Fitting Discrete Relaxation Spectrum using LASSO

Contents

1 Introduction

A classic problem in rheology is finding the discrete relaxation spectrum from measurements of the complex modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$. We assume that measurements of $G'(\omega)$ and $G''(\omega)$ are available at a set of frequencies $\omega = \{\omega_1, \cdots, \omega_n\}$. The goal is to simultaneously fit $G'(\omega)$ and $G''(\omega)$ to a set of N discrete Maxwell modes $\mathcal{M} = \{g_j, \tau_j\}$ with $j = 1, \cdots, N$.

$$\begin{aligned} G'(\omega) \approx P'(\omega) &= \sum_{j=1}^{N} g_j \frac{\omega^2 \tau_j^2}{1+\omega^2\tau_j^2} = \sum_{j=1}^{N} g_j k'(\omega\tau_j) \\ G''(\omega) \approx P''(\omega) &= \sum_{j=1}^{N} g_i \frac{\omega \tau_j}{1+\omega^2\tau_j^2} = \sum_{j=1}^{N} g_j k''(\omega\tau_j), \end{aligned} \tag{1}$$

where $g_j > 0$ and $\tau_j > 0$ are the modulus and timescale characterizing the j^{th} relaxation mode, respectively. $k'(z) = z^2/(1+z^2)$ and $k''(z) = z/(1+z^2)$ are the kernels corresponding to the storage and loss moduli, respectively.

$\mathcal{M}$ is called the discrete relaxation spectrum (DRS). There are specialized programs for computing $\mathcal{M}$ from experimental data.

2 Problem

- Given a set of n data points $\{\omega_i, G'(\omega_i), G''(\omega_i)\}$ fit a discrete spectrum by minimizing the error using the "SMEL Test" outlined in the Method section.

$$\chi^2 = \frac{1}{4n_d} \sum_{i=1}^{n_d} \left[w_i' \left(D_i' - P'(\omega_i)\right)^2 + w_i'' \left(D_i'' - P''(\omega_i)\right)^2 \right], \tag{2}$$

  With LASSO this becomes,

$$\chi^2_{\text{LASSO}}(\{g_j\}) = \chi^2(\{g_j\}) + \alpha \sum_{j=1}^{N} |g_j| \,. \tag{3}$$

- Compare the properties of the inferred spectrum with that obtained from a standard program like pyReSpect

3 Method

1. **Setup Data and Parameters**

   - Collect experimental observations, $\mathcal{D} = \{\omega_i, D_i' = G'(\omega_i), D_i'' = G''(\omega_i)\}$. Stack these moduli into a $2n_d \times 1$ column vector $\mathbf{D}$ so that $\mathbf{D}_i = D_i'$ and $\mathbf{D}_{n_d+i} = D_i''$;
   - Denote the boundaries of the frequency window $\omega_{\min} = \min\{\omega_i\}$ and $\omega_{\max} = \max\{\omega_i\}$; mark the boundaries of the modes $\tau_{\min} = 0.1/\omega_{\max}$ and $\tau_{\max} = 10/\omega_{\min}$ by extending the experimental domain by one decade on either side;
   - Set mode density $\rho_N = 10$ modes/decade. Set the number of modes $N = \rho_N \cdot \text{int}(\log_{10}(\tau_{\max}/\tau_{\min}))$;
   - Set the intermediate timescales τ_j on a logarithmically equispaced grid via,

$$\frac{\tau_j}{\tau_{\min}} = \left(\frac{\tau_{\max}}{\tau_{\min}}\right)^{\dfrac{j-1}{N-1}}, \tag{4}$$

     Thus, $\tau_1 = \tau_{\min}$ and $\tau_N = \tau_{\max}$.

2. **Setup for LASSO**

   - Furnish two $n_d \times N$ kernel matrices $\mathbf{K}'_{i,j} = k'(\omega_i \tau_j)$, and $\mathbf{K}''_{i,j} = k''(\omega_i \tau_j)$. Stack $\mathbf{K}'$ above $\mathbf{K}''$ to produce the $2n_d \times N$ feature matrix $\mathbf{K}$, so that $\mathbf{K}_{i,j} = \mathbf{K}'_{i,j}$ and $\mathbf{K}_{n_d+i,j} = \mathbf{K}''_{i,j}$;

- Let $\mathbf{g} = [g_1, \cdots, g_N]^T$ be a column vector of coefficients to be determined so that $\mathbf{D} \approx \mathbf{Kg}$ (eqn 1);
- Define a $2n_d \times 2n_d$ diagonal matrix of weights $\mathbf{W}_{ii} = 1/\sqrt{|\mathbf{D}_i|}$ for weighted least-squares;
- Transform the data vector $\mathbf{D}$ and the feature matrix $\mathbf{K}$ using these weights, $\hat{\mathbf{D}} = \mathbf{WD}$ and $\hat{\mathbf{K}} = \mathbf{WK}$. The least-squares objective function (eqn 2) can be succinctly represented as,

$$\chi^2 = \frac{1}{4n_d}(\hat{\mathbf{D}} - \hat{\mathbf{K}}\mathbf{g})^T(\hat{\mathbf{D}} - \hat{\mathbf{K}}\mathbf{g}). \tag{5}$$

  The standard unregularized normal equations are $\hat{\mathbf{K}}^T\hat{\mathbf{K}}\mathbf{g} = \hat{\mathbf{K}}^T\hat{\mathbf{D}}$;
- Use the `scikit-learn` function `LassoCV` with three-fold cross-validation to determine an optimal value of α in eqn 3. Solve and determine the coefficients $\mathbf{g}$;
- Assess the quality of the fit using the coefficient of determination, or R^2, as a proxy for the quality of the fit. Test if $R^2 \geq 0.95$ (or some other reasonable threshold).

4 Results

5 Summary

6 References