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# Application of Tunable Resistive Pulse Sensing

Eva Weatherall[1,2] and Geoff R. Willmott[1,3,†]

[1]The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington
[2]Callaghan Innovation, PO Box 31-310, Lower Hutt 5040, New Zealand
[3]The Departments of Physics and Chemistry, The University of Auckland, New Zealand
[†]Corresponding author
Email: g.willmott@auckland.ac.nz
Phone: (64) (0)9 9737599
Fax: (64) (0)9 3737445

## Supplementary Information: Data Handling

A tunable resistive pulse sensing (TRPS) measurement yields a number size distribution, in which the size is derived from the insulating volume of the particle (see main text). If a single parameter is used to describe this distribution, information is necessarily lost. However, if there is a requirement for one parameter (e.g. for size calibration), the mode is often most appropriate provided that the distribution is monomodal. The uncertainty in a mode is at least the width of a histogram bin. Bin widths can be calculated systematically, although there is no established consensus for such a calculation.[1]

When collecting data, a threshold for the pulse amplitude is necessary to distinguish resistive pulses from electronic noise (Figure S1(a)). The mode should lie clearly above this threshold. Distribution means and medians are affected by skew as well as the current threshold. Often the skew of a particle size distribution may favour a log-normal distribution, as in the case of aggregates of engineered nanoparticles,[2] in which case a geometric mean and standard deviation can most effectively describe the distribution.

For TRPS, it is particularly important to understand the difference between methods commonly used to calculate a distribution mean[3] and those used widely with dynamic light scattering (DLS). The usual measure of mean size for TRPS is the number-average particle radius, where there are $N_i$ particles of radius $r_i$, given by

$$\bar{r}_N = \frac{\sum N_i r_i}{\sum N_i}.$$

The mass-average and volume-average particle radii are respectively defined as

$$\bar{r}_m = \frac{\sum N_i r_i^4}{\sum N_i r_i^3}, \text{ and}$$

$$\bar{r}_V = \left(\frac{\sum N_i r_i^3}{\sum N_i}\right)^{1/3}.$$

In DLS, data are obtained from the scattered light intensity, correlated in time. Particle size distributions are derived using algorithms which find a fit to the correlations. As a result, the measure of average size obtained using DLS (Z-average, $x_Z$), although well-defined,[4] is different from other methods. The Z-average is calculated using

$$\frac{1}{\bar{x}_Z} = \int_0^\infty \frac{1}{x} G \, d\left(\frac{1}{x}\right),$$

where $G$ is a normalized distribution of autocorrelation decay rates, equivalent to a fraction of scattered intensity. Therefore, $x_Z$ is a harmonic intensity-averaged particle size. (Note that this is different to the Z-average defined by Slomkowski *et al.*[3]).

Dispersity is a measure of the breadth of a distribution. Particle-radius dispersity is given by the ratio of mass-average radius to the number-average radius,[5]

$$D_r = \frac{\bar{r}_m}{\bar{r}_N}.$$

Analyses of DLS have usually employed a polydispersity index (PDI) to describe distribution breadth. This quantity is taken from a coefficient in the polynomial fit to the logarithm of one of the measured correlation functions.[4] Note that the International Union of Pure and Applied Chemistry consider the word ‘polydispersity’ to be ill-defined (and in fact tautologous).[5]

An important practical example concerns the difference between number and volume size distributions. If particle diameter is used to define histogram bins on the horizontal axis, the relative proportion within a particular bin scales with the cube of the diameter when moving between number and volume distributions. $x_Z$ is derived from measurements of intensity, proportional to the square of the particle volume. Therefore, a number distribution derived from DLS uses experimental data scaled with the sixth power of the particle diameter. This is the reason for recommendations not to use number distributions derived from light scattering,[4] and common warnings in the literature regarding light scattering data for polydisperse distributions.

Robust comparison of TRPS with DLS requires careful reconciliation of the data, as in the example in Figures S1(b) and S1(c). DLS data are typically available as a volume size distribution for logarithmically-spaced bins. If the data distribution within each bin is unknown, reconciliation is best achieved by distributing the known individual TRPS results into the same logarithmic bins. The use of logarithmic bins means that the area under the graph does not represent the total population (as in a histogram), so individual points are best plotted and joined with lines to guide the eye. To convert data between number and volume distributions, the proportions within each bin can be scaled with the cube (or cube root) of the corresponding particle diameter for each bin.

Figure S1: Data for a soy bean oil in water emulsion from Somerville *et al.*[6] (a) TRPS particle diameter distributions as a function of emulsion storage time. The left-most bin for each histogram is at the lower threshold discussed in the text. (b) Direct comparison of TRPS and DLS size distributions by number, reconciled as discussed in the text. (c) The same data plotted by particle volume.

## References

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