

Determination of the relative number distribution of particle sizes using photon correlation spectroscopy

T. W. Taylor, S. M. Scrivner, C. M. Sorensen and J. F. Merklin

We investigate the determination of relative number distributions of particle sizes using photon correlation spectroscopy (PCS). To distinguish our work from earlier results, we have studied the extraction of the number distribution, relative number as a function of size, from the intensity distribution, relative scattered intensity vs size, and set limits on its usefulness. Expressions relating the scattered intensity distribution to the number distribution are presented. These results are connected to the output of two common PCS analysis techniques, the method of cumulants, and the inverse Laplace transform. These results are tested, and limits are set by generating a synthetic intensity autocorrelation function from a known number distribution and comparing the recovered number distribution to the input. We find good agreement for distributions narrower than a geometric width of 1.40.

I. Introduction

The possibility of performing *in situ* size distribution measurements for a suspension of particles in the submicron range using photon correlation spectroscopy has attracted considerable attention in the past decade. The cumulant method proposed by Koppel¹ represents one way of characterizing the nonexponentiality of the scattered electric field autocorrelation function. In this method the exponent is expanded in integral powers of time, the coefficients of which are called cumulants and are related to the moments of the distribution. This method is often limited to two or perhaps three cumulants because of noise and is considered only useful for narrow distributions.²⁻⁴

More recently multiexponential or histogram techniques have been studied wherein the autocorrelation function is represented by a finite sum of exponentials or integrals of exponentials with constant amplitude over a finite range.⁵⁻⁷ These methods are attractive in that they give a more straightforward picture of the distribution, they can fit broader distributions than the cumulant method, and they can detect bimodality.

In this paper we study the conversion of *intensity distribution* information, determined by the above

methods of analysis of the autocorrelation function, into *number distribution* information. Below we present a method of extracting number distribution information from the results of both the cumulant and multiexponential analysis methods. The procedure is limited to Rayleigh scatterers which scatter light proportional to the sixth power of their radius. This causes the small particle part of the size distribution to be hard to detect, thus setting limits on the width of a distribution that one can measure using PCS.

We also extend the analysis of size distribution from the usual hydrodynamic regime to the kinetic regime, defined by the mean free path of the gas molecules being large compared to the diffusing particle radius. The diffusion coefficient varies as inverse radius in the hydrodynamic regime, inverse radius squared in the kinetic regime.

II. Theory

The analysis of PCS data to determine number distributions depends heavily on two things: the functional dependence of the scattered intensity on particle size and the dependence of the linewidth, or equivalently the diffusion coefficient, on particle size. For Rayleigh particles ($r \ll \lambda$ and/or $\theta \ll 1$), the scattered intensity in the scattering plane is isotropic and has a particle radius dependence given by

$$I(r) \propto r^6. \quad (1)$$

The intensity autocorrelation function for a suspension of Brownian diffusing particles with no interparticle interactions can be written as

The authors are with Kansas State University, Manhattan, Kansas 66506.

Received 14 June 1985.

0003-6935/85/223713-05\$02.00/0.

© 1985 Optical Society of America.

$$\langle I(t)I(0) \rangle = \langle I \rangle^2 + A \exp(-2\Gamma t), \quad (2)$$

where the linewidth is given by

$$\Gamma = Dk^2. \quad (3)$$

D is the diffusion coefficient, A is a constant that depends on the coherence of the scattered light on the photocathode, and $\mathbf{k} = [(4\pi n)/\lambda_0] \sin\theta/2$ is the scattered wave vector. The index of refraction of the suspension is n , the incident wavelength is λ_0 , and the scattering angle is θ .

The diffusion coefficient D depends on the ratio of the mean free path of the molecules l to the particle's radius r . When $l/r \ll 1$, the particles are in the hydrodynamic regime, and D is given by the Stokes-Einstein diffusion constant

$$D_{SE} = \frac{K_B T}{6\pi\eta r}, \quad (4)$$

where K_B is the Boltzmann constant, T is the temperature, and η is the shear viscosity of the suspension.

In the other extreme, $l/r \gg 1$, the particle is in the kinetic regime, and the diffusion coefficient is given by⁸

$$D_{CE} = \frac{3}{8\rho r^2} \left(\frac{mK_B T}{2\pi} \right)^{1/2}, \quad (5)$$

where ρ is the mass density of the surrounding medium, and m is the mass of the medium particle.

We will restrict the analysis to the hydrodynamic and the kinetic regimes with

$$\Gamma_H = C_H/r \quad (6a)$$

or

$$\Gamma_K = C_K/r^2, \quad (6b)$$

where C_H and C_K are the appropriate constants found from Eqs. (3), (4), and (5).

A. Cumulants

Throughout the remainder of this paper, we will refer to the normalized intensity autocorrelation function as

$$g^{(2)}(t) = \langle I(t)I(0) \rangle / C, \quad (7)$$

where the normalization constant C is chosen so that $g^{(2)}(\infty) = 1$.

If a distribution of particle sizes is present, there is a corresponding distribution of diffusion coefficients, or equivalently, a distribution of linewidths. Hence the correlation function can be rewritten as

$$g^{(2)}(t) = 1 + A \left| \int_0^\infty d\Gamma G(\Gamma) \exp(-\Gamma t) \right|^2, \quad (8)$$

where $G(\Gamma)d\Gamma$ is the fraction of the total intensity of light scattered from particles with linewidth Γ within $d\Gamma$.

Koppel¹ proposed the cumulant technique as a method of analysis for polydisperse systems. In the cumulant technique the correlation function is fit to the form

$$g^{(2)}(t) = 1 + A \left[\exp \left(-\mu_1 t + \frac{\mu_2}{2!} t^2 - \frac{\mu_3}{3!} t^3 + \dots \right) \right]^2, \quad (9)$$

where μ_i is the i th cumulant, and the cumulants are related to the moments of the scattered intensity distribution function. The first cumulant is the mean linewidth,

$$\mu_1 = \langle \Delta\Gamma \rangle, \quad (10)$$

and the second cumulant is the variance of the intensity distribution about the mean,

$$\mu_2 = \langle \Delta\Gamma^2 \rangle, \quad (11)$$

with $\Delta\Gamma = \Gamma - \langle \Gamma \rangle$. Using the first two cumulants a polydispersity index can be defined as

$$Q = \mu_2/\mu_1^2 = \frac{\langle \Delta\Gamma^2 \rangle}{\langle \Gamma \rangle^2}. \quad (12)$$

Equation (12) conveniently, although not directly, relates the nonexponentiality of $g^{(2)}(t)$ to the polydispersity of the particles.

As a general rule many experimentalists assume, as an experimental guide, that when $Q < 0.05$, the distribution is monodisperse. However, Barger^{3,9} has shown that this may be in error. He showed for a relatively broad Gaussian number distribution of Rayleigh particles ($\sigma_r \sim 0.35$), $g^{(2)}(t)$ deviated little from exponential behavior ($Q \sim 0.04$). Furthermore, an assumption of monodispersity for this system would produce a 30% error in the mean size of the particles inferred from the mean linewidth.

We will extend Barger's work to the zeroth-order lognormal (ZOLD) and Schultz distributions in both the hydrodynamic and kinetic diffusion regimes. The normalized ZOLD has the form

$$N_L(r) = \frac{\exp \left[\frac{-(\ln \sigma)^2}{2} \right]}{\sqrt{2\pi r_0 \ln \sigma}} \exp \left[\frac{(-\ln r/r_0)^2}{2(\ln \sigma)^2} \right], \quad (13)$$

where the parameters are the most probable size r_0 and the geometric width σ . The normalized Schulz distribution has the form

$$N_S(r) = \frac{(Z+1)^{Z+1}}{\langle r \rangle \Gamma(Z+1)} \left(\frac{r}{\langle r \rangle} \right)^Z \exp[-(Z+1)r/\langle r \rangle], \quad (14)$$

where the parameters are $\langle r \rangle$, the mean radius, and Z , the width parameter. $\Gamma(Z+1)$ is the gamma function.

The moments of the linewidth distribution $G(\Gamma)$ are given by

$$\langle \Gamma^n \rangle = \int \Gamma^n G(\Gamma) d\Gamma. \quad (15)$$

Using Eqs. (1) and (6), the moments become

$$\langle \Gamma^n \rangle_H = C_H \int_0^\infty r^{6-2n} N(r) dr, \quad (16a)$$

$$\langle \Gamma^n \rangle_K = C_K \int_0^\infty r^{6-2n} N(r) dr, \quad (16b)$$

where the subscripts H and K denote the hydrodynamic and kinetic diffusion regimes, respectively. These moments are normalized so that the total scattered intensity is unity.

The normalized mean radius $\langle r \rangle/r_0$ and the standard deviation $\sigma_r = \langle \Delta r^2 \rangle^{1/2}/\langle r \rangle$ of the number distri-

Table I. Normalized Mean Radius, Standard Deviation σ , Mean Linewidth, and Polydispersity Index (Q) for the ZOLD and Schulz Distributions in both the Hydrodynamic H and Kinetic K Diffusion Regimes

$N(r)$	Regime	$\langle r \rangle / r_0$	σ^2	$\langle \Gamma \rangle$	Q
ZOLD	H	$\exp(1.5 \ln^2 \sigma)$	$\exp(\ln^2 \sigma) - 1$	$\frac{C_H}{r_0} \exp(-6.5 \ln^2 \sigma)$	$\exp(\ln^2 \sigma) - 1$
ZOLD	K	$\exp(1.5 \ln^2 \sigma)$	$\exp(\ln^2 \sigma) - 1$	$\frac{C_K}{r_0^2} \exp(-12 \ln^2 \sigma)$	$\exp(4 \ln^2 \sigma) - 1$
Schulz	H	$(Z + 1)/Z$	$(Z + 1)^{-1}$	$\frac{C_H}{\langle r \rangle} \left(\frac{Z + 1}{Z + 6} \right)$	$(Z + 5)^{-1}$
Schulz	K	$(Z + 1)/Z$	$(Z + 1)^{-1}$	$\frac{C_K (Z + 1)^2}{\langle r \rangle^2 (Z + 6)(Z + 5)}$	$\frac{4Z + 18}{(Z + 4)(Z + 3)}$

butions along with the mean linewidth and polydispersity index calculated from Eqs. (11), (12), and (16) are given in Table I.

B. Inverse Laplace Transform

The inverse Laplace transform method has been used to determine the intensity distribution $G(\Gamma)$ from $g^{(2)}(t)$ in recent years. It has been tested on synthetic data^{6,10-13} and applied to various real systems, e.g., vesicle aggregation^{11,14} and polymer solutions.¹¹

The method can be used to determine directly the distribution of scattered intensities $G(\Gamma)$. There are several ways of representing $G(\Gamma)$: as evenly spaced histograms; as logarithmically spaced histograms, or as logarithmically spaced delta functions. We will represent $G(\Gamma)$ as logarithmically spaced delta functions so that Eq. (8) becomes

$$g^{(2)}(t) = 1 + A \left| \sum_i a_i \exp(-\Gamma_i t) \right|^2, \quad (17)$$

where a_i is the relative intensity of light scattered by a particle with $\Gamma_i = D_i k^2$. Our purpose here is to extend this technique to relate the scattered intensities a_i to the actual relative number density of particles n_i .

Since the delta functions are logarithmically spaced, the a_i values are elements of the intensity distribution in $\ln \Gamma$ space, $G(\ln \Gamma)$. They are readily converted to intensities in r space using the relation

$$G(\ln \Gamma) d(\ln \Gamma) = I(r) dr, \quad (18)$$

where $I(r) dr$ is the fraction of the intensity scattered by particles with radii between r and $r + dr$. Thus $I(r)$ can be written in terms of the amplitudes of the delta functions

$$I_H(r) = \sum_i (\Gamma_i / C_H) a_i \delta(r - C_H / \Gamma_i) \quad (19a)$$

and in the kinetic regime

$$I_K(r) = \sum_i 2(\Gamma_i / C_K)^{1/2} a_i \delta(r - [C_K / \Gamma_i]^{1/2}). \quad (19b)$$

Using Eqs. (1), (2), and (19) we find that the dependence of the number on the radius is identical in both the hydrodynamic and kinetic diffusion regimes:

$$N(r_i) \propto a_i / r_i^7. \quad (20)$$

This shows the important and often problematic effect that large particles will dominate the intensity autocorrelation function due to the r^7 factor, thus masking the presence of the smaller particles.

III. Synthetic Data Generation and Fitting

To determine the limits of the above formalism, a ZOLD with $r_0 = 10$ nm and σ in the range of 1.05–1.5 was used to generate intensity autocorrelation functions. This was accomplished by composing an intensity distribution function of 400 evenly spaced delta functions where the spacing was chosen so that the entire distribution was sampled. The normalized amplitudes of the delta functions were determined from the number distribution and the appropriate diffusion regime using Eqs. (1) and (18).

The sample time was chosen according to the criterion that the correlation function for a particle with linewidth $\Gamma = \langle \Gamma \rangle$ will have decayed to $\exp(-10)$ by the last channel. This insured that the distribution

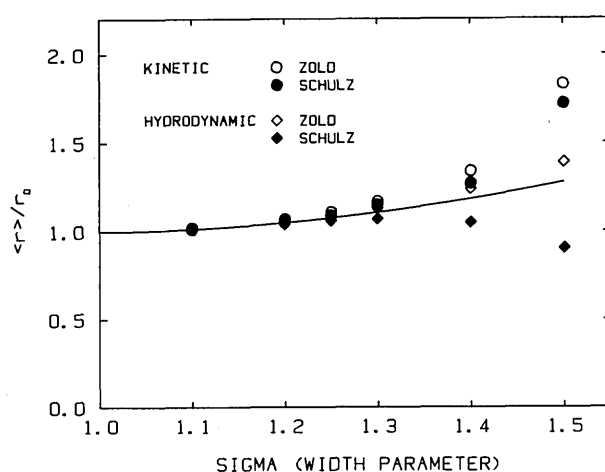


Fig. 1. Normalized mean radius $\langle r \rangle / r_0$ of the distribution vs the width of the input ZOLD distribution using the cumulant technique and assuming either a ZOLD or Schulz distribution in the appropriate diffusion regime. The line is the expected value from the input distribution.

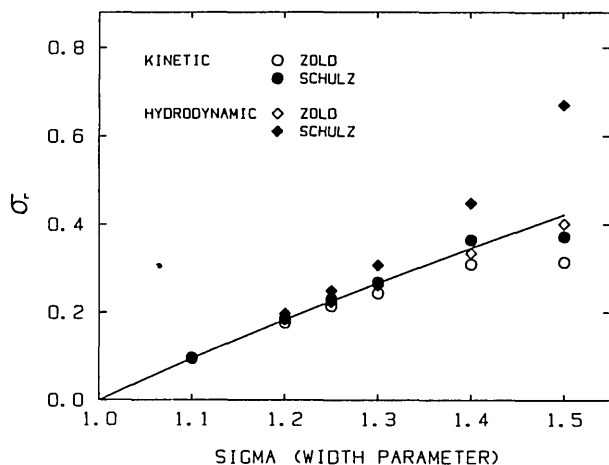


Fig. 2. Normalized standard deviation of the distribution σ_r vs the width of the input ZOLD distribution using the cumulant technique and assuming either a ZOLD or Schulz distribution in the appropriate diffusion regime. The line is the expected value from the input distribution.

function was adequately sampled. A 256-point electric field autocorrelation function was constructed as

$$g^{(1)}(t) = \sum_{j=1}^{256} \sum_{i=l}^{400} G(\Gamma_i) \exp(-\Gamma_i t_j), \quad (21)$$

where $t_j = j\Delta t$, Δt is the sample time, and $G(\Gamma)$ is given in the appropriate diffusion regime by

$$G_H(\Gamma_i) = \frac{r_i^8 N(r_i)}{C_H}, \quad (22a)$$

$$G_K(\Gamma_i) = \frac{r_i^9 N(r_i)}{2C_K}. \quad (22b)$$

The intensity autocorrelation function was constructed from the field autocorrelation function using the Siegert relation and a relative random noise of 2×10^{-4} was added to $g^{(2)}(t)$ to simulate the noise on an experimentally measured correlation function.

Both the cumulant extrapolation^{2,10} and the two exponential^{9,10,15} analysis techniques were used to determine the first two cumulants. The first cumulant differed by <1% between the two techniques, while the second cumulant varied <15%. The average values of the cumulants were used to recover the number distribution.

The multiple delta function technique was performed as outlined by Pike⁵ with $\omega_{\max} = 6$ corresponding to the random noise added to the correlation function. The shifting procedure, in which the Γ_i values are shifted a fraction of the distance $\Gamma_{i+1} - \Gamma_i$ and the correlation function refit, was used to obtain more detail in the intensity distribution function $G(\ln \Gamma)$.

IV. Results

Using the mean decay rate and the polydispersity index obtained from the cumulant method and Table I, the normalized mean radius and standard deviation

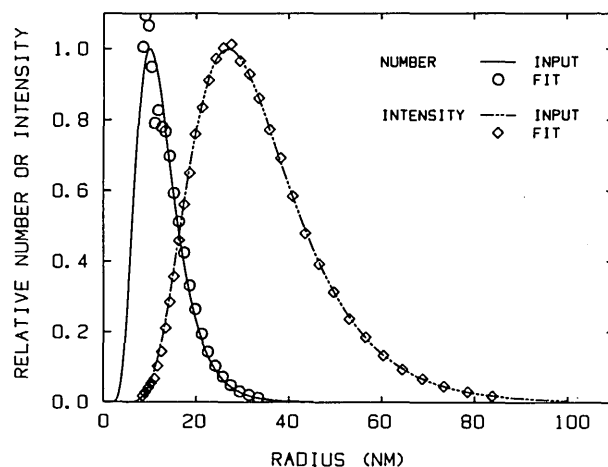


Fig. 3. Relative number and scattered intensity vs radius for a ZOLD distribution of width $\sigma = 1.5$. The data points were found using the multiple delta function technique.

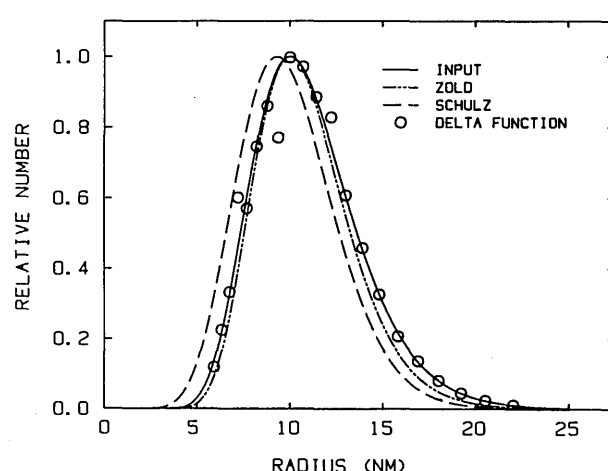


Fig. 4. Relative number vs radius for a ZOLD distribution of width $\sigma = 1.3$. The data points are from the multiple delta function technique, and the curves are from the cumulant technique assuming either a ZOLD or Schulz distribution.

of both the ZOLD and Schulz number distributions were determined. Calculated values of these moments using the known input number distribution were also determined and are represented by the solid curves in Figs. 1 and 2. The recovered mean radius agrees well with the input value, Fig. 1, up to $\sigma \sim 1.45$ and then begins to deviate. It is satisfying that, although a distribution must be assumed to recover the moments of the number distribution, these recovered moments appear to be distribution independent. Figure 2 shows the same behavior when the recovered standard deviation is compared with the input deviation. Thus for distributions with a geometric width, $\sigma > 1.45$, or normalized standard deviation, $\sigma_r > 0.4$, the cumulant method has a significant error.

In Fig. 3 the input intensity distribution function

$I(r)$ is compared with the recovered $I(r)$ values obtained from delta function techniques. These results are for $\sigma = 1.5$ and the kinetic regime. Excellent agreement is seen between the input and recovered intensities. However, when the intensities were converted into the number distribution $N(r)$ and compared with the input number distribution, the lack of agreement is quite evident. The dominance of the large particles in the scattered intensity completely washes out the appearance of the smaller particles. This stresses the significance of recognizing that accurate knowledge of the intensity distribution does not necessarily imply accurate knowledge of the size distribution.

The results for a number distribution with $\sigma = 1.3$ are shown in Fig. 4. Here the agreement is good over the entire distribution. The Schulz and ZOLD distributions determined from the cumulant method are also included to indicate their good agreement with the input number distribution.

V. Discussion

The conversion of the intensity autocorrelation function measured by PCS to a number distribution is a tricky but important problem. Not only must one contend with the difficulties of data analysis but also with the conversion of intensity information into number information. Although an accurate representation of the intensity distribution can be achieved, this does not guarantee accurate recovery of the number distribution. The r^6 factor involved in the scattered intensity tends to wash out the intensity scattered by the small particles, causing increased error in the determination of the number of small particles.

The results presented here indicate that the problem can be handled sufficiently well within limits. The cumulant technique appears to have merits in its ease of use. Although a unimodal two-parameter number distribution must be assumed, the first two moments of the distribution, $\langle r \rangle$ and $\langle \Delta r^2 \rangle$, can be determined with reasonable accuracy regardless of the assumed distribution up to a limiting width. Beyond this limit significant errors begin to emerge.

Analysis of the intensity autocorrelation function to determine the scattered intensity distribution, $G(\ln \Gamma)$ is difficult due to the ill-conditioning of the inverse Laplace transform. In this paper we have shown that, although a good representation of $G(\ln \Gamma)$ or equivalently $I(r)$ may be obtained, an adequate conversion to $N(r)$ is not always possible and is limited by the width of the distribution. It is somewhat surprising that both the cumulant and the multiple delta function techniques are limited by the same width for the ZOLD, $\sigma \sim 1.45$. This work is important not only because of its numerous applications but also because it sets limits on the usefulness of the techniques and identifies trends that are expected for any particle size distribution.

This work was supported by NSF grant CHE-8218415 and DOE grant DE-AC01-80ER10677 and Kansas State University Engineering Experiment Station grant 0607.

References

1. D. E. Koppel, "Analysis of Macromolecular Polydispersity in Intensity Correlation Spectroscopy: The Method of Cumulants," *J. Chem. Phys.* **57**, 4814 (1972).
2. P. N. Pusey, "Macromolecular Diffusion," in *Photon Correlation and Light Beating Spectroscopy*, H. Z. Cummins and E. R. Pike, Eds. (Plenum, New York, 1974), p. 387.
3. C. B. Barger, "Measurement of a Continuous Distribution of Spherical Particles by Intensity Correlation Spectroscopy: Analysis by Cumulants," *J. Chem. Phys.* **61**, 2134 (1974).
4. B. Chu, "Correlation Function Profile Analysis in Laser Light Scattering. I. General Review on Methods of Data Analysis," in *The Application of Laser Light Scattering to the Study of Biological Motion*, J. C. Earnshaw and M. W. Steer, Eds. (Plenum, New York, 1983), p. 53.
5. E. R. Pike, "The Analysis of Polydisperse Scattering Data," in *Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems*, S. Chen, B. Chu, and R. Nossal, Eds. (Plenum, New York, 1981), p. 179.
6. E. Gulari, E. Gulari, Y. Tsunashima, and B. Chu, "Photon Correlation Spectroscopy of Particle Distributions," *J. Chem. Phys.* **70**, 3965 (1979).
7. S. Provencher, "Inverse Problems in Polymer Characterization—Direct Analysis of Polydispersity with Photon Correlation Spectroscopy," *Makromol. Chem.* **180**, 201 (1979).
8. R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1958).
9. R. L. McCally and C. B. Barger, "Application of Intensity Correlation Spectroscopy to the Measurement of Continuous Distributions of Spherical Particles," *J. Chem. Phys.* **67**, 3151 (1978).
10. B. Chu and A. Dinapoli, "Extraction of Distributions of Decay Times in Photon Correlation of Polydisperse Macromolecular Solutions," in *Measurement of Suspended Particles by Quasi-Elastic Light Scattering*, B. E. Dahneke, Ed. (Wiley, New York, 1983), p. 81.
11. S. Bott, "Polydispersity Analysis of QELS Data by a Smoothed Inverse Laplace Transform," in *Measurement of Suspended Particles by Quasi-Elastic Light Scattering*, B. E. Dahneke, Ed. (Wiley, New York, 1983), p. 129.
12. N. Ostrowsky, D. Sornette, P. Parker, and E. R. Pike, "Exponential Sampling Method for Light Scattering Polydispersity Analysis," *Opt. Acta* **28**, 1059 (1981).
13. G. C. Fletcher and D. J. Ramsay, "Photon Correlation Spectroscopy of Polydisperse Samples. I. Histogram Method with Exponential Sampling," *Opt. Acta* **30**, 1183 (1983).
14. D. Sornette and N. Ostrowsky, "Kinetics of Growth of Phospholipid Vesicles," in *Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems*, S. Chen, B. Chu, and R. Nossal, Eds. (Plenum, New York, 1981), p. 351.
15. J. R. Ford and B. Chu, "Correlation Function Profile Analysis in Laser Light Scattering. III. An Iterative Procedure," *Photon Correlation Techniques in Fluid Mechanics*, E. O. Schulz-DuBois, Ed. (Springer-Verlag, New York, 1983).