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Inverse Transformation: Unleashing Spatially Heterogeneous Dynamics with an Alternative Approach to XPCS Data Analysis

Ross N. Andrews^{a,*}, Suresh Narayanan^a, Fan Zhang^b, Ivan Kuzmenko^a, and Jan Ilavsky^a

^aAdvanced Photon Source, Argonne National Laboratory, Argonne, IL 60559, USA

^bMaterials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Abstract

X-ray photon correlation spectroscopy (XPCS), an extension of dynamic light scattering (DLS) in the X-ray regime, detects temporal intensity fluctuations of coherent speckles and provides scattering vector-dependent sample dynamics at length scales smaller than DLS. The penetrating power of X-rays enables probing dynamics in a broad array of materials with XPCS, including polymers, glasses and metal alloys, where attempts to describe the dynamics with a simple exponential fit usually fails. In these cases, the prevailing XPCS data analysis approach employs stretched or compressed exponential decay functions (Kohlrausch functions), which implicitly assume homogeneous dynamics. In this paper, we propose an alternative analysis scheme based upon inverse Laplace or Gaussian transformation for elucidating heterogeneous distributions of dynamic time scales in XPCS, an approach analogous to the CONTIN algorithm widely accepted in the analysis of DLS from polydisperse and multimodal systems. Using XPCS data measured from colloidal gels, we demonstrate the inverse transform approach reveals hidden multimodal dynamics in materials, unleashing the full potential of XPCS.

1. Introduction

Dynamic light scattering (DLS)(Berne & Pecora, 1976) and X-ray photon correlation spectroscopy (XPCS) (Sutton *et al.*, 1991; Grübel *et al.*, 2000; Grübel *et al.*, 2008; Shpyrko, 2014) operate on identical principles (Figure 1). DLS uses coherent illumination from a laser source, whereas XPCS uses coherent X-rays produced by third-generation synchrotron sources. Electron density variations within the XPCS or DLS sample cause scattering of incident light with wavelength λ by angle 2θ on length scales given by $q = \frac{4\pi}{\lambda} \sin\theta$.

Interference of the scattered waves yields a speckle pattern in the far field. Temporal changes in $I(q, \tau)$ correspond to changes in the sample, revealing meso- or atomic scale fluctuations. Pinhole-camera based XPCS (Sandy *et al.*, 1999) and multispeckle DLS (Kirsch *et al.*, 1996) employ a 2D detector that reveals a series of two-dimensional images

Correspondence: RossNAndrews@gmail.com.

*Simulated g_2 s vs. q result from building a Toeplitz matrix A with elements given by the desired autocorrelation function, in this case

$a(t) = e^{-q^2 t}$. Given a vector of random data $\mathbf{X}$, the discrete process $\mathbf{G}$ with autocorrelation function $a(t)$ is given by $\mathbf{G} = \mathbf{LX}$, where Cholesky decomposition $A = \mathbf{LL}^T$ gives the lower triangular matrix $\mathbf{L}$.

over time across a range of q s, whereas traditional DLS uses a point detector that gives a single stream of intensity at a fixed q . Bonse-Hart USAXS-XPCS originally used a point detector (Zhang *et al.*, 2011), but recent advancements allow simultaneous collection of multiple data streams at a fixed q (Zhang *et al.*, 2015).

$$g_2(q, t) = \frac{\langle I(q, \tau)I(q, \tau + t) \rangle}{\langle I(q, \tau) \rangle^2} \quad (1)$$

Self convolution of the time-dependent intensity $I(q, \tau)$ produces a normalized intensity autocorrelation function $g_2(q, t)$ as a function of lag time t at a scattering vector q (Equation 1). As shown in the simulated $I(q, \tau)$ traces* in Figure 1, dynamics ordinarily become faster with smaller length scale (higher q), though sample dynamics can show more complex q dependence, notably de Gennes narrowing in the vicinity of structural correlations (Lumma *et al.*, 2000).

The shorter wavelength of X-rays ($\lambda \approx 1 \text{ \AA}$) compared to laser light ($\lambda \approx 5000 \text{ \AA}$) reduces challenges introduced by sample absorption and multiple scattering, broadening the range of suitable XPCS samples beyond dilute or index-matched samples for DLS. XPCS enables investigation of atomic and mesoscopic dynamics in a diverse array of materials including polymers (Mochrie *et al.*, 1997), colloids (Dierker *et al.*, 1995; Spannuth *et al.*, 2011), metallic glasses (Leitner *et al.*, 2012; Ruta *et al.*, 2012), magnetic systems (Konings *et al.*, 2011) and metal alloys (Brauer *et al.*, 1995). Ongoing enhancements in detector technology (Dufresne *et al.*, 2016) and next generation synchrotrons will further expand the time and length scales observable with XPCS. With the ever-broadening scope of XPCS comes a wide array of dynamics that rarely follow simple exponential relaxation.

XPCS data analysis typically employs (Madsen *et al.*, 2010) stretched or compressed exponentials ((Kohlrausch, 1854a; Kohlrausch, 1854b; Berberan-Santos *et al.*, 2008)), known as Kohlrausch functions, to accommodate this diverse array of dynamics. Though sample characterization with a stretching exponent mathematically suggests homogeneous dynamics, "...there is no way to judge whether a model is advocating homogeneous or [heterogeneous] dynamics based on just the fact that the Kohlrausch function is invoked or employed" (Ngai, 2011). Stretched and compressed exponentials have a heterogeneous interpretation through relation of the Kohlrausch exponent to the width of a distribution. However, the complexity or entropy of the distribution of exponential functions corresponding to a stretched or compressed exponential ordinarily exceeds the knowledge available from the data considering error in the measurement. Unless prior knowledge about the dynamics suggests sample heterogeneity should follow stretched exponential relaxation, interpreting the Kohlrausch exponent as a distribution corresponds to overfitting the data – less complicated distributions consistent with the observation likely exist.

Figure 2 outlines models used to fit dynamics in DLS or XPCS. For classical diffusion of dilute monodisperse spheres, DLS and XPCS g_2 s show simple exponential decay. Polydisperse sample dynamics no longer fit well to a simple exponential. Modeling in DLS routinely employs a heterogeneous approach, assuming g_2 results from a linear

superposition of many simple exponentials with different relaxation rates Γ . Cumulant analysis of polydisperse DLS data characterizes moments of the underlying distribution of relaxation rates by fitting parameters corresponding to the mean (Γ), variance (μ_2) and skewness (μ_3) (Frissen, 2001). This approach, however, assumes underlying dynamics have a single mode. The most flexible approach to DLS data analysis directly seeks a solution for the underlying distribution of relaxation rates using CONTIN or MULTI-Q. These inverse Laplace transformation techniques do not require *a priori* assumption of the distribution shape.

Random uncertainty in the data means that inverse Laplace transformation does not have a unique or well-behaved solution. Regularized inverse transformation seeks the simplest distribution that sufficiently explains the observation. DLS analysis generally uses the program CONTIN developed by Provencher in the 1980s to solve this regularized inverse problem. Given a DLS autocorrelation function $g_2(q, t)$, CONTIN performs a numerical inverse Laplace transform, returning a distribution of relaxation rates and thus an intensity distribution of diffusion coefficients and hydrodynamic radii. For a series of DLS autocorrelation functions measured at multiple angles (multiple q) from a sample in the dilute limit, the MULTI-Q extension of CONTIN collectively analyzes all the data sets using a q^2 -dependent inverse Laplace transform.

Current XPCS analysis methods, with few exceptions (Trappe *et al.*, 2007), employ stretched exponential analysis rather than the inverse transform approach used in DLS of heterogeneous samples, even though spatially heterogeneous dynamics occur in XPCS (Micoulaut, 2016; Ballesta *et al.*, 2008). In principle, stretched or compressed exponential fitting reflects a two parameter cumulant-like approach, where Γ describes the position of the distribution and the Kohlrausch exponent α its shape, because the Kohlrausch exponential function and an underlying distribution have an exact mathematical relationship (Pollard, 1946). However, the complexity of the distribution giving a stretched exponential function after Laplace transformation imparts a significant amount of prior information about the solution that may not have physical justification. In addition, many different Laplace transformed distributions will give a good fit within the error bounds of the data.

This work applies inverse transform analysis methods to XPCS data as an alternative to compressed or stretched exponential fitting of heterogeneous dynamics. The area detector approach to XPCS simultaneously acquires g_2 s at multiple q positions by default, enabling use of the MULTI-Q extension of CONTIN. We will demonstrate the use of modified versions of CONTIN and MULTI-Q to XPCS data beginning with the classical case of dilute monodisperse spheres, and continuing into compressed exponential dynamics. These examples demonstrate that inverse transform analysis reveals information obscured by conventional Kohlrausch exponential fitting.

2. Results and Discussion

We illustrate inverse transformation analysis of XPCS auto-correlation functions by comparing the results of Kohlrausch, CONTIN and MULTI-Q fitting on three different XPCS data sets: classical diffusion (§2.1), obvious (§2.2) and subtle bimodal compressed

exponential relaxation (§2.3). XPCS data was acquired at beamline 8-ID-I at Argonne National Laboratory using the ANL-LBL FastCCD camera. Frames were acquired at a rate of 60 Hz, and two time correlation analysis (Fluerasu *et al.*, 2005) was used to confirm the sample was at steady state. The images were converted to 1D g_2 s using Argonne's program XPCSGUI (Sikorski *et al.*, 2011). For classical diffusive dynamics, simple exponential fitting, CONTIN and MULTIQ analysis yield essentially the same conclusion. After describing modifications to CONTIN and MULTIQ, we illustrate their use with double compressed exponential decay observed in a concentrated colloidal gel. In the final example, least squares fitting of a Kohlrausch function suggests a single compressed exponential decay, where subsequent inverse transform analysis reveals a bimodal ensemble of compressed exponential dynamics.

2.1. Simple Exponential Dynamics and Classic CONTIN

Classical diffusion observed from a monodisperse, dilute sample of nanoparticles provides a benchmark for comparing analysis approaches because the conclusion should not depend on the analytical method selected. Using this sample, we introduce and illustrate the formulation and working principles of CONTIN and MULTIQ and compare these results with simple exponential fitting. A simple exponential function describes g_2 s associated with a dilute monodisperse suspension, and the relaxation rate determined from measurements at different q scales as $\Gamma \propto q^2$. CONTIN analysis correspondingly gives a series of single-peaked distributions whose center of mass shifts along the relaxation rate axis with q^2 . Likewise, a q^2 -dependent inverse Laplace transform (MULTIQ) gives a single peak describing the entire data set.

2.1.1. Simple Exponential Fit—

$$g_2(t) = a + be^{-2\Gamma t} = a + be^{-\Upsilon t} \quad (2)$$

Figure 3 shows a series of XPCS autocorrelation functions acquired from a dilute sample of monodisperse spheres measured between $q = 0.0024 \text{ \AA}^{-1}$ and $0.0052 \text{ \AA}^{-1}$ along with the fit of each using a simple exponential function (Equation 2). A constant of proportionality b and flat background a account for variations in experimental setup and/or processing artifacts. The inset shows that the relaxation rate $\Upsilon = 2\Gamma$ obtained for each $g_2(q, t)$ follows Γq^2 . Simple exponential with q^2 length $\propto$ relaxation scale dependence describes classical diffusion, as expected from simple Brownian motion.

2.1.2. CONTIN Analysis—Since its introduction over three decades ago, DLS experiments consistently employ the program CONTIN (Provencher, 1979; Provencher, 1982*a*; Provencher, 1982*b*) for interpreting intensity autocorrelation functions as distributions of simple exponential relaxation rates. Scattered intensity fluctuation from particles of polydisperse size will give an overall time correlation function composed of different exponential decays. Laplace transformation[†] $\mathcal{L}[\Psi(\Upsilon)](t)$ of this time constant distribution $\Psi(\Upsilon)$ gives the g_2 expected from such a collection of particles (Equation 3), where Υ relates to the size through the Stokes-Einstein relation. CONTIN gives unnormalized distributions, in

which case $\beta = 1$; the coherence factor b comes from integration of the distribution $b = \beta \int \Psi(\Upsilon) d\Upsilon$.

$$g_2(t) = a + \beta \underbrace{\int_0^\infty \Psi(\Upsilon) e^{-\Upsilon t} d\Upsilon}_{\mathcal{L}[\Psi(\Upsilon)](t)} \quad (3)$$

$$g_2(t) = \underbrace{\frac{a'}{(1+\beta')}}_a + \underbrace{\frac{1}{(1+\beta')}}_\beta \int_{\Upsilon_{\text{Min}}}^{\Upsilon_{\text{Max}}} \Psi(\Upsilon) e^{-\Upsilon t} d\Upsilon \quad (4)$$

$$(1 + \beta')g_2(t) = a' + \int_{\Upsilon_{\text{Min}}}^{\Upsilon_{\text{Max}}} \Psi(\Upsilon) e^{-\Upsilon t} d\Upsilon \quad (5)$$

$$g_2(t_j) = a' - \beta' g_2(t_j) + \sum_{i=1}^N c_i \Psi(\Upsilon_i) e^{-\Upsilon_i t_j} \quad (6)$$

$$\underbrace{\begin{bmatrix} g_2(t_1) \\ \vdots \\ g_2(t_M) \end{bmatrix}}_{\mathbf{g}_2} = \underbrace{\begin{bmatrix} 1 & -g_2(t_1) & c_1 e^{-\Upsilon_1 t_1} & \dots & c_N e^{-\Upsilon_N t_1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & -g_2(t_M) & c_1 e^{-\Upsilon_1 t_M} & \dots & c_N e^{-\Upsilon_N t_M} \end{bmatrix}}_{\mathbf{K}} \underbrace{\begin{bmatrix} a' \\ \beta' \\ \Psi(\Upsilon_1) \\ \vdots \\ \Psi(\Upsilon_N) \end{bmatrix}}_{\mathbf{S}} \quad (7)$$

Inverse transform analysis seeks the function $\Psi(\Upsilon)$ given only the measurement $g_2(t)$ – an inverse problem. CONTIN solves this by first formulating the integral equation as a linear matrix problem $\mathbf{g}_2 = \mathbf{KS}$. Converting the Laplace transform in Equation 3 to matrix form involves rewriting a and β in terms of new variables a' and β' (Equation 4), selection of the limits of integration Υ_{min} and Υ_{max} (Equation 5), and discretizing the integral using quadrature weights c_i (Equation 6). The linear matrix transform $\mathbf{K}$ with dimensions $M \times N + 2$ maps the vector $\mathbf{S}$, consisting of $i = 1 \dots N$ distribution intensities $\Psi(\Upsilon_i)$, a' and β' to a

[†]The syntax of the Laplace transform used here, where it transforms a distribution of time constants to the time domain $\mathcal{L}[\Psi(\Upsilon)](t) \rightarrow g_2(t)$, differs from its usage in differential equations where it maps the time domain to the frequency (“ s ”) domain $\mathcal{L}[f(t)](s) \rightarrow F(s)$.

vector $j = 1 \dots M$ of autocorrelation intensities $g_2(t_j)$ in the time domain, $\mathbf{g}_2 = \mathbf{KS}$ (Equation 7).

Given the vector $\mathbf{g}_2$ with elements resulting from measurement and temporal autocorrelation of the speckle intensity $I(q, \tau)$ at a fixed q , inverse transformation seeks restoration of $\mathbf{S}$ using the transform kernel $\mathbf{K}$. However, even if the kernel $\mathbf{K}$ has an inverse, the solution resulting from explicit inverse transformation $\mathbf{K}^{-1}\mathbf{g}_2 = \mathbf{S}$ will pass noise from the measurement into the solution, ordinarily resulting in an unlikely (jagged) result for $\mathbf{S}$. The measurement error also renders this direct inverse problem ill-conditioned (Equation 8). Within the error bounds of the measurement, many different solutions give an acceptable fit to the data. The concept of parsimony dictates selection of the simplest solution from this set sufficient to explain the observation.

In the context of dynamic distributions in soft matter, given the choice between a broad distribution of time constants and a series of sharp peaks, the parsimony argument selects the least informative, highest entropy (smoothest) distribution as the most likely solution. Rather than finding a solution based upon misfit (χ^2) alone, CONTIN finds a solution $\mathbf{S}$ at a fixed Λ by minimizing a functional $V(\Lambda)$ incorporating goodness of fit and solution smoothness (Equation 9). The Lagrange multiplier Λ controls the relative weight given to the fit and smoothness terms. Determination of the most likely value for Λ does not come from the data or model, but from some external prior knowledge about expected characteristics of the solution.

$$\mathbf{g}_2 = \mathbf{KS} + \varepsilon \quad (8)$$

$$V(\Lambda) = \underbrace{\chi^2}_{\text{Fit}} + \Lambda \underbrace{\int \left(\frac{d^2\Psi(\mathbf{r})}{d\mathbf{r}^2} \right)^2 d\mathbf{r}}_{\text{Smoothness}} \quad (9)$$

Provencher developed a rejection probability metric $\mathcal{P}_{\text{rej}}$ based upon Fisher's F-test (Provencher, 1982a) for automatic determination of the best Λ . Figure 4 shows the progression of the misfit χ^2 , degrees of freedom N_g , rejection probability $\mathcal{P}_{\text{rej}}$ and some examples of solutions for $\Psi(\mathbf{r})$ that result during a typical CONTIN search for the most likely value for Λ , Λ_{opt} . For small values of Λ in Equation 9, CONTIN essentially minimizes only the goodness of fit $V(\Lambda) = \chi^2$, and recovers the least squares solution; noise in the data passes through, giving a jagged solution. As Λ increases, the solution becomes more smooth, at the cost of worsening the fit (increasing χ^2) and reducing the degrees of freedom N_g . At large Λ , CONTIN effectively minimizes the regularizer that penalizes curvature $V(\Lambda) = \int \left(\frac{d^2\Psi(\mathbf{r})}{d\mathbf{r}^2} \right)^2 d\mathbf{r}$, giving a smooth solution that mostly ignores the data. CONTIN's internal metric finds a compromise solution between the two extremes, choosing Λ_{opt} at the

50 % probability to reject, $\mathcal{P}_{\text{rej}} = 1/2$. This value for Λ_{opt} and the corresponding solution $\Psi(\Upsilon)$ “should not be used blindly” (Provencher, 1984), but interpreted along with other prior knowledge about the solution and/or the behavior of the solution and χ^2 as a function of Λ . In practice, we find that automatic selection of Λ using $\mathcal{P}_{\text{rej}} = 1/2$ almost always gives the most logical result for $\Psi(\Upsilon)$.

In Figure 4, the multi peaked solutions at small Λ have χ^2 similar to the solution at Λ_{opt} , which consists of a single large peak with a small shoulder. Occam’s razor (parsimony) rejects the jagged solutions at $\Lambda < \Lambda_{\text{opt}}$ because a less complicated solution with a similar χ^2 ($\Psi(\Upsilon)$) resulting from minimization of $V(\Lambda_{\text{opt}})$ suffices. At the same time, the measurement requires the shoulder, because its exclusion in the region $\Lambda > \Lambda_{\text{opt}}$ causes a precipitous increase in χ^2 . The increase in χ^2 beyond the point $V(\Lambda_{\text{opt}})$ reveals that $\mathcal{P}_{\text{rej}} = 1/2$ relates to the “point of inflection” (Schnablegger & Glatter, 1991) and MaxEnt methods (Bauer *et al.*, 1995; Ilavsky, 2008).

2.1.3. CONTIN Fitting of XPCS Data—

$$g_2(q, t) = a + \beta \int \Psi(\Upsilon) e^{-\Upsilon t} d\Upsilon \quad (10)$$

Figure 5 shows sequential application of unmodified CONTIN with the simple exponential kernel in Equation 10 to the g_2 s analyzed in Figure 3 to reveal a series of $\Psi(\Upsilon)$ with similar shape. As expected from conventional fitting, the $\Psi(\Upsilon)$ coalesce around a single diffusion coefficient $2\mathcal{D}$ after shifting each abscissa by q^2 to $\Psi(2\mathcal{D} = 2\Gamma/q^2 = \Upsilon/q^2)$. Significant changes in $\Psi(\Upsilon)$ shape between data sets result from inverse transformation sensitivity to termination effects in g_2 and/or noise in the data. Inverse transformation of a truncated relaxation, as in the high q g_2 data in Figure 4 (magenta), leads to spurious peaks at longer Υ . Collective simultaneous analysis of g_2 at all q with MULTI Q helps mitigate both these complications.

2.1.4. MULTI Q Analysis—

$$g_2(g, t) = a + \beta \int \Psi(\Upsilon) e^{-\Upsilon q^2 t} d\Upsilon \quad (11)$$

Provencher extended CONTIN to MULTI Q (Provencher & Št pánek, 1996) for global analysis of DLS data measured at multiple angles (multiple q). DLS of a dilute system typically observes q^2 -dependent dynamics, so MULTI Q includes the measurement q point in the inverse transform kernel.[‡] While CONTIN gave a distribution for each q point where Υ has

[‡] MULTI Q can also resolve data measured at multiple q points into two distributions with different q -dependency (Provencher & Št pánek, 1996).

dimensions of inverse time (s^{-1}), MULTIQ gives a global distribution for all q where Υ now has dimensions of a diffusion coefficient ($\text{\AA}^2 s^{-1}$).

Equation 11 shows the q^2 -dependent Laplace transform model assuming constant background a and contrast β . Rewriting a and β and discretization as before (Equation 6) gives the linear matrix equation (Equation 12). MULTIQ solves a similar inverse problem as CONTIN, except that the vector of measured data now consists of L blocks corresponding to each of the $k = 1 \dots L$ measurement points q_k ; the transform matrix K likewise consists of blocks K_k with dimensions $M \times N + 2$. The solution vector S remains the same as with CONTIN, since MULTIQ seeks a single solution for all the measured data.

$$g_2(q_k, t_j) = a' - \beta' g_2(q_k, t_j) + \sum_{i=1}^N c_i \Psi(\Upsilon_i) e^{-\Upsilon_i q_k^2 t_j} \quad (12)$$

$$\underbrace{\begin{bmatrix} g_2(q_1, t_1) \\ \vdots \\ g_2(q_1, t_M) \\ \vdots \\ g_2(q_L, t_1) \\ \vdots \\ g_2(q_L, t_M) \end{bmatrix}}_{\mathbf{g}_2} = \underbrace{\begin{bmatrix} K_1 \\ K_2 \\ \vdots \\ K_L \end{bmatrix}}_{\mathbf{K}} \underbrace{\begin{bmatrix} a' \\ \beta' \\ \Psi(\Upsilon_1) \\ \vdots \\ \Psi(\Upsilon_N) \end{bmatrix}}_{\mathbf{S}} \quad (13)$$

$$K_k = \begin{bmatrix} 1 & -g_2(q_k, t_1) & c_1 e^{-\Upsilon_1 t_1 q_k^2} & \dots & c_N e^{-\Upsilon_N t_1 q_k^2} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & -g_2(q_k, t_M) & c_1 e^{-\Upsilon_1 t_M q_k^2} & \dots & c_N e^{-\Upsilon_N t_M q_k^2} \end{bmatrix} \quad (14)$$

As with CONTIN, MULTIQ gives an unnormalized distribution, and $\beta = 1$ for β independent of q . But, because contrast and background often change as a function of length scale q , MULTIQ can find backgrounds $a(q)$ and scale factors $\beta(q)$ for each g_2 , in addition to a global distribution function (15). The q -dependent scale factor $\beta(q)$ accounts for differences in contrast; MULTIQ scales the g_2 by defining $\beta = 1$ for data from the highest q point, and the contrast b of this data set comes from integration of the distribution $b = \beta \int \Psi(\Upsilon) d\Upsilon$. With $a(q)$ and $\beta(q)$ functions of q , the matrix formulation (Equation 14) now has vectors in place of scalars for a' and β' in S , with expanded blocks in K_k . Defining q_o as the q value of the

last data set, Laplace transformation of a single distribution $\Psi(\Upsilon)$ describes the entire data set by including the q dependency as the ratio q/q_o (Equation 15).

2.1.5. MULTIQ Fitting of XPCS—

$$g_2(q, t) = a(q) + \beta(q) \int \Psi(\Upsilon) e^{-\Upsilon \left(\frac{q}{q_o}\right)^2 q_o^2 t} d\Upsilon \quad (15)$$

Figure 6 shows application of MULTIQ to the XPCS data analyzed with simple exponential fitting (Figure 3) or sequential inverse transformation using CONTIN (Figure 5). MULTIQ stacks all nine ($L = 9$ in Equation 13) $g_2(t)$ s into a single input vector $\mathbf{g}_2$ and populates nine transform blocks $\mathbf{K}_k$ according to the q_k point of the $g_2(q_k, t_{1...M})$ (Equation 14) into the matrix $\mathbf{K}$. The resulting solution $\mathbf{S}$ consisting of background(s) a' , scale factor(s) β' and a single distribution $\Psi(\Upsilon)$ simultaneously describes all nine g_2 s.

The lower inset in Figure 6 shows the solution for $\Psi(\Upsilon)$ obtained by MULTIQ. This solution consists of a single broad peak at the same diffusion coefficient $2\mathcal{D} = \Upsilon q_o^{-2}$ as the multiple CONTIN solutions plotted as a function of Υq^{-2} (Figure 5), but without spurious peaks resulting from deficiencies in the input data. The inset shows backgrounds $a(q)$ and relative contrast $\beta(q)$ determined by MULTIQ. Reintegrating $\Psi(\Upsilon)$ according to the q point of the measurement according to Equation 15 gives the fit shown by the solid lines.

Three different methods of analysis, simple exponential, CONTIN and MULTIQ fitting, gave similar results – a q^2 -dependent distribution exponential functions – but the implications of the simple exponential fit differ from the results of inverse transformation. A simple exponential fit results from Laplace transformation of a delta function, while inverse transformation gives a distribution of finite width. Equation 16 characterizes these three results using the global sum of fitting residuals as shown in Table 1. The simple exponential gives a better fit than either CONTIN or MULTIQ, a result that may seem surprising since inverse transformation has more fitting parameters available. However, inverse transformation seeks the best solution given only the data, absent any preconceptions about what the solution should look like. The error in the measurement and the ill-posed nature of inverse transformation renders the most likely solution more polydisperse than the sample itself. Independent knowledge about the polydispersity of the sample, perhaps from SAXS or DLS, could justify biasing the solution in favor of a better fit by selecting a smaller Lagrange multiplier than that selected from the smoothness criteria ($\mathcal{P}_{\text{rej}} = 1/2$) alone.

$$\mathcal{R} = \sum_k \sum_j \frac{|g_2(q_k, t_j)_{\text{Fit}} - g_2(q_k, t_j)_{\text{Data}}|}{\sigma(q_k, t_j)} \quad (16)$$

2.2. Compressed/Stretched Exponential Dynamics and Modified CONTIN

In contrast to X-ray scattering, the Rayleigh-Gans-Debye approximation applies to light scattering only in limited circumstances due to the long wavelength of laser light. In addition, the short wavelength of X-rays means multiple scattering occurs much less frequently in small angle X-ray scattering compared to small angle light scattering. Because XPCS accommodates a broader scope of materials, a simple exponential often fails to describe the measured g_2 s, and typical XPCS data analysis employs stretched or compressed exponential functions (Madsen *et al.*, 2010). The original DLS implementation of CONTIN and MULTIQ solves an inverse Laplace transformation that could analyze stretched, but not compressed, exponential dynamics. We describe changes to CONTIN and MULTIQ that enable its use with faster than exponential dynamics (compressed) often observed in XPCS.

2.2.1. Bimodal Compressed Exponential Relaxation—

$$g_2(t) = a + b_1 \exp[-2(\Gamma_1 t)^{\alpha_1}] + b_2 \exp[-2(\Gamma_2 t)^{\alpha_2}] \quad (17)$$

Figure 7 shows XPCS data from a concentrated colloidal gel displaying two obvious relaxations that require addition of a second Kohlrausch function to the model (Equation 17). Both relaxations have different Kohlrausch exponents, the faster dynamics giving $\alpha_1 \approx 1.9$, and the slower $\alpha_2 \approx 1.3$; both Γ_1 and Γ_2 follow $\propto q^1$, consistent with compressed exponential relaxation.

The two-time correlation function of the measurement (Figure 8) shows temporally homogeneous dynamics, meaning that the bimodal relaxation results from spatially heterogeneity. Rather than *ad hoc* addition of explicit terms to fitting models, the popularity of inverse transform analysis in DLS comes from the absence of an underlying assumption about the characteristics of the dynamics (other than requiring a smooth, nonnegative solution);[§] the inverse transform approach inherently accommodates multiple relaxations. However, use of inverse transformation with the compressed exponential relaxation in Figure 7 requires modification of classic CONTIN and MULTIQ.

2.2.2. Interpreting Stretched and Compressed Exponential Functions as Distributions of Simple Exponentials and Gaussians—

$$g_2(q, t) = a + b \exp[-2(\Gamma t)^\alpha] \quad \begin{array}{l} 0 < \alpha < 1 \text{ Stretched} \\ 1 < \alpha < 2 \text{ Compressed} \end{array} \quad (18)$$

Certain systems have underlying microscopic dynamics that show stretched exponential behavior, justifying use of a Kohlrausch exponential function. In other cases, stretched exponentials appear empirically to describe heterogeneous phenomena, where the Kohlrausch exponent characterizes the shape of the underlying distribution. While the

[§]Solutions in this work come from CONTIN's selection of Λ_{opt} alone, without the "peak-constrained solution" option.

stretched exponential results from Laplace transformation of Pollard's distribution, thus linking the Kohlrausch exponent with underlying heterogeneity, the complexity of this distribution often exceeds the information available from the measurement. Many common distributions give an apparent stretched exponential decay after Laplace transformation, even though the shape of the underlying distribution significantly deviates from Pollard's exact result for a stretched exponential function. Inverse transform analysis seeks the simplest heterogeneous explanation for the measurement, without an *a priori* assumption about the shape of the distribution.

The exponential relaxation that Kohlrausch (Kohlrausch, 1854*b*; Kohlrausch, 1854*a*) introduced in 1854 (Equation 18) appears in a variety of systems. Membrane dynamics follow $\alpha = 2/3$ (Zilman & Granek, 1996), relaxation phenomena at the glass transition has two "magic" numbers $\alpha = 3/5$ and $3/7$ (Phillips, 1996), and jamming often gives $\alpha = 3/2$ (Cipelletti *et al.*, 2003; Cipelletti *et al.*, 2000). Use of a stretched exponential function here defines a homogeneous approach, wherein microscopic dynamics adopt nonclassical behavior (Arbe *et al.*, 1998).

An alternative interpretation justifies nonexponential relaxations as reflecting underlying heterogeneity in, for example, fluorescence decay (Lee *et al.*, 2001), supercooled liquids (Ediger, 2000; Cipelletti & Ramos, 2005), or soft matter dynamics (Richert, 2002), where the stretching exponent α empirically reflects the shape of a time constant distribution. Such an approach has intuitive justification since a stretched exponential comes from a Pollard distribution of exponentials (Pollard, 1946), explicitly linking it to an underlying distribution; Laplace transformation of the probability density function $\rho(\alpha, k, \Gamma)$ (Equation 19) gives a stretched exponential function.

Laplace transformation of Dirac's delta function gives the sharpest possible exponential decay from any uniformly positive distribution; any other arbitrary nonnegative distribution gives slower than exponential decay. Any Kohlrausch function has an alternative representation as a distribution $\exp[-(\Gamma t)^{\alpha_1}] = \int \rho(\gamma) \exp[-(\gamma t)^{\alpha_2}] d\gamma$ of faster-decaying Kohlrausch functions ($\alpha_2 > \alpha_1$). In addition, compressed exponentials ($\alpha < 1$) do not have a representation as a distribution of simple exponentials (because $\alpha_2 \not> \alpha_1$). Inverse Laplace transformation cannot resolve a compressed exponential decay into a

$$e_{\alpha < 1}^{-(\Gamma t)^{\alpha}} = \mathcal{L}[\text{Pollard's } \rho(\gamma)](t) = \int_0^{\infty} \exp[-\gamma t] \quad (19)$$

$$\underbrace{\int_0^{\infty} \frac{\Gamma}{\pi} \exp\left[-\cos\left(\frac{\pi\alpha}{2}\right)u^{\alpha}\right] \cos\left[\Gamma\gamma u - \sin\left(\frac{\pi\alpha}{2}\right)u^{\alpha}\right] du d\gamma}_{\text{Pollard's } \rho(\alpha, \gamma, \Gamma)}$$

$$e_{\alpha < 2}^{-(\Gamma t)^\alpha} = \mathcal{G} [\text{Pollard's } \rho(\gamma^2)](t) = \int_0^\infty 2\gamma \exp[-(\gamma t)^2] \quad (20)$$

$$\underbrace{\int_0^\infty \frac{\Gamma}{\pi} \exp\left[-\cos\left(\frac{\pi\alpha}{4}\right)u^{\alpha/2}\right] \cos\left[\Gamma\gamma^2 u - \sin\left(\frac{\pi\alpha}{4}\right)u^{\alpha/2}\right] du d\gamma}_{\text{Pollard's } \rho(\frac{\alpha}{2}, \gamma^2, \Gamma)}$$

distribution of simple exponentials. Because compressed exponential functions decay more slowly than a Gaussian function, by substitution into Pollard's relation (Hansen *et al.*, 2013), compressed exponential relaxation results from Gaussian transform of a distribution (Equation 20).

A heterogeneous ensemble of classical diffusion gives kinetics slower than exponential since the collective dynamics result from a linear superposition of exponential decays with different Γ ; in certain cases, particular distributions of Γ may cause collective dynamics to masquerade as stretched exponential decay. Inverse Laplace transformation assumes classical microscale dynamics and attempts to find a distribution of exponential functions that explains the observation. The rationale for inverse Gaussian transformation follows a similar argument. A heterogeneous ensemble of ballistic diffusion gives kinetics slower than a Gaussian since the collective dynamics result from a linear superposition of Gaussian decays with different Γ . While inverse Laplace transformation in the classical case gives a distribution of diffusion coefficients, inverse Gaussian transformation gives a distribution of velocities. Molecular dynamic simulations showed that a heterogeneous ensemble of ballistic motion gives what appears to be compressed exponential relaxation, as stated by Del Gado and Kob (Del Gado & Kob, 2007):

“...for these intermediate and large wave vectors the motion can be considered as nearly ballistic. Note that these moving entities do have different masses and therefore different thermal velocities. Since $F_s(q, t)$ is the average over the different local relaxation functions, assuming that each of them is of the Gaussian form given above, it must be expected that $F_s(q, t)$ decays more slowly than a Gaussian in time, i.e., that the exponent in the CE [compressed exponential] is less than 2.0, in agreement with our results...”

Either compressed or stretched exponential functions have exact representations as the Laplace ($\mathcal{L}$, Equation 19) or Gaussian ($\mathcal{G}$, Equation 20) transform (Alecu *et al.*, 2006) of Pollard's distribution. However, different distributions of relaxation rates give similar profiles after transformation into the time domain, a common limitation of decay curve analysis. (Lindsey & Patterson, 1980). Inverse transformation has more flexibility than the use of predefined distributions, functions, or cumulants, since it involves no *a priori* assumption about the solution, seeking only the simplest explanation for the observation.

2.2.3. CONTIN Modified for XPCS—

$$g_2(t) = a + \beta \int \exp(-\Upsilon t^\xi) \Psi(\Upsilon) d\Upsilon \quad (21)$$

DLS analysis often uses the term “CONTIN analysis” as jargon meaning inverse Laplace transformation. However, the program solves any linear inverse problem $f(x) = \int K(x, y)g(y)dy$, seeking a solution $g(y)$ given data $f(x)$ and an integral transform $K(x, y)$. Generalization of the original exponential kernel used by CONTIN for inverse Laplace transformation in DLS (Equation 3) to Equation 21 accommodates the diverse dynamics observed with XPCS. Adding a predefined exponent ξ on time allows either inverse Laplace transformation ($\xi = 1$), as in conventional analysis, or inverse Gaussian transformation ($\xi = 2$).[¶]

While ξ can mathematically have any value, a noninteger value for ξ in Equation 21 corresponds to a distribution of distributions; $\xi > 2$, to our knowledge, does not have meaning.

$$g_2(t) = a + \beta \underbrace{\int_0^\infty \Psi(\Upsilon) e^{-\Upsilon t^2} d\Upsilon}_{\mathcal{G}[\Psi(\Upsilon)](t)} \quad (22)$$

Kohlrausch exponential fitting in Figure 12 revealed compressed exponentials ($a \approx 1.3$). Solving for an underlying distribution with CONTIN requires an inverse Gaussian transform ($\xi = 2$, Equation 22). Applying this Gaussian integral transform kernel with modified CONTIN to each g_2 sequentially gave a series of distributions $\Psi(\Upsilon)$ with a similar bimodal shape. Scaling the abscissa of each distribution by the length scale $\Psi(\Upsilon) \rightarrow \Psi(\Upsilon q^{-2})$ reveals distributions concentrated around a similar (Υq^{-2}) point, consistent with the length scale dependency of ballistic diffusion and the result from conventional fitting in Figure 12. The Kohlrausch function raises the time constant to the stretching exponent (Equation 18), while the kernel in Equation 22 does not. For this reason, compressed exponential dynamics that follow $\Gamma \propto q^1$ from Kohlrausch fitting will give a series of distributions after inverse Gaussian transformation (Equation 22) whose mode scales with $\Upsilon \propto q^2$; the stretched exponential dynamics (Figure 3) $\Gamma \propto q^2$ gave a series of distributions that also scale with $\Upsilon \propto q^2$.

2.2.4. MULTIQ Modified for XPCS—

$$g_2(q, t) = a(q) + \beta(q) \int \Psi(\Upsilon) \exp\left[-\Upsilon \left(\frac{q}{q_0}\right)^n q_0^n t^\xi\right] d\Upsilon \quad (23)$$

[¶]The form of the Gaussian transform used here, $\exp[-\Upsilon q^2 t^2]$, comes from the intermediate scattering function for ballistic motion $R(q, t) = \exp[-Tq^2 t^2/(2m)]$, (Del Gado & Kob, 2007), where T is the temperature and m is the mass that undergoes ballistic motion.

Modification of CONTIN for use with XPCS consisted of generalizing the time exponent ξ in the inverse transform kernel to accommodate faster or slower than exponential dynamics (Equation 21). Inverse Laplace or Gaussian transformation of either stretched or compressed exponential dynamics thus reveals an ensemble of simple exponential or Gaussian decays. Collective analysis of the entire data set using a single distribution may require adjustment of the kernel's dependence on length scale q . For XPCS analysis herein, the MULTIQ kernel includes not only a selection for the time exponent ξ , but also adjustable length scale dependence n (Equation 23).

$$g_2(q, t) = a(q) + \beta(q) \int \Psi(\Gamma) e^{-\Gamma \left(\frac{q}{q_0}\right)^2 q_0^2 t^2} d\Gamma \quad (24)$$

Collective MULTIQ analysis of the g_2 s in Figure 15 uses Equation 24 with $n = 2$ and $\xi = 2$, describing a q^2 -dependent inverse Gaussian transform (Equation 24). A single q^2 -dependent distribution $\Psi(\Gamma)$ of relaxation rates fits all 16 g_2 s after q^2 -dependent Gaussian transformation. The MULTIQ result of an ensemble of q^2 -dependent ballistic diffusion parallels the result found using conventional fitting in Figure 12 and sequential CONTIN analysis (Figure 14). Inverse transformation finds simpler distributions than the Pollard distribution (Equation 20) corresponding to the conventional compressed exponential fits determined (Figure 7).

Table 2 compares the three fitting techniques used to analyze this data set in terms of the sum of global fitting residuals $\mathcal{R}$.

2.2.5. Effect of Data Error on Inverse Transformation—Added noise in the measurement corresponds to loss of information and inverse transformation will give a less complicated (higher entropy) distribution. Figure 11 illustrates this effect by taking the data used in Figure 15, adding increasing amounts of random error, and performing MULTIQ. Larger amounts of error cause increased weighing of the smoothness constraint in the MULTIQ result for $\Psi(\Gamma)$, until ultimate loss of the bimodal characteristics of the solution, at which point the degrees of freedom N_g falls precipitously. MULTIQ automatically selects increasing values of the Lagrange multiplier Λ , giving more weight to the smoothness constraint in Equation 9 to avoid passing noise into the result.

2.3. Subtle Bimodal Compressed Exponential Relaxation

Clear separation between two decays in the time domain makes addition of a second Kohlrausch function to the model obvious, as in the previous example. Inverse Gaussian transform using CONTIN or MULTIQ needed no modification to recover a bimodal distribution, since they make no *a priori* assumption about the form of the solution. Avoidance of an *a priori* assumption has a significant advantage since one cannot always immediately identify a bimodal distribution by sight (for example, in cases where the two decays have similar time constants). In this example, MULTIQ reveals bimodal dynamics even though Kohlrausch fitting gives an acceptable fit to a single compressed exponential decay.

2.3.1. Analysis with Kohlrausch Function—

$$g_2(t) = a + b \exp[-2(\Gamma t)^\alpha] \quad (25)$$

Kohlrausch exponential analysis according to Equation 25 of XPCS g_2 s from a concentrated colloidal gel reveals compressed exponential relaxation ($\alpha > 1$, Figure 12) with $\Gamma \propto q^1$. Some misfit occurs, but addition of a second Kohlrausch function as before does not appear warranted; a single compressed exponential function gives a reasonable fit to the data.

Two-time correlation analysis reveals temporally homogeneous dynamics (Figure 13), meaning either the microscale dynamics exhibit compressed exponential decay or the sample possesses spatially heterogeneous ballistic dynamics. Assuming the latter, inverse transform analysis seeks a heterogeneous ensemble of ballistic diffusion constants.

2.3.2. Analysis With CONTIN Modified for XPCS—

$$g_2(t) = a + \beta \underbrace{\int_0^\infty \Psi(\Upsilon) e^{-\Upsilon t^2} d\Upsilon}_{\mathcal{E}[\Psi(\Upsilon)](t)} \quad (26)$$

Unlike the previous example of unambiguous bimodal compressed exponential relaxation, CONTIN analysis of this data using inverse Gaussian transformation does not give a clear result (Figure 14). At particular q points, CONTIN recovers a bimodal distribution; at others, a broad monomodal distribution results. Differences in measurement error between data sets likely explain these inconsistent results. Manual adjustment (rather than automatic selection based upon $P_{\text{rej}} = 1/2$) of each Lagrange multiplier could reveal equivalent results across q , though this intervention can significantly bias the results. As an alternative, collective MULTIQ analysis of the entire data set mitigates the effect of measurement noise.

2.3.3. Analysis With MULTIQ Modified for XPCS—

$$g_2(q, t) = a(q) + \beta(q) \int \Psi(\Upsilon) e^{-\Upsilon \left(\frac{q}{q_0}\right)^2 q_0^2 t^2} d\Upsilon \quad (27)$$

Individual inverse transform analysis gave a series of distributions with different profiles. Simultaneous inverse transform analysis seeks a single solution that explains the entire data set. Using the model in Equation 27, collective analysis gives a single, subtle bimodal distribution (Figure 14). Unlike conventional analysis with a single Kohlrausch function, MULTIQ gives a good global fit to the data using a distribution significantly different than the Pollard distribution of Gaussian functions corresponding to the best fit compressed exponential function. In this case, inverse transform analysis revealed additional dynamic behavior hidden by conventional analysis.

Table 3 compares the three fitting techniques used to analyze this data set in terms of the sum of global fitting residuals $\mathcal{R}$.

3. Conclusions

In this paper, we present an inverse transformation-based data analysis method as an alternative to the widely used Kohlrausch function in the analysis of XPCS data, seeking to overcome the stringent homogeneous assumption imposed by Kohlrausch analysis and unveil the dynamic heterogeneity hidden in the data. This method is analogous to the CONTIN and MULTI-Q algorithms widely accepted in DLS analysis of polydisperse and multimodal systems. To adapt CONTIN and MULTI-Q to XPCS analysis, we added the inverse Gaussian transform for accommodating the faster than exponential relaxation often observed in XPCS.

The modified version of CONTIN developed here accommodates stretched and compressed exponential dynamics by virtue of an inverse Laplace or Gaussian transform, and modifications to MULTI-Q allow for arbitrary q -dependency. Simple exponential, CONTIN and MULTI-Q analysis give similar conclusions when applied to classical diffusion observed in XPCS g_2 s from a dilute solution of monodisperse spheres.

We illustrated inverse Gaussian transform analysis of two experimental data sets displaying compressed exponential relaxation. The data exhibited in this work came from measurement of samples at steady state (temporally homogeneous, but spatially heterogeneous), as demonstrated by two-time correlation analysis. Inverse transformation applied to temporally evolving dynamics has a less obvious physical interpretation that we do not attempt to address here. Inverse transform analysis resolves dynamics in terms of spatial heterogeneity, giving a distribution of classical (with inverse Laplace transformation) or ballistic (with inverse Gaussian transformation) diffusion coefficients. In contrast to conventional exponential or Kohlrausch analysis, inverse transform analysis does not assume *a priori* a particular form for the solution, and natively accommodates mono- or multimodal stretched or compressed exponential dynamics. Addition of a second Kohlrausch function can extend classical analysis to bimodal dynamics, but only when double relaxation in the time domain appears clearly (§2.2.1). The second case illustrated dynamics giving a reasonable fit to a single Kohlrausch function (§2.3.1) that resolves into a subtle bimodal distribution of ballistic diffusion using inverse transform analysis.

Inverse transform analysis interprets multimodal compressed or stretched exponential dynamics in terms of spatial heterogeneity. Rather than lumping the dynamic diversity observed in XPCS into a stretching exponent that, for heterogeneous dynamics, amounts to parameterizing the shape of a nontrivial Pollard distribution, inverse transformation can reveal underlying dynamic behavior hidden by Kohlrausch exponential analysis.

The author will provide source codes, a compiled Windows executable, and a Python/Qt GUI for the program used in this work (CONTIN XPCS) for free upon request.

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Figure 1.

Principles of DLS and XPCS. Coherent X-ray (XPCS) or laser (DLS) light impinges on a sample, and local contrast variation gives a speckle pattern. Internal sample dynamics result in time-dependent scattering intensity $I(q, \tau)$ as measured by a 2D detector. The dynamics of $I(q, \tau)$, and the relaxation rate of the resulting autocorrelation function $g_2(q, t)$, usually have dependence on the length scale q of the measurement.

$$g_2(t) = \begin{cases} a + b \exp[-2\Gamma t] & \text{Simple} \\ a + b \exp[-2(\Gamma t)^\alpha] & \text{Kohlrausch} \\ a + b \exp[-2\Gamma t] \left(1 + \frac{t^2 \mu_2}{2!} - \frac{t^3 \mu_3}{3!}\right)^2 & \text{Cumulant} \\ a + \beta \int \Psi(\Upsilon) \exp[-\Upsilon t] d\Upsilon & \text{CONTIN} \end{cases}$$

$$g_2(q, t) = a + \beta \int \Psi(\Upsilon) \exp[-\Upsilon q^2 t] d\Upsilon \quad \text{MULTIQ}$$

Figure 2.

Techniques for analysis of DLS and XPCS temporal autocorrelation functions $g_2(t)$. We introduce the parameter Υ representing a relaxation rate that reflects the transform used, a definition used later with inverse Gaussian transformation (*vide infra* §2.2.3). Classic XPCS analysis uses the Kohlrausch exponent α to account for deviation from simple exponential decays, whereas DLS assumes this results from dynamic heterogeneity through cumulant or inverse transform approaches. The method of cumulants characterizes the underlying monomodal distribution using parameters Γ , μ_2 and μ_3 . Inverse transformation seeks the underlying distribution $\Psi(\Upsilon)$ itself by solving the inverse Laplace transform (CONTIN) or simultaneously solving a single q^2 -dependent inverse Laplace transform on multiple data sets $g_2(q, t)$ measured at different q (MULTIQ).

Figure 3.

Simple exponential fitting of an XPCS measurement on a dilute suspension of nanoparticles. Correlating speckle intensity from a 2D detector gives a series of nine g_2 s across a q range spanning $q = 0.0024 \text{ \AA}^{-1}$ (orange) to $0.0052 \text{ \AA}^{-1}$ (red). For clarity, the plot shows only four g_2 s, while the inset shows the relaxation rates ($\Gamma = 2\Gamma$) determined from all nine g_2 s. The lines show a fit to a simple exponential function (Equation 2). Plotting $\Gamma = 2\Gamma$ thereby obtained on a log-log scale against q with a best fit to q^2 (solid) and q^1 (dashed) reveals that the dynamics scale with length according to q^2 , consistent with classical diffusion.

Figure 4.

Result from a typical procedure for selection of the Lagrange multiplier Λ , showing the goodness of fit χ^2 (blue), degrees of freedom N_g (green) and rejection probability P_{rej} (red) as a function of Λ . The filled gray curves show examples of distributions $\Psi(T)$ found at certain Λ , with the intensity at each mode scaled to the same value.

Figure 5.

Data from Figure 3 analyzed using CONTIN. Inverse Laplace transform of each g_2 according to Equation 10 yields a series of distributions $\Psi(\Upsilon)$ (upper inset). All the $\Psi(\Upsilon)$ obtained retain a similar shape, and dynamics at lower q (orange) decay more slowly than higher q (magenta), reflected in the shifting of the distribution mode from largest Υ at high q to lower Υ at low q . The lower inset shows the result from shifting each abscissa by q^{-2} , $\Psi(\Upsilon) = \Psi(2\Gamma) \rightarrow \Psi(2\mathcal{D} = 2\Gamma q^{-2} = \Upsilon q^{-2})$. $\Psi(\Upsilon q^{-2})$ coalesce around the diffusion coefficient $2\mathcal{D}$ (Figure 3).

Figure 6.

Simultaneous analysis with MULTIQ using a q^2 -dependent inverse Laplace transformation (Equation 11) that yields a single distribution of diffusion coefficients $\Psi(\Gamma)$ describing all nine $g_2(q, t)$ s (lower inset), nine backgrounds $a(q)$ and scale factors $\beta(q)$ (upper inset). Taking the solution $\Psi(\Gamma)$ and applying a q^2 -dependent Laplace transform nine times gives a good global fit to the data (lines, four of nine data sets shown).

Figure 7.

XPCS measurement on a gel between $q = 0.044 \text{ \AA}^{-1}$ (orange) and $0.064 \text{ \AA}^{-1}$ showing two distinct relaxations. The plot shows the data (point) and the fit (lines) using Equation 17 from four of 16 g_2 s. The lower inset shows the time constants Γ_1 and Γ_2 from all 16 g_2 s with best fits to $\propto q^1$ (dashed) and $\propto q^2$ (solid); the upper inset shows the corresponding values of the Kohlrausch exponents α_1 and α_2 .

Figure 8.
Two-time correlation function of the measurement giving the g_2 s in Figure 7 showing temporal homogeneity.

Figure 9.

Sequential application of CONTIN to g_2s from Figure 7 using Equation 22 giving a series of distributions $\Psi(T)$ (upper inset). Reintegration of each $\Psi(T)$ gives a good fit (lines) to the data (points). The lower inset shows the result after rescaling $\Psi(T)$ by q^2 .

Figure 10.

Simultaneous analysis of all g_2 s from Figure 7 using Equation 24. MULTIQ gives a single bimodal distribution describing the entire data set (lower inset); the dashed line results from conversion of the average Kohlrausch exponential determined from conventional fitting in Figure 7 ($a_1 = 1.3$, $a_2 = 1.9$) to a distribution using Pollard's relation (Equation 20) and shifting $\rho(\gamma^2)$ arbitrarily along the abscissa. Reintegration according to the q point of the measurement gives a good fit (lines) to the g_2 data (points). The upper inset shows MULTIQ's determination of the background a and scale parameters β as a function of q .

Figure 11.

Effect of added measurement error (left) on MULTIQ inverse transformation result (right). The left plot shows g_2 at one q from the data in Figure 7 with 0, 1, 3, 5, and 7 % additional random Gaussian error (points), compared to the Kohlrausch fitting of the original data set (black) from Figure 7. The right shows the MULTIQ inverse transformation result for a global distribution, stacked according to added error. The fit (solid colorized lines) results Gaussian transformation of the corresponding distribution on the right, all stacked vertically according to the amount of added error. The inset shows the resulting values for goodness of fit (χ^2 , green), good parameters (N_g , blue) and Lagrange multiplier (Λ , red) as a function of added random Gaussian error (**+Error**).

Figure 12.

Kohlrausch exponential fitting of XPCS data (points) acquired from a sample of colloidal gel between $q = 0.036$ (orange) and 0.057 (red) $\text{\AA}^{-1}$. The upper inset shows the value of the Kohlrausch exponent α as a function of q ; each g_2 displays compressed exponential relaxation ($\alpha > 1$). The lower inset shows the value of the time constant Γ , along with a best fit to $\propto q^2$ (solid line) and $\propto q^1$ (dashed).

Figure 13. Two-time correlation of the measurement giving the g_2 s in Figure 12 showing temporal homogeneity.

Figure 14.

Sequential CONTIN analysis of data from Figure 12 giving the results shown in the upper inset; the lower inset shows the same $\Psi(\Gamma)$ after rescaling by q^{-2} .

Figure 15.

MULTIQ fitting with Equation 27 of data from Figure 12 giving the global distribution shown in the lower inset with background a and scale factor β shown in the upper inset. The dashed line shows the Pollard distribution $\rho(\gamma^2)$ (Equation 20) obtained from the Kohlrausch exponent determined in Figure 12 ($a = 1.2$), shifted arbitrarily along the abscissa.

Table 1

Sum of fitting residuals (Equation 16) for each method of g_2 analysis from XPCS of a solution of dilute monodisperse spheres

Method	$\mathcal{R}$
Simple Exponential §2.1.1	0.37
CONTIN §2.1.3	0.45
MULTIQ §2.1.5	1.8

Table 2

Sum of fitting residuals for each fitting technique

Method	$\mathcal{R}$
Double Kohlrausch	0.68
CONTIN	0.47
MULTIQ	1.2

Table 3

Sum of fitting residuals for each fitting technique

Method	$\mathcal{R}$
Kohlrausch	3.5
CONTIN	2.1
MULTIQ	3.7