

Correlated scattering may directly reveal local structure in amorphous matter

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Abstract

INTRODUCTION

If we expand the electron density of the object under study in terms of the spherical harmonics $Y_{\ell m}$,

$$\rho(\mathbf{r}) = \sum_{\ell m} g_{\ell m}(r) Y_{\ell m}(\Omega)$$

where $g_{\ell m}(r)$ is a radial function. Then by Theorem 1, the Fourier transform of this function is

$$\hat{\rho}(\mathbf{q}) = \sum_{\ell m} G_{\ell m}(q) Y_{\ell m}(\Omega)$$

where

$$G_{\ell m}(q) = \sqrt{(2\ell+1)\pi} i^{-\ell} q^{-\ell+\frac{1}{2}} \int_0^\infty g_{\ell m}(s) J_{\ell+1/2}(2\pi qs) s^{\ell+\frac{1}{2}} ds$$

when the scattering $|\hat{\rho}(\mathbf{q})|^2$ thus expanded is substituted into (7) we obtain

$$M_{\lambda\mu}(q) = \int Y_{\lambda\mu}(\Omega) \left| \sum_{\ell m} G_{\ell m}(q) Y_{\ell m}(\Omega) \right|^2 d\Omega$$

this can be written more productively by in terms of a Gaunt integral

$$\begin{aligned} M_{\lambda\mu}(q) &= \sum_{\ell m} \sum_{LM} G_{\ell m}(q) G_{LM}^*(q) \int Y_{\lambda\mu}(\Omega) Y_{\ell m}(\Omega) Y_{LM}^*(\Omega) d\Omega \\ &= \sum_{\ell m} \sum_{LM} (-1)^M N_{\ell L \lambda} G_{\ell m}(q) G_{LM}^*(q) \begin{pmatrix} \ell & L & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & L & \lambda \\ m & -M & \mu \end{pmatrix} \end{aligned}$$

where we have employed the Wigner $3j$ -symbols and the coefficient

$$N_{\ell L \lambda} = \sqrt{\frac{(2\ell+1)(2L+1)(2\lambda+1)}{4\pi}}$$

alternatively, we may wish to employ the Wigner-Eckart theorem, in which case this reads

$$M_{\lambda\mu} = \sum_{\ell L} \langle L || Y_{\lambda} || \ell \rangle \sum_{mM} G_{\ell m}(q) G_{LM}^*(q) C_{\lambda\mu LM}^{\ell m}$$

where $\langle L || Y_{\lambda} || \ell \rangle$ is the *reduced matrix element* independent of m and M , and $C_{\lambda\mu LM}^{\ell m}$ is a Clebsh-Gordon coefficient.

Let $h_{\ell m} = |\langle L || Y_{\lambda} || \ell \rangle C_{\lambda\mu LM}^{\ell m}|^{1/2} G_{\ell m}$, so that we may write

$$M_{\lambda\mu} = \sum_{\ell L} \sum_{mM} h_{\ell m}(q) h_{LM}(q) \exp\{i\theta_{\ell m LM}\}$$

where θ is the phase of $G_{\ell m}(q) G_{LM}^*(q)$. So long as we can rotate the Kam bases such that we can ignore all but the $\mu = 0$ term (PROOF NEEDED), then because $m + M + \mu = 0$, we can write

$$M_{\lambda\mu} = \sum_{\ell L} \sum_m h_{\ell m}(q) h_{L(-m)}(q) \exp \{i\theta_{\ell m LM}\}$$

Let matrix $H = (h_{\ell k})$, where $k = m + 1$, $k = 1 \dots 2\ell + 1$ re-indexes m , and 1_n be a vector with unity in the first n positions, and zero everywhere else. Then we can write the modulus of $M_{\lambda\mu}$ very compactly in Dirac notation

$$|M_{\lambda\mu}| = \langle 1_\lambda | H \Pi H^T | 1_\lambda \rangle$$

with Π a permutation matrix of the form

$$\Pi = \begin{bmatrix} & & 1 \\ & \ddots & \\ 1 & & \end{bmatrix}$$

such that the multiplication $A\Pi$ swaps the columns of A . Note that the elements of H are functions of λ and q ; their indexing defines the dependence on ℓ, m, L and M .

Now, the Kam coefficients take the form (dbl chk but I think this is only OK for autocorrelator)

$$C_\lambda(q_1, q_2) = \langle 1_\lambda | H_1 \Pi H_1^T | 1_\lambda \rangle \langle 1_\lambda | H_2 \Pi H_2^T | 1_\lambda \rangle$$

for an autocorrelator $q_1 = q_2$,

$$\sqrt{C_\lambda(q, q)} = \langle 1_\lambda | H \Pi H^T | 1_\lambda \rangle$$

the vector \mathbf{C}_λ may be written

$$\sqrt{\mathbf{C}_\lambda(q, q)} = T H \Pi H^T \mathbf{1}$$

where T is a matrix with ones in the lower diagonal and zeros otherwise and $\mathbf{1}$ is a vector of all ones. Note that if found, the $h_{\ell m}$ coefficients completely specify the real-space electron density up to a phase. Further, that phase is constrained to discrete values $\theta_{\ell m LM} = \{0, 1, 2, 3\}$. Thus, these coefficients contain nearly all the information about the electron density. The problem of inferring them, however, is quite poorly conditioned.

Further, the conditioning of the problem can be improved if we relax our inferred variables to be

$$x_{\ell L} = \sum_m h_{\ell m} h_{L(-m)}$$

in this case, we obtain

$$\sqrt{\mathbf{C}_\lambda(q, q)} = TX\mathbf{1}$$

where our independent variables are now contained in the $\lambda_{max} \times \lambda_{max}$ matrix X (*vs.* the $\lambda_{max} \times (2\lambda_{max} + 1)$ matrix H). X gives the (rotationally smeared) magnitudes of the symmetries along the diagonal, cross terms off diagonal. Further, because the inference is now linear (instead of quadratic), this could be solved directly using the principles of compressed sensing via *e.g.* basis pursuit. We expect X to be sparse, because ...

NEED: rotation trick to eliminate μ is acceptable

NOTES: We have ignored cross correlators. Need to figure out what information loss there is due to ignoring them, and how we might be able to employ that info.

KAM EXPANSION

We assume that we measure the coherent scattering from a system consisting of identical copies of a specific particle or molecule with electron density $\rho(\mathbf{r})$. The effects of inter-particle interference or solvent contribution are ignored until later. Let the scattering from a single molecule with orientation ω to scattering vector \mathbf{q} be

$$M(\omega, \mathbf{q}) = \left| \int \rho(R_\omega \mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \right|^2 \quad (1)$$

Note that ω might be *e.g.* a tuple of three Euler angles, and R_ω is a rotation operator. We further assume that during the experiment, we expose the sample to light for a very short period of time (much shorter than rotational diffusion) and then refresh the sample and repeat. One such exposure will be called a “shot”, and the observed intensity for shot indexed n can be written

$$I_n(\mathbf{q}) = \sum_{\omega_i \in \Gamma_n} M(\omega_i, \mathbf{q}) + \text{interference terms}$$

Here, Γ_n is the set of orientations for each molecule i for a specific shot n . The orientations are assumed to be distributed uniformly on the three dimensional unit ball, and the cardinality of Γ_n , which we denote m_n (the number of molecules in shot n) is Poisson distributed with some mean parameter m that depends on the concentration and beam spot size.

Kam was the first to demonstrate that the correlation function

$$C(\mathbf{q}_1, \mathbf{q}_2) = \left\langle \delta I_n(\mathbf{q}_1) \delta I_n(\mathbf{q}_2) \right\rangle_n \quad (2)$$

where $\delta I_n(\mathbf{q}) = I_n(\mathbf{q}) - S(q)$, contained detailed information about the electron density of the system under study. We can demonstrate this connection between the electron density and correlation function as follows.

The first important thing to realize is what is meant by $\langle \cdot \rangle_n$ – this is an average over two quantities: first, the specific orientations within each shot, and second, the number of molecules in each shot. Using the definition of I_n , we can split the first term in an expansion of (2) into “coherent” and “incoherent” terms, respectively

$$I_n(\mathbf{q}_1) I_n(\mathbf{q}_2) = \sum_{\omega_i \in \Gamma_n} M(\omega_i, \mathbf{q}_1) M(\omega_i, \mathbf{q}_2) + \sum_{\omega_i \in \Gamma_n} \sum_{\omega_j \neq i \in \Gamma_n} M(\omega_i, \mathbf{q}_1) M(\omega_j, \mathbf{q}_2)$$

and then perform the expectation, using the fact that the orientations are identically distributed and independent

$$\begin{aligned} \langle I_n(\mathbf{q}_1) I_n(\mathbf{q}_2) \rangle_n &= \int p(m_n) \int p(\vec{\omega}) \left\{ \sum_{\omega_i \in \Gamma_n} M(\omega_i, \mathbf{q}_1) M(\omega_i, \mathbf{q}_2) \right. \\ &\quad \left. + \sum_{\omega_i \in \Gamma_n} \sum_{\omega_j \neq i \in \Gamma_n} M(\omega_i, \mathbf{q}_1) M(\omega_j, \mathbf{q}_2) \right\} dm_n \\ &= \int p(m_n) \left\{ m_n \int M(\omega, \mathbf{q}_1) M(\omega, \mathbf{q}_2) d\omega \right. \\ &\quad \left. + (m_n^2 - m_n) \int M(\omega, \mathbf{q}_1) d\omega \int M(\omega, \mathbf{q}_2) d\omega \right\} dm_n \\ &= \int p(m_n) \left\{ m_n \int M(\omega, \mathbf{q}_1) M(\omega, \mathbf{q}_2) d\omega + \frac{(m_n^2 - m_n)}{m^2} S(q_1) S(q_2) \right\} dm_n \end{aligned}$$

We can expand the integral

$$\int M(\omega, \mathbf{q}_1) M(\omega, \mathbf{q}_2) d\omega \quad (3)$$

in the spherical harmonics

$$M(\omega, \mathbf{q}) = \sum_{mm'\ell} M_{\ell m}(q) Y_{\ell m'}(\Omega) R_{m'm}^\ell(\omega) \quad (4)$$

where $M_{\ell m}$ is a complex coefficient, $Y_{\ell m'}$ is a spherical harmonic, Ω is the angular orientation of \mathbf{q} , and $R_{m'm}^\ell$ is a Wigner rotation matrix.

Substituting this into (3) and using first the orthogonality theorem

$$\int R_{m'm}^{(\ell)}(\omega) R_{M'M}^{(L)}(\omega) d\omega = \frac{1}{2\ell + 1} \delta_{\ell L} \delta_{mM} \delta_{m'M'}$$

and then the addition theorem

$$\sum_{m'} Y_{\ell m'}(\Omega_1) Y_{\ell m'}^*(\Omega_2) = \frac{2\ell + 1}{4\pi} P_\ell(\cos \psi)$$

where P_ℓ is a Legendre polynomial, and ψ is the angle subtended by Ω_1 and Ω_2 , we obtain

$$\int M(\omega, \mathbf{q}_1) M(\omega, \mathbf{q}_2) d\omega = \frac{1}{4\pi} \sum_{\ell} P_{\ell}(\cos \psi) \left[\sum_{m=-\ell}^{\ell} M_{\ell m}(q_1) M_{\ell m}^*(q_2) \right] \quad (5)$$

Finally, substituting this back into

$$[\text{NEEDFUL EXPRESSION}] \quad (6)$$

This is the central result of Kam, which we will call ‘‘Kam’s Expansion’’. The term in square brackets is a coefficient of an expansion of the correlation in Legendre polynomials. These coefficients,

$$C_{\ell}(q_1, q_2) = \sum_{m=-\ell}^{\ell} M_{\ell m}(q_1) M_{\ell m}^*(q_2)$$

can be obtained from an experimentally measured correlation function by simple projection,

$$C_{\ell}(q_1, q_2) = 2\pi(2\ell + 1) \int_0^{\pi} C(q_1, q_2, \psi) P_{\ell}(\cos \psi) \sin \psi d\psi$$

Note that the $\ell = 0$ term corresponds to information that is isotropic, dependent only on the magnitudes q_1 and q_2 . This information can be readily re-introduced into any modeling scheme by treating the structure factor $S(q)$ – which contains all of this isotropic information – as a separate source of information in addition to measured correlation functions. Further, by Friedel’s theorem, $M(\omega, \mathbf{q}) = M(\omega, -\mathbf{q})$, so we expect $C(\mathbf{q}_1, \mathbf{q}_2) = C(q_1, q_2, \psi)$ to be even around $\psi = 0$. Consequentially, only terms even in ℓ should contribute to the sum in (??).

MODEL COMPARISON

$$M_{\ell m}(q) = \int Y_{\ell m}(\Omega) M(0, q, \Omega) d\Omega \quad (7)$$

via *e.g.* a finite point-sampling algorithm. The normalization here makes these coefficients directly relatable to those measured by experiment, Equation (??) shows that said coefficients can be obtained from experiment by projecting the measured correlation function onto the Legendre polynomials,[?]

where we have written $C(\mathbf{q}_1, \mathbf{q}_2) = C(q_1, q_2, \psi)$ to emphasize the dependence of the correlation function on the angle between the scattering vectors.

Now the coefficients $C_{\ell}(q_1, q_2)$ can be matched between a computed model and measured experiment. Alternatively, one could attempt direct inversion, as discussed by Kam, and later Kirian, Saldin, Spence *et. al.*

USEFUL FACTS

The following theorem directly demonstrates that the angular component of the spherical harmonics are preserved under Fourier transformation. It employs a specific radial component to form the *solid spherical harmonics*,

$$P_{\ell m}(\mathbf{x}) = \sqrt{\frac{4\pi}{2\ell+1}} r^\ell Y_{\ell m}(\theta, \phi)$$

but is general for any radial form of the spherical harmonics in n dimensions.

Theorem 1 (Stein and Weiss, Thm 3.10, p. 158). *Suppose $n \geq 2$, and function $f \in L^2(E_n) \cap L^1(E_n)$ has form $f(\mathbf{x}) = f_0(x)P_{\ell m}(\mathbf{x})$, where $P_{\ell m}(\mathbf{x})$ is a solid spherical harmonic. Then \hat{f} has form $\hat{f}(\mathbf{x}) = F_0(x)P_{\ell m}(\mathbf{x})$ where*

$$F_0(r) = 2\pi i^{-\ell} r^{-(n+2\ell-2)/2} \int_0^\infty f_0(s) J_{(n+2\ell-2)/2}(2\pi r s) s^{(n+2\ell)/2} ds$$

and J is a Bessel function of the first kind.

We further employ the well-known fact that a spherical harmonic of degree ℓ can be represented via a linear combination of spherical harmonics, also of degree ℓ , in a rotated basis.

Lemma. *For any linear combination of spherical harmonics of the form $\sum_{m=-\ell}^\ell a_{\ell m} Y_{\ell m}(\Omega)$, and any rotation operator R_ω , there exists a second linear combination of harmonics $\sum_{m=-\ell}^\ell b_{\ell m} Y_{\ell m}(\Omega)$ of same degree ℓ such that*

$$\sum_{m=-\ell}^\ell a_{\ell m} Y_{\ell m}(\Omega) = \sum_{M=-\ell}^\ell b_{\ell M} Y_{\ell M}(R_\omega \Omega)$$

whose coefficients obey $\sum_{m=-\ell}^\ell a_{\ell m}^2 = \sum_{M=-\ell}^\ell b_{\ell M}^2$.

Proof. It was demonstrated in [REF] that any spherical harmonic can be represented in a rotated basis by spherical harmonics of the same degree

$$Y_{\ell m}(\Omega) = \sum_{M=-\ell}^\ell d_{mM}^{(\ell)} Y_{\ell M}(R_\omega \Omega)$$

where the coefficients obey $\sum_{M=-\ell}^\ell [d_{mM}^{(\ell)}]^2 = 1$.

Given a linear combination of such rotated spherical harmonics

$$\sum_{m=-\ell}^\ell a_{\ell m} Y_{\ell m}(\Omega) = \sum_{m=-\ell}^\ell a_{\ell m} \sum_{M=-\ell}^\ell d_{mM}^{(\ell)} Y_{\ell M}(R_\omega \Omega)$$

we may rearrange the finite sums

$$\sum_{m=-\ell}^{\ell} a_{\ell m} Y_{\ell m}(\Omega) = \sum_{M=-\ell}^{\ell} A_{\ell} d_{mM}^{(\ell)} Y_{\ell M}(R_{\omega} \Omega)$$

where we have written $A \equiv \sum_{m=-\ell}^{\ell} a_{\ell m}^2$. Since $\sum_{M=-\ell}^{\ell} [d_{mM}^{(\ell)}]^2 = 1$, it follows directly that $\sum_{M=-\ell}^{\ell} [A_{\ell} d_{mM}^{(\ell)}]^2 = \sum_{m=-\ell}^{\ell} a_{\ell m}^2$. Identifying $A_{\ell} d_{mM}^{(\ell)} = b_{\ell M}$ completes the proof.