Acorn™, a new, simple, inexpensive method for non-invasive particle size measurement of suspensions and droplets

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ABSTRACT

Nanoscale particle sizing of colloidal suspensions can be performed with Acorn,™ a new, patented handheld device, that combines remote delivery and detection of laser light, and a direct measurement of particle size, without the use of digital correlators. The former is achieved through a singlemode backscatter fiber optic probe, while the latter is made possible through the implementation of a statistical processing algorithm, which recovers the average particle diameter from the integration time dependent coherence of the scattered intensity. Real-time measurement of the factorial moments, or the coherence of the scattered intensity, is made with a field programmable gate array. A fiber optic backscatter probe permits remote interrogation of samples either by dipping the probe into the solution or by placing the probe outside the container. Acorn™ provides a rapid measurement of the average diameter in the range of 2 to 5000 nm over a broad range of concentrations.

Keywords: particle sizing, dynamic light scattering, backscatter fiber optics, colloidal suspensions.

1 INTRODUCTION

Dynamic light scattering (DLS) [1] is a well-known and well-established technique for measuring particle/droplet sizes from a few nanometers to one or two micrometers; a dynamic size range encompassing all colloidal systems. As such it is an ideal for characterizing emerging nanotechnology materials. However, accurate particle sizing is possible normally in only very dilute suspensions where multiple scattering and particle-particle interactions are insignificant. In such cases an auto-correlation function (ACF) formed from the scattered laser-light can be analyzed to yield intensity-weighted particle size distribution (PSD) information.

Because of the inherent traditional instrument design, and the need for a digital correlator, current commercial instruments tend to be large, bulky, complicated to use and expensive. As such they are mainly used for R&D purposes. We describe a system based on the use of an integrated fiber-optic probe, that is, small, portable and inexpensive; ideal for formulators and as a QC tool as well as R&D. Statistical signal processing of the scattered laser-light signal leads to a new method of determining particle size that circumvents the need for digital autocorrelation.

Major practical advantages of the new instrument are the ability to accommodate non-dilute systems and to work in remote or environmentally challenging situations. Additionally, the technique works over a dynamic size range much larger than that attainable using DLS, encompassing sizes that, hitherto, have been the domain of Fraunhofer diffraction.

2 THEORETICAL BACKGROUND

Dhadwal *et al* [2] described a direct method of particle sizing based on the real-time measurement of the factorial moments of the photo-electron stream arising from the laser light scattered by a colloidal suspension of particles. In particular, they showed that the degree of coherence of the scattered field can be derived from the first two factorial moments and is given by

$$\beta = \frac{\langle n^2 \rangle - \langle n \rangle^2 - \langle n \rangle}{\langle n \rangle^2} \tag{1}$$

where, $\langle \cdots \rangle$ denotes ensemble average, β is the coherence factor and n is the average number of photons counted in a given integration time interval. An alternative expression, based on a Gaussian noise process with a Lorentzian power spectrum, relates the degree of coherence to a normalized integration time variable ξ (=$\gamma\Delta$T),

$$\beta = \frac{\beta_S}{2\xi^2}\left[\exp(-2\varsigma) + 2\xi - 1\right] \tag{2}$$

where β_S is spatial coherence, usually close to unity, Δt is the integration time and $\gamma = Q^2 D$ is the characteristic linewidth parameter, $Q = (4n\pi/\lambda)\sin(\theta/2)$ is the Bragg wavenumber, n is the refractive index of the medium, λ is the free space wavelength of the laser source, and θ is the scattering angle. The Stokes-Einstein equation $D = k_B T/6\pi\eta r$, relates the translational diffusion coefficient D, at infinite dilution, to an equivalent spherical particle radius r; k_B is Boltzmann's constant, T is the absolute temperature of the medium, and η is the viscosity of the medium.

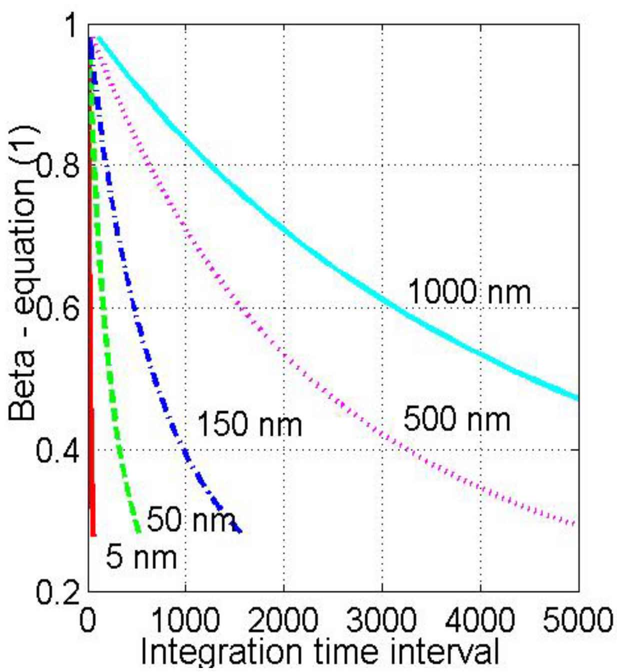

Figure 1: Degree of coherence as a function of the integration time interval ΔT.

Figure 1 shows a plot of equation (2) over a range of particle diameters. Data is generated for a typical dynamic light scattering experiment at a backward scattering angle of 146°. From this Figure it can be clearly seen that measurement of the degree of coherence using equation (1) can lead to a rapid determination of particle size. Dhadwal *et al* [2] demonstrated the potential of this technique through the use of a Brownian motion simulator and simultaneous experimental measurements with a conventional dynamic light scattering apparatus, which typically, requires a laboratory bench. They made measurements of β at several values of the integration, and by using a non-linear least squares curve-fitting procedure recovered the average particle diameter using equation (2). Experimental measurements confirmed that a twenty to sixty second duration was sufficient for a 4% precision. To overcome computational difficulties arising from nonlinear curve fitting, they proposed linear and quadratic approximations, which would be necessary for a handheld device.

In this paper we have extended those ideas to show that a portable, handheld and battery-operated particle sizing device can be constructed at modest cost. Expansion of equation (2) leads to linear (equation (3)) and quadratic (equation (4)) approximations:

$$\beta(\Delta T) = \beta_S \left[1 - \frac{2}{3}\gamma\Delta T \right] \quad (3)$$

and

$$\beta(\Delta T) = \beta_S \left[1 - \frac{2}{3}\gamma\Delta T + \frac{1}{3}\gamma^2\Delta T^2 \right] \quad (4)$$

For example, using the linear approximation it is possible to recover γ from two measurements of β, and hence particle diameter. Figure 2 shows the range of validity of ΔT for the linear (squares) and quadratic (triangles) approximations for broad range particle size. It can be noted that a single value of the larger integration time will not suffice for the entire range of particle size. Additionally, the quadratic approximation, while more accurate, would still require non-linear curve fitting to extract the size information.

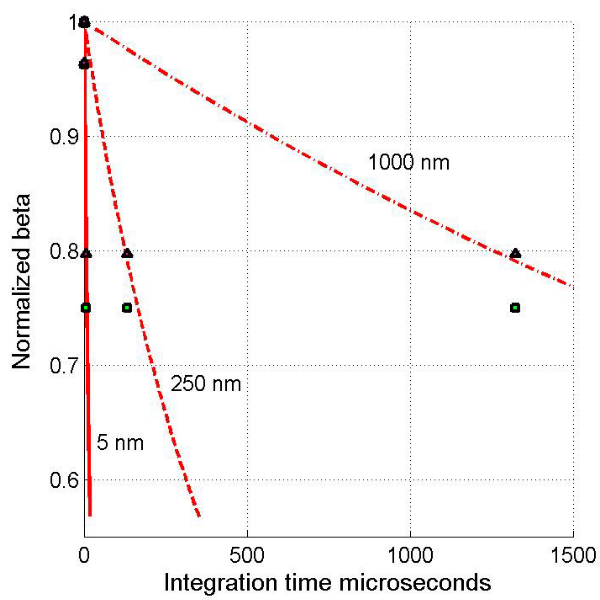

Figure 2: Linear (squares – equation (3)) and quadratic (triangles – equation (4)) approximations to equation (2).

3 EXPERIMENTAL RESULTS

There are three components of a portable handheld particle sizing instrument: a fiber optic delivery and detection probe; application specific integrated circuits that can take the burden of processing the photon streams in real time to provide measurements of the degree of coherence and an embedded processor system for controlling the flow

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of information between the display and a mass storage device.

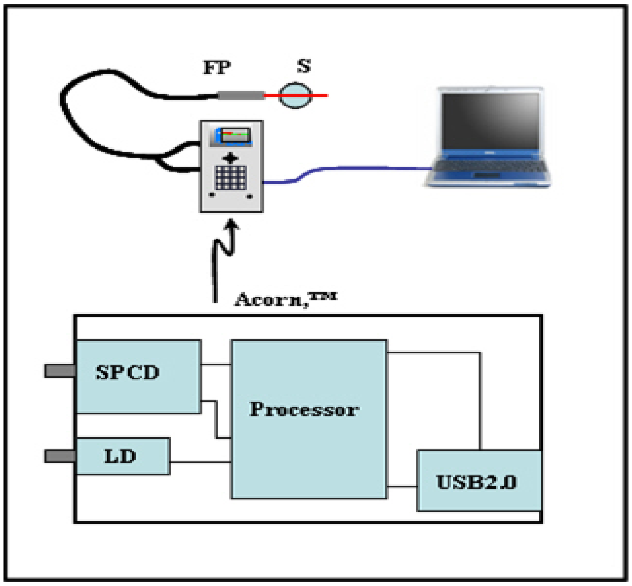

Figure 3: Set-up for obtaining data using the described technique.

The set-up in figure 3 was used to obtain real-time particle size information utilizing the techniques discussed above. A back-scatter fiber probe (FP), described by Dhadwal *et al* [3], uses two singlemode optical fibers mounted in the same cylindrical body, but inclined with respect to each other so as to define a measurement volume, about 2 mm in front of the tip as shown in Figure 4. The two-fiber arrangement can be designed for a backward scattering angle very close to 180^{o}. In the DLS community it is generally believed that measurement of the scattered intensity at 180^{o} mitigates ambiguity arising from multiple scattering. While this may be true, separation of the incident and scattered light paths becomes a serious issue, as this can lead to unknown homodyne mixing at the detector, giving rise to uncertainty in particle size. Figure 5 shows a measured spot size (~ a diameter of 400 μm) at the center of the scattering volume.

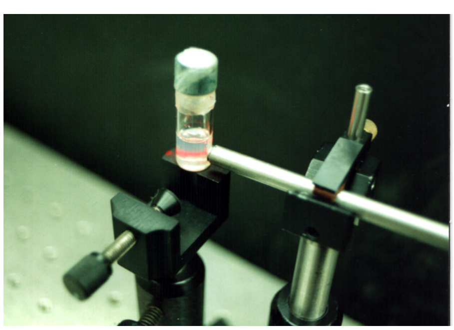

Figure 4: Photograph showing the backscatter probe placed outside a 10 mm round glass cell.

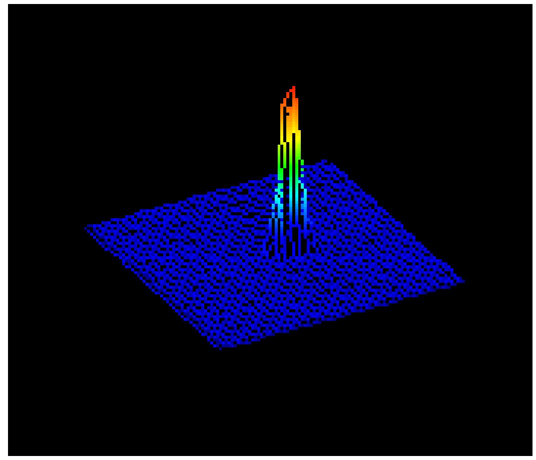

Figure 5: Laser beam profile at the center of the scattering volume.

In the experimental set-up a helium-neon laser was used for the measurements, but in the portable device a suitable semiconductor laser diode (LD) will be employed. The backward scattered photons are detected by a single photon counting system (SPCD). Factorial moments are measured using a dedicated 8-bit counter. The counter and the flow of data is controlled via a USB2.0 interface (FX2) using a laptop computer. An embedded processor in the handheld device eliminates the need for a laptop computer.

4 RESULTS AND CONCLUSION

Samples of aqueous solutions of a range of polystyrene latex spheres, purchased from Bangs Laboratories, were prepared. A real-time procedure for measuring the average particle diameter, equation (3), was tested. Simultaneous measurements were also made with a conventional Brookhaven Instrument Corporation BI9000 correlator. For the latter measurements samples were diluted appropriately using filtered DI water and the count-rate checked to ensure the absence of multiple scattering and that particle-particle interactions are insignificant. Figures 6 and 7 show the real-time estimates of particle diameter as a function of accumulation time for nominal 25 nm and 85 nm samples of polystyrene latex spheres. For the former sample a good estimate was obtained after 10 s, whereas the latter sample required about 40 s. These two measurements were performed $\Delta T=1$ μs and $K=30$ for the 25 nm sample and $K=40$ for the 85 nm sample ($\Delta T_2=K\,\Delta T$).

As illustrated in Figure 2, the linear model gives a good estimate of size provided that K does not exceed some maximum value, which can be determined. However, the same value of K does not provide sufficient accuracy for the larger particle size. Work is currently in progress on a procedure, to determine the optimum value of K for any size in the range of one or two nm to several thousand nm.

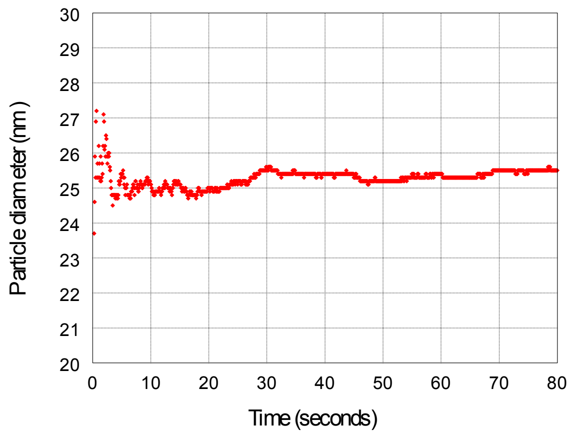

Figure 6: Real time measurement of particle sizing – 25 nm PLS

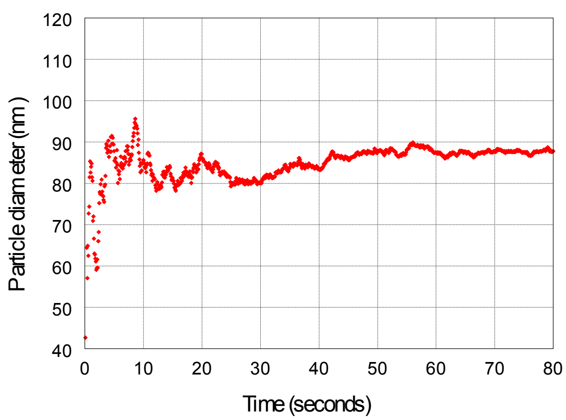

Figure 7: Real time measurement of particle sizing – 85 nm PLS

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