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CONTIN XPCS: Software for Inverse Transform Analysis of X-Ray Photon Correlation Spectroscopy Dynamics

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Abstract

X-ray photon correlation spectroscopy (XPCS) and dynamic light scattering (DLS) both reveal dynamics using coherent scattering, but X-rays permit investigating of dynamics in a much more diverse array of materials. Heterogeneous dynamics occur in many such materials, and we showed how classic tools employed in analysis of heterogeneous DLS dynamics extend to XPCS, revealing additional information that conventional Kohlrausch exponential fitting obscures. This work presents the software implementation of inverse transform analysis of XPCS data called CONTIN XPCS, an extension of traditional CONTIN that accommodates dynamics encountered in equilibrium XPCS measurements.

1. Introduction

X-ray photon correlation spectroscopy (XPCS) (Sutton *et al.*, 1991; Grübel *et al.*, 2000; Grübel *et al.*, 2008; Shpyrko, 2014) and dynamic light scattering (DLS) (Berne & Pecora, 1976) both use coherent scattering for observation of material dynamics. With idealized monodisperse, dilute materials, both XPCS and DLS reveal simple exponential (Brownian) dynamics. However, the analytical treatment of measurements showing divergence from simple exponential dynamics differ considerably between XPCS and DLS, despite their operational similarity. Traditional DLS analysis commonly interprets nonexponential relaxation in terms of underlying dynamic heterogeneity using cumulant (Friskén, 2001) or CONTIN analysis (Provencher, 1979; Provencher, 1982*a*; Provencher, 1982*b*), whereas XPCS analysis uses a Kohlrausch function. (Kohlrausch, 1854*a*; Kohlrausch, 1854*b*; Madsen *et al.*, 2010; Berberan-Santos *et al.*, 2008) We demonstrated the use of modified CONTIN with XPCS measurements (Andrews *et al.*, 2017) from XPCS data sets showing classic simple diffusive kinetics, compressed exponential dynamics and bimodal compressed exponential dynamics. The mathematical functions commonly used for DLS and XPCS analysis, as well as our notation for CONTIN- and MULTI-Q-XPCS analysis, are summarized in Fig. 1. This work describes the software implementation of inverse transform methods for XPCS data analysis.

Simultaneous analysis of $g_2(t)$ s measured at multiple q points mitigates effect of noise and truncation of the data, but also allows testing of more complicated hypothesis involving multiple q -dependent distributions. Here, $g_2(t) = \frac{\langle I(q, \tau) \rangle \langle I(q, \tau + t) \rangle}{\langle I(q, \tau) \rangle^2}$, and $q = 4\pi/\lambda \sin \theta$, where

λ is the X-ray wavelength and 2θ is the scattering angle. The original version of MULTI_Q (Provencher & Št pánek, 1996) defined a model using a Laplace transform of two distributions $\Psi(\Gamma)$ and $\Psi'(\Gamma)$, one independent of length scale and one with conventional q^2 dependence of Brownian motion. In a solution of polystyrene in cyclohexane, q^2 -dependent diffusion of the gel occurred in the presence of q -independent structural relaxation (Nicolai *et al.*, 1990). Analysis of concentrated poly(styrene) in diethyl malonate DLS data with MULTI_Q over two grids isolated these two dynamic modes (Fig. 2). Measurements from four different scattering angles between 30° and 140° ($q = 0.00117$ to $0.00150 \text{ \AA}^{-1}$) resolved the q^2 -dependent distribution corresponding to concentration fluctuations from a q -independent distribution attributed to density fluctuations. The characteristics of these samples measured with DLS and analyzed with MULTI_Q, semidilute solutions and plasticized polymers (Provencher & Št pánek, 1996), have some similarity with samples currently used with XPCS, suggesting applicability of this double distribution MULTI_Q approach for XPCS data analysis.

Classical use of the Kohlrausch function in XPCS for spatially heterogeneous dynamics assumes not only monomodal underlying dynamics, but the presence of a nontrivial Pollard (Pollard, 1946) distribution that gives a stretched exponential function after Laplace transformation. As an alternative to Kohlrausch exponential analysis of heterogeneous dynamics, we demonstrated the use of modified CONTIN (Andrews *et al.*, 2017) with XPCS data sets showing simple diffusive and compressed exponential dynamics. In the final example presented there, inverse transform analysis revealed a bimodal distribution of ballistic relaxation rates not obvious based upon classical Kohlrausch function analysis.

The modification of the CONTIN and MULTI transform kernel for use with XPCS is shown in the equations below. User-defined parameters ξ (the type of transform), q (the length scale dependence of the distribution) describe the type of dynamic model employed for inverse transformation. Selection of the classic inverse Laplace transform uses $\xi = 1$ describing slower than exponential dynamics. Faster than exponential decays require an inverse Gaussian transform, $\xi = 2$.

Equation 1 shows the adjustable transform model for analysis of a single g_2 , while Equations 2, 3, and 4 collectively analyze multiple g_2 s measured a multiple q . In Equation 4 the first transform includes a function $S(q)$ for more complicated dynamic dependence on length scale q .

$$g_2(t) = a + \beta \int \Psi(r) e^{-r t^\xi} dr \quad (1)$$

$$g_2(q, t) = a + \beta \int \Psi(r) e^{-r q^n t^\xi} dr \quad (2)$$

$$g_2(q, t) = a + \beta \int \Psi(r) e^{-r q^n t^\xi} + \Psi'(r) e^{-r q^{n'} t^{\xi'}} dr \quad (3)$$

$$g_2(q, t) = a + \beta \int \Psi(r) e^{-r q^n t^\xi S(q)^{-1}} + \Psi'(r) e^{-r q^{n'} t^{\xi'}} dr \quad (4)$$

2. Program

2.1. Structure

The program XPCS CONTIN consists of a Python GUI frontend and a Fortran back-end. The Python GUI loads the data, allows user selection of parameters and starts the compiled Fortran CONTIN/MULTIQ executable. Python writes the input values to STDIN of the Fortran executable using Brendan Arnold's FortranFormat library; when the Fortran program finishes, FortranFormat reads the output back into Python. Python dynamically updates the progress of CONTIN through the file system. The Fortran backend is the original CONTIN MULTIQ (Provencher, 1979; Provencher, 1982a; Provencher, 1982b; Provencher, 1984) written in FORTRAN66. Modifications to CONTIN MULTIQ allow user selection from Python of the time exponent and q -dependency of the transform, and exchange of other data between Python and Fortran through the file system. This modified version, called CONTIN XPCS, compiles and runs on Windows 7 or 10 machines. Analysis of typical XPCS data sets using nominal CONTIN XPCS inversion parameters requires about a minute on an average desktop computer. This software will analyze any XPCS data set, either as a standalone desktop application or integrated as part of online data analysis at the beamline. Argonne National Laboratory currently has CONTIN XPCS installed at 8-ID-I the XPCS beamline.

2.2. Interface

Figure 3 shows the user interface for XPCS CONTIN allowing definition of the transform type and selection of other parameters. CONTIN for batchwise analysis requires a user selection for the type of transform ξ and setting q independence by selecting q^n with $n = 0$. Pressing **Run CONTIN Batch** will analyze each g_2 individually and give one distribution for each g_2 . For MULTIQ, setting n to a nonzero value takes into account q^n dependence of the data set. Pressing **Run MULTIQ** will analyze all g_2 at once and give a single distribution $\Psi(T)$. Checking **Add Second Distribution** allows addition of $\Psi'(T)$ resulting from a different type of inverse transformation and q dependency. The **Distribution Solution** defines the lower $T_{\min}$ and upper $T_{\max}$ limits of integration, and the number of points (**Bins**) for discretization of the dT integral. CONTIN and MULTIQ automatically determine the most likely value for the Lagrange multiplier Λ the weights the relative

amounts of fit and smoothness (Eq. 5). In most cases, while we find the automatic selection the best intuitive choice, one should investigate the solution behavior in the vicinity of $\mathcal{P}_{\text{rej}} = 1/2$. Here, $\mathcal{P}_{\text{rej}}$ represents a rejection probability metric as defined in (Andrews *et al.*, 2017). XPCS CONTIN exports the distribution solution and inverse transform parameters into text files.

$$V(\Lambda) = \underbrace{\chi_{\text{Fit}}^2 + \Lambda \int \left(\frac{d^2\Psi(r)}{dr^2} \right)^2 + \left(\frac{d^2\Psi'(r)}{dr^2} \right)^2 dr}_{\text{Smoothness}} \quad (5)$$

2.3. Data Input Format

CONTIN XPCS requires the value of $g_2(q, t)$ and the points q and t of the measurement. This file containing a single array must have the format shown in the following array. The array consists of a single column of times t corresponding to all the g_2 , the g_2 and the error σ , the lag time points of each g_2 must be equal. A single row appended to the top of the array contains the q points of the measurement, followed by zeros to fill the remainder of the row. Instructions appear in the supporting information for modification of XPCSGUI in use at Argonne National Laboratory to output this array by default.

$$\begin{pmatrix} q_1 & q_2 & q_3 & \cdots & 0 \\ t_1 & g_2(q_1, t_1) & \sigma(q_1, t_1) & \cdots & \sigma(q_n, t_1) \\ t_2 & g_2(q_1, t_2) & \sigma(q_1, t_2) & \cdots & \sigma(q_n, t_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ t_m & g_2(q_1, t_m) & \sigma(q_1, t_m) & \cdots & \sigma(q_n, t_m) \end{pmatrix}$$

The program will look for the Kohlrausch exponential fit files and static SAXS intensity $I(q)$ and display them in a plot for reference, but their absence does not inhibit the rest of the program or inverse transformation.

2.4. GUI

The Python/Qt GUI, shown in Figure 4, displays the input data as a three dimensional plot of g_2 vs. $\log t$ vs. q (d). Presence of the fit file. TAUFIT2ASCII will populate the plots of the time constant γ (a) and Kohlrausch exponent (b) from the XPCS-GUI fit model $g_2(t) = a + \beta \exp[-(t/\gamma)^a]$. After selection of the inverse transform parameters as detailed in Figure 3 and processing, the solution and its characteristics appear in the remaining panels (e,f,g,h). The solution $\Psi(T)$ (and $\Psi'(T)$ with addition of a second distribution) appears in (e). The data and CONTIN fit corresponding to the selected q point (**Select g2**) in addition to the fitting residuals appear in (f). CONTIN determines a Lagrange multiplier automatically by first testing a series of 30 (**Search Points**) from small to large. CONTIN then performs a more detailed search in the region where $\mathcal{P}_{\text{rej}}$ crosses from $0 \rightarrow 1$ to identify the value closest to $\mathcal{P}_{\text{rej}} = 1/2$. CONTIN then uses this value to determine and report the solution shown in (e). Panel (h) shows the relative χ^2 , background $a(q)$ (**Multiple** selected for

Backgrounds) and contrast/scaling factor $\beta(q)$. CONTIN XPCS exports the solution into text files that contain the inverse transform parameters and the distribution solution(s).

3. Conclusion

DLS traditionally uses inverse Laplace transform analysis for describing exponential decays in terms of an ensemble of classical dynamics, as results from, for example, dynamics occurring in suspensions of particles with polydisperse radii. We demonstrated the extension of the inverse transform technique to XPCS data analysis by including the inverse Gaussian transformation for faster than exponential dynamics (Andrews *et al.*, 2017). The examples showed that inverse Gaussian transform analysis can reveal dynamics hidden by conventional Kohlrausch exponential analysis. In this work, we presented the software implementation of this technique in the program CONTIN XPCS.

The supporting information contains the source code for the Fortran backend and the Python frontend, and a user manual that describes compiling and installation instructions from the source code and analysis of the test data sets supplied. The results of these test data appeared in our earlier publication. The author will provide a ready-to-use version that includes the compiled Fortran executable and a full distribution of Python for free upon request.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Synopsis

This work describes the software package `CONTIN XPCS` for inverse transform analysis of X-ray photon correlation spectroscopy.

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

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

$$g_2(q, t) = a + \beta \int \Psi(\Upsilon) e^{-\Upsilon q^2 t} + \Psi'(\Upsilon) e^{-\Upsilon t} d\Upsilon \quad \text{MULTIQ}$$

Fig. 1.

Principles of DLS and XPCS. Figure based upon our earlier work (Andrews *et al.*, 2017). Techniques for analysis of DLS and XPCS temporal autocorrelation functions $g_2(t)$. Γ shows relaxation rate in its conventional definition. We introduce the parameter Υ that represents a relaxation rate whose units reflect the transform used. Classic XPCS analysis uses the Kohlrausch exponent α to account for deviation from simple exponential decay, 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). Inclusion of the measurement q allows inverse transform analysis into two distributions, $\Psi(\Upsilon)$ and $\Psi'(\Upsilon)$, each with different q dependency (q^2 and q^0 , respectively). a , b , α , and β are constants.

Fig. 2. *MULTIQ* extraction of q -independent relaxation from q^2 -dependent diffusion from DLS data of concentrated poly(styrene) in diethyl malonate. Figure reproduced from Provencher's original introduction of the *MULTIQ* technique (Provencher & Št pánek, 1996).

CONTIN/MULTIQ Transform and MULTIQ Kernel q Dependence

First Distribution (CONTIN/MULTIQ): ☒ Exp ☐ Gauss ☐ e^ 1.00

☐ q^0 (CONTIN) ☐ q^1 ☒ q^2 ☐ q^3 ☐ q^ 0.00 ☐ S(q) File

☒ *Add Second Distribution (MULTIQ):* ☒ Exp ☐ Gauss ☐ e^ 1.00

☒ q^0 ☐ q^1 ☐ q^2 ☐ q^3 ☐ q^ 2.00

Distribution Solution Log(Upsilon) = -7.00 to 7.00 Bins 150

Lagrange Multiplier ☒ Search points 30 ☐ Fix @ 10^-5.00

Background ☐ None ☐ Single ☒ Multiple

Weights ☐ None ☐ Poisson ☐ Constant ☒ Input ☐ Internal

Run CONTIN Batch Run MULTIQ Stop Export Reset

Result ☐ Rescale MULTIQ ☐ Rescale CONTIN by q^-2.00

Lagrange Multiplier Used -4.23 Probability to Reject 0.451

Sum Deviations 1.046 Degrees of Freedom 36.01

Fig. 3.

The CONTIN XPCS interface for user selection of parameters

Figure 4.

CONTIN XPCS Python/Qt GUI. Plots show the relaxation rate γ (a) and Kohlrausch exponent α (b) from conventional fitting with a Kohlrausch exponential function, and a 3D plot of the input g_2 data as a function of scattering vector q on one axis and lag time $\log t$ on the other axis (d) – these data come from the input file(s). The selected inverse transform parameters in the interface (c, **Gauss** and **q²** for the first distribution and **Gauss** and **q⁰** for the second) correspond to the model $g_2(q, t) = a + \beta \int \Psi(r) e^{-r q^2 t^0} + \Psi'(r) e^{-r q^0 t^2} dr$.

Pressing “Run MULTIQ” finds the distribution solutions $\Psi(T)$ and $\Psi'(T)$ shown in (e), the background $a(q)$ and scale parameters $\beta(q)$ shown in (h). The fit and data for the selected q point highlighted in blue (d) appear in panel (f). Panel (g) shows CONTIN’s search for the most likely value for the Lagrange multiplier Λ , displaying the goodness of fit χ^2 , degrees of freedom N_g and rejection probability $\mathcal{P}_{\text{rej}}$ as a function of Λ . MULTIQ performs a second search for Λ (large points) after rescaling the data by $\beta(q)$ determined during a preliminary analysis (small points). The most likely solution occurs at the point where $\mathcal{P}_{\text{rej}} = 1/2$, indicated by the vertical magenta line in (g).