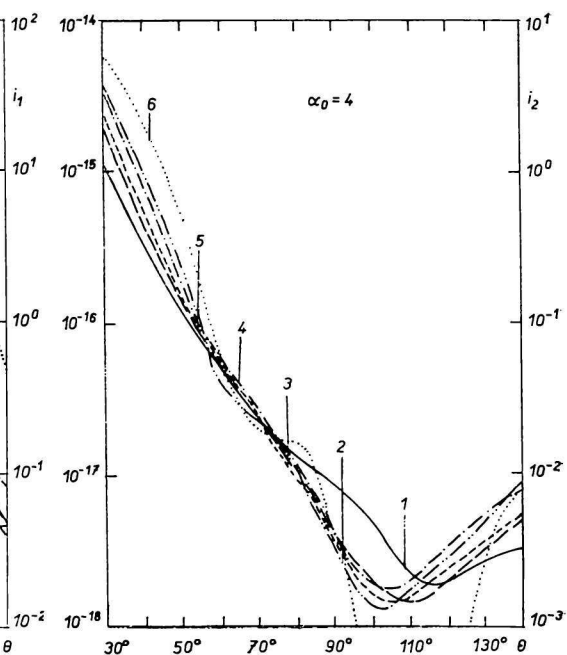


Fig. 4d

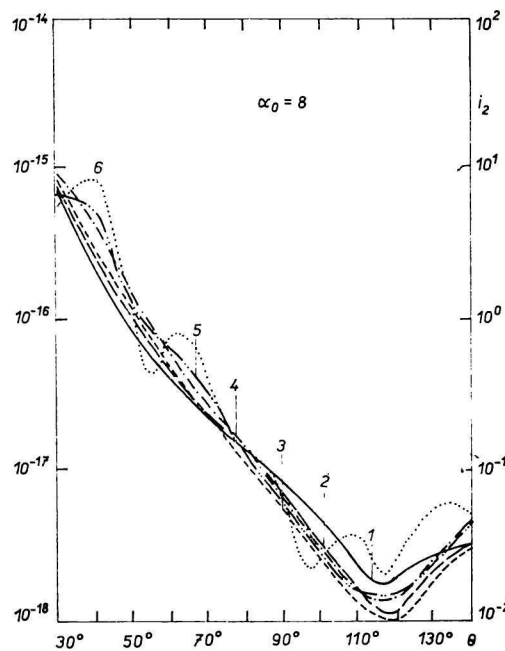


Fig. 4e

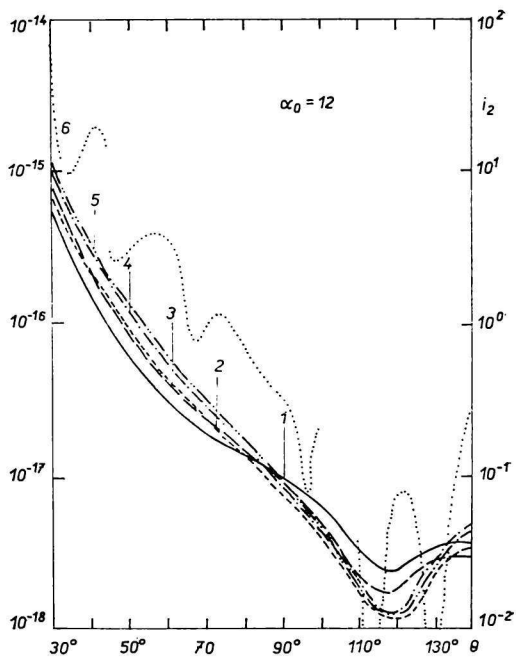


Fig. 4f

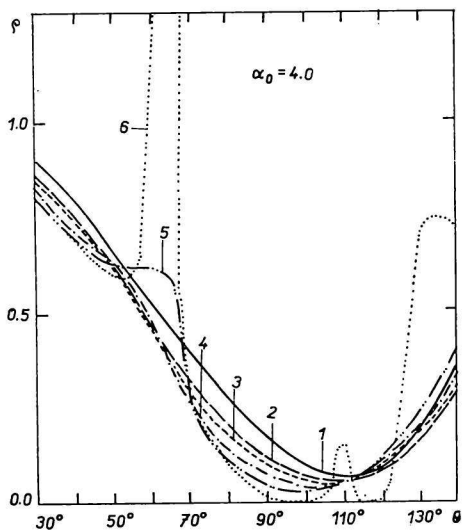


Fig. 4g

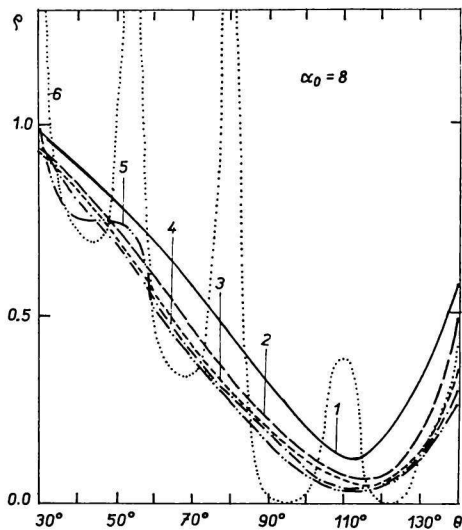


Fig. 4h

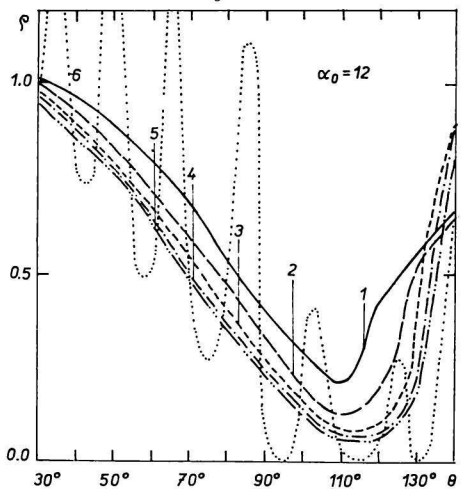


Fig. 4i

Fig. 4. The angular dependence of scattering functions and polarization ratio for  $m = 1.10$ .  
 1.  $K = 2.5$ ; 2.  $K = 5$ ; 3.  $K = 10$ ; 4.  $K = 20$ ;  
 5.  $K = 50$ ; 6.  $K = \infty$ .

$a, b, c$  vertical component  
 $d, e, f$  horizontal component  
 $g, h, i$  polarization ratio

the curves turn downwards from an angle about  $110^\circ$ . This curvature is more pronounced at  $\alpha_0 = 8$  for all degrees of polydispersity. The situation is similar at  $\alpha_0 = 12$ , however, in contrast to Fig. 4a the radiation envelope attains an oscillating character at high polydispersity and in the range of angles  $100-140^\circ$ .

The "flattening" of the curves with an increasing polydispersity for  $\alpha_0 = 4$  and  $\alpha_0 = 8$  or the indication of undulation at  $\alpha_0 = 12$  and higher degrees of polydispersity can be seen also in the  $i_2^*$  vs.  $\theta$  plots. Moreover, at  $\alpha_0 = 4$  there appeared a shift of the position of the minimum with increasing polydispersity. For  $K = 50$  and  $K = 2.5$  it is situated at  $\theta = 100^\circ$  and  $\theta = 115^\circ$ , respectively.

An analogous shift of the minimum for  $\alpha_0 = 4$  between  $95-115^\circ$  occurred also in the angular dependence of the polarization ratio  $\rho(\theta)$  while for  $\alpha_0 = 8$  and

$\alpha_0 = 12$  the minimum had a constant position regardless the changing angle. For  $\alpha_0 = 4$  and  $\alpha_0 = 8$ , a flattening of curves  $\rho(\theta)$  with increasing polydispersity was observed while for  $\alpha_0 = 12$  undulation was indicated at  $K = 5$  and  $K = 2.5$ .

It can be concluded for all dependences studied that the higher the  $\alpha_0$  value the lower is the degree of polydispersity at which the flattening of the corresponding curves begins.

Thus the theoretical calculations show that the combination of the results of the intensity and polarization measurements can be used for evaluating the nature of dispersion studied.

As known,  $i^*(\theta)$  curves are important with regard to the influence of polydispersity on working dependences of the minimum intensity method while  $\rho(\theta)$  relationships involve another method of particle size determination. In this connection let us consider the extremes in the dependences on Figs. 4d, 4f, 4g, and 4h. Since according to Figs. 4d and 4g the positions of minima in the region of angles 95–115° were shifted as a consequence of polydispersity, the corresponding extremes of dependences  $i_s^*(\theta)$  and  $\rho(\theta)$  cannot be used for determining a mean diameter of particles in polydisperse systems. On the other hand, in spite of a negligible effect of polydispersity on the position of minima in Figs. 4f and 4h in the region of angles 112–118° these minima are situated practically in the domain of appearance of maxima on the corresponding dependences for a monodisperse system. Therefore, it is hardly possible to coordinate these minima to any neighbouring minimum. As can be seen, the determination of the mean particle diameter based on the appearance of minima on the curves  $i^*(\theta)$ ,  $\rho(\theta)$  in the region of higher angles is rather difficult.

It becomes also evident that a detailed distribution analysis of the above-mentioned systems cannot be carried out by comparing the experiment and theory since the majority of dependence studied is rather monotonous.

*Acknowledgements.* The author wish to express his gratitude to Dr L. Sakál (Institute of Inorganic Chemistry, Slovak Academy of Sciences) for his valuable assistance in calculations performed at the UNO Computing Centre, Bratislava.

## References

1. Shifrin, K. S., *Rasseyanie sveta v mutnoi srede*. (Scattering of Light in Non-transparent Medium.) Gostechizdat, Moscow, 1951.
2. Kerker, M., *The Scattering of Light and other Electromagnetic Radiation*. Academic Press, New York, 1969.
3. Kerker, M., Matijević, E., Espenscheid, W. F., Farone, W. A., and Kitani, S., *J. Colloid Sci.* **19**, 213 (1964).
4. Shifrin, K. S., Perelman, A. Y., and Punina, V. A., *Proc. A. I. Vocikov Main Geophys. Obs.* **183**, 19 (1966).
5. Evva, F., *Z. Phys. Chem.* **202**, 208 (1953).
6. Denman, H. H., Heller, W., and Pangonis, W. J., *Angular Scattering Functions for Spheres*. Wayne State University Press, Detroit, 1966.
7. Gumprecht, R. O. and Sliepceovich, C. M., *Ricatti-Bessel Functions for Large Arguments and Orders*. University of Michigan, Ann Arbor, 1951.
8. Gumprecht, R. O. and Sliepceovich, C. M., *Functions of First and Second Derivatives of Legendre Polynomials*. University of Michigan, Ann Arbor, 1951.

Translated by D. Berek