Correlated scattering may directly reveal local structure in amorphous matter

Thomas J. Lane

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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

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

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

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

if we let $H_{\ell m}^{LM}(q) = G_{\ell m}(q) \, G_{LM}^*(q)$, then this can be written more productively by in terms of a Gaunt integral

$$M_{\lambda\mu}(q) = \sum_{\ell m} \sum_{LM} H_{\ell m}^{LM}(q) \int Y_{\lambda\mu}(\Omega) \, Y_{\ell m}(\Omega) \, Y_{LM}^*(\Omega) \, d\Omega$$

$$= \sum_{\ell m} \sum_{LM} (-1)^M \, N_{\ell L\lambda} \, H_{\ell m}^{LM}(q) \begin{pmatrix} \ell & L & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & L & \lambda \\ m & -M & \mu \end{pmatrix}$$

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

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

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.

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

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

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

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

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

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

We can expand the integral

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

in the spherical harmonics

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

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

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

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

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

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

Finally, substituting this back into

$$
[\text{NEEDFULLEXPRESSION}] \tag{6}
$$

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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

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

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*

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

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 $\sum_{M=-\ell}^\ell \left[d_{mM}^{(\ell)}\right]^2 = 1$.

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 $\sum_{M=-\ell}^\ell \left[d_{mM}^{(\ell)}\right]^2 = 1$, it follows directly that $\sum_{M=-\ell}^\ell \left[A_\ell \, d_{mM}^{(\ell)}\right]^2 = \sum_{m=-\ell}^\ell a_{\ell m}^2$. Identifying $A_\ell \, d_{mM}^{(\ell)} = b_{\ell M}$ completes the proof.