# Model-Independent Statistical Averages of the Hydrodynamic Radius via Dynamic Light Scattering

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**ABSTRACT:** I present new, robust, and measurable nonparametric statistical averages that summarize major features of the distribution of the hydrodynamic radius. I explain how these descriptive statistical averages—the mean, standard deviation, and skewness of the intensity-weighted distribution—are obtained. Next, I demonstrate that—unlike the well-known and widely used Z-average and polydispersity index—these statistical averages bear a direct and physically meaningful interpretability. At the same time, these statistical averages are straightforward to obtain from experimental correlograms, and therefore, they merit a place in characterizing particle systems via DLS.

Dynamic light scattering (DLS) is a half-centennial experimental technique,[1,2] and it has become essential in characterizing the size distribution of colloidal particle systems.[3] DLS is considered a mature technique, yet even nowadays, there are still ongoing efforts to render the technique more accessible and the analyses more transparent.[4-7]

DLS begins with the so-called electric field auto-correlation function $g_1(t)$ of identical particles:

$$1) \quad g_1(t) = e^{-\Gamma t}$$

where $\Gamma$ is the so-called relaxation rate, which is a function of the diffusion coefficient of the particles, polarization mode,[8,9] and the amplitude of the scattering vector (also known as momentum transfer). If DLS probes the translational diffusion of particles with hydrodynamic radius r, then $\Gamma(r,q) = q^2 D_T(r)$ and $D_T(r) = k_B T / (6\,\pi\,\eta\,r)$ where $k_B$ is the Boltzmann constant, T the temperature, $\eta$ the viscosity of the solvent in which the particles are dispersed, q the momentum transfer $q = \frac{4\pi}{\lambda} n \sin\left(\frac{\theta}{2}\right)$, $\theta$ the scattering angle, $\lambda$ the wavelength of the scattered light, and n the effective refractive index of the dispersion. In case of polydispersity, the electric field auto-correlation function is expressed by the well-known Laplace transform via the probability density function of the distribution of $\Gamma$

$$2) \quad g_1(t) = \int_0^\infty f_\Gamma(\Gamma)\, e^{-\Gamma t}\, d\Gamma.$$

In a DLS experiments one records the so-called intensity auto-correlation function $g_2(t)$, and the two are tied together by the Siegert relation:

$$3) \quad g_2(t) = \alpha + \beta\, |g_1(t)|^2,$$

where $\alpha \approx 1$ and $0 < \beta \leq 1$ is an experimental and instrumentation pre-factor. These two are regarded as an adjustable parameter when fitting the experimental data points.[10-12]

In particle sizing, the aim is at obtaining information about the distribution of particle sizes and not on either the decay rates or diffusion constants. Accordingly, one can reformulate Equation 2, and express $g_1(t)$ via the intensity-weighted distribution of the hydrodynamic radius

$$4) \quad g_1(t) = \int_0^\infty f_r(r)\, e^{-\frac{\kappa}{r} t}\, dr$$

where $\kappa = q^2 k_B T / 6\,\pi\,\eta$. In fact, $f_\Gamma(\Gamma)$ and $f_r(r)$ are intimately related, and one can be computed from the other via the rule of transforming random variables:[8]

$$5) \quad f_r(r) = f_\Gamma\left(\Gamma(r)\right) \cdot |\partial_r \Gamma(r)|.$$

Obtaining the true $f_r(r)$—in adequate details no matter the complexity of the distribution—by analyzing the experimental data $g_2(t)$ is the ultimate goal of DLS particle size analysis. Success, however, cannot be guaranteed, which owes to fundamental limits posed by the fact that Equation 2 and 4 are integral transform embodying ill-conditioned inverse problems, whose numerical inversion is highly sensitive to a) experimental noise present in $g_2(t)$,[13-15] and b) the algorithm used to invert numerically the integral transform.[16,17] Therefore, 'absolute' methods of analyses that exhibit a much weaker dependence on experimental noise have become highly relevant, and reporting the results of nonparametric model-free analysis on two statistical averages of the intensity-weighted distribution of the hydrodynamic radius (the Z-average and the polydispersity index),[18-20] has become de facto a standard in DLS.[21]

The Z-average hydrodynamic radius ($r_Z$) and the polydispersity index (PDI) are directly related to the so-called cumulant analysis of polydispersity.[18-20] The essence of the cumulant analysis (and its variations) is expanding the negative exponential function into its Maclaurin series (a polynomial around $t = 0$)

$$6)\quad e^{-\Gamma t} = 1 - \Gamma + \tfrac{1}{2}\Gamma^2 t^2 - \tfrac{1}{6}\Gamma^3 t^3 + \cdots .$$

From Eq 6, any polydisperse auto-correlation function may be expressed via the statistical moments of $f_\Gamma(\Gamma)$

$$7)\quad \langle \Gamma^m \rangle = \int_0^\infty \Gamma^m f_\Gamma(\Gamma) d\Gamma.$$

The first two terms—a linear and a quadratic term—are used for quantifying the Z-average hydrodynamic radius and the polydispersity index: $r_Z$ is defined through the inverse of the mean value of $\Gamma$,

$$8)\quad r_Z = \kappa / \langle \Gamma \rangle$$

and PDI is the normalized variance of the distribution of $\Gamma$

$$9)\quad \mathrm{PDI} = \left\langle \Gamma^2 \right\rangle / \langle \Gamma \rangle^2 - 1.$$

The mean and the variance of the distribution of $\Gamma$ have a clear and physically intuitive meaning if it comes to the analysis of relaxation rates. Indeed, so far, several thousands of peer-reviewed publications have cited the method,[18-20] which indicates that statistical averages, even if their information content is limited to a summary, are appreciated. Next, one can follow the same route (Eq 6) and apply it to Eq 4, and it is not difficult show that

$$10)\quad r_Z = \frac{1}{\int r^{-1} f_r(r) dr}$$

and

$$11)\quad \mathrm{PDI} = \frac{\int r^{-2} f_r(r) dr}{\left(\int r^{-1} f_r(r) dr\right)^2} - 1.$$

Therefore, at a given scattering angle, a) the z-average radius is the harmonic mean of the intensity-weighted probability function of the hydrodynamic radius, and b) the polydispersity index is more complex expression of ‘inverted’ averages. That is, in the context of hydrodynamic radius, the physical interpretation of the statistical averages obtained via the cumulat method is rather obscure and unintuitive, especially when it comes to describe polydispersity.

The question I address here is whether—from the same kind of DLS experiments—one could obtain statistical averages that describe the intensity-weighted distribution of the hydrodynamic radius in a direct and physically intuitive manner, such as mean, relative standard deviation, and skewness of the distribution of r. The answer is positive, and instead of series expansion, I will address this question through integrating the exponential function (Eq 4) in time

$$12)\quad I_p \equiv \int_0^\infty t^p\, g_1(t)\, dt.$$

I will show that via temporal integration one can readily obtain physically intuitive statistical averages. For this, I consider that Eq 12 may be written as a double integral,

$$13)\quad I_p = \int_0^\infty t^p \left( \int_0^\infty f_r(r)\, e^{-\frac{\kappa}{r} t}\, dr \right) dt,$$

and to benefit from Eq 13, one needs to recognize two things. First, the order of integration in time and in radius may be exchanged

$$14)\quad I_p = \int_0^\infty f_r(r) \left( \int_0^\infty t^p\ e^{-\frac{\kappa}{r} t} \right) dt\, dr.$$

Second, the inner part of Eq 14 confined within the brackets may be defined as the p-th temporal moment of the exponential term

$$15)\quad M_p = \int_0^\infty t^p e^{-\frac{\kappa}{r} t} dt,$$

and evaluating this integral provides a closed form valid for nonnegative integers $(p > -1)$

$$16)\quad M_p = p! \left(\frac{r}{\kappa}\right)^{1+p}$$

and if p is not an integer, the factorial becomes the gamma function: $\mathrm{Gamma}[1 + p]$. Now, the temporal integral of Eq 12-14 can be expressed as

$$17)\quad I_p = \int_0^\infty f_r(r) M_p dr.$$

I know of precedents of temporal integration with $p = 0$ only. It was used to define coherence time corresponding to random optical fields in statistical optics,[22,23] and it was used to the estimate harmonic mean of the diffusion coefficient via DLS.[24] To the best of my knowledge, the potential to describe the hydrodynamic radius has not been recognized elsewhere. However, the relevance of Eq 17 becomes evident when I substitute the first three nonnegative integer values of p: $M_0 = r/\kappa$, $M_1 = (r/\kappa)^2$, $M_2 = 2(r/\kappa)^3$, and subsequently evaluate Eq 17

$$18)\quad I_0 = \frac{1}{\kappa}\int_0^\infty f_r(r)\, r\, dr = \frac{1}{\kappa}\langle r \rangle$$

$$19)\quad I_1 = \frac{1}{\kappa^2}\int_0^\infty f_r(r)\, r^2\, dr = \frac{1}{\kappa^2}\langle r^2 \rangle$$

$$20)\quad I_2 = \frac{2}{\kappa^3}\int_0^\infty f_r(r)\, r^3\, dr = \frac{2}{\kappa^3}\langle r^3 \rangle.$$

The surprising result is that the temporal integrations yield the raw statistical moments of the distribution of the hydrodynamic radius (identically as defined in Eq 7 for the relaxation rate).

From these raw moments, the standard deviation and skewness may be easily computed: $\sigma = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$ and $\gamma_1 = \sigma^{-3}\,(2\langle r \rangle^3 - 3\langle r \rangle \langle r^2 \rangle + \langle r^3 \rangle)$. Therefore, I just proved that by integrating the experimental autocorrelation function, one has the potential to quantify nonparametric statistical averages that summarize the major features of the intensity-weighted distribution of the hydrodynamic radius.

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