I. INTRODUCTION

In X-ray diffraction one analyzes quantities like the unit scattering power of a sample of N scatterers in a volume V. If the scatterers are distributed with a density $\rho(u),\ u \in V$, then the total scattering power for the sample is given by

$$I_N(s) = \int_V P(u) exp(-2\pi i s \cdot u)\ du$$

where $P(u) = \int_V \rho(u' + u)\rho(u')du'$ is the autocorrelation of ρ; $I_N(s)$ is the measured intensity in the direction S, of radiation diffracted from a beam of wavelength λ propagating in the direction S_0, with $s = (S - S_0)/\lambda$ (equation 2.11 in Guinier).[1] $I_N(s)$ clearly depends on the configuration of the given sample through $P(u)$, and thus on the separations of scatterers and the relative frequencies of such separations. Ergodic theory enables us to relate $I_N(s)$ to part of the spectrum of a certain group of unitary operators acting on a Hilbert space. In this paper we prove that

$$I_N(s)ds \cong |V|\ d\!< E_s\tilde{f}, \tilde{f} >$$

with equality in the limit of an infinite sample, where E_s is a spectral family of projection operators of those unitary operators acting on a certain Hilbert space, $\tilde{f}$ is an element of this space, and ds is a volume element of $\mathbf{R}^3$ (the radial direction corresponding to the wavelength λ). In this way ergodic theory demonstrates a link between $I_N(s)$ and E_s.

II. THE THEORY

Let X be the set of all "configurations with hard core restriction", that is, the set of all sets of countably many points in $\mathbf{R}^3$ (points representing the positions of scatterers) such that the distance between any two points is at least one. Define a metric on X as follows. Enumerate the countable set of all finite collections of open balls in $\mathbf{R}^3$ such that for each finite set: (1) the configuration of their centers satisfies the hard core condition, (2) all centers have rational coordinates, and (3) all radii are rational and less than 1/2. Let $B_c(\epsilon)$ be the open ball with center c and radius ϵ, and to each such ball define the continuous function $f_{c,\epsilon} : \mathbf{R}^3 \to \mathbf{R}$ by

$$f_{c,\epsilon}(u) = \begin{cases} \epsilon - \|u - c\| & \text{if } u \in B_c(\epsilon) \\ 0 & \text{otherwise} \end{cases}$$

where $\|v\|$ denotes the usual euclidean norm in $\mathbf{R}^3$. Let C_n denote the set of open balls in the n$^{\text{th}}$ collection in the enumeration above, and let $\delta_j(x)$ be the position of the j^{th} particle of x. Define the function $f_n : X \to \mathbf{R}$ as follows: $f_n(x) = \prod_{B_c(\epsilon)\in C_n} \sum_j f_{c,\epsilon}(\delta_j(x))$. Finally, define the metric $d : X \times X \to \mathbf{R}$ by $d(x, y) = sup_n|f_n(x) - f_n(y)|/n$. To prove X is compact in the metric topology one need only show it has the property that any sequence of configurations has a subsequence which converges.[2] This is straightforward using Cantor diagonalization and the Bolanzo-Weierstrass theorem applied to bounded cubes, as follows.

Lemma : The space X is compact.

Proof : Given a configuration $x \in X$ we may enumerate the points of x as follows. Form a lattice in $\mathbf{R}^3$ from the vectors $n_1(1/\sqrt{3}, 0, 0)$, $n_2(0, 1/\sqrt{3}, 0)$, $n_3(0, 0, 1/\sqrt{3})$, where $n_1, n_2, n_3 \in \mathbf{Z}$. Enumerate the corresponding lattice boxes $\{(u_1, u_2, u_3) \in \mathbf{R}^3 |\, 1/\sqrt{3}\, n_i \leq u_i < 1/\sqrt{3}\,(n_i + 1),\ i = 1, 2, 3\}$ so as to spiral outward from the origin. Then in each copy (translate) of the half-open-half-closed box $[0, 1/\sqrt{3}) \times [0, 1/\sqrt{3}) \times [0, 1/\sqrt{3})$ there exists at most one point of the configuration x (by hard core condition). Define $x(j)$ as the position of the particle of x in j^{th} box, B_j (let $x(j) = \{\eta\}$ if no such particle exists). Let $\overline{B}_j$ be the closure of B_j and assign $\mathbf{B}_j = \overline{B}_j \cup \{\eta\}$ the usual product topology. Let $x_i,\ i \geq 1$, be any sequence of configurations in X. Then $x_i(1)$ is a sequence in $\mathbf{B}_1$. By the Bolanzo-Weierstrass theorem[2] there exists a convergent subsequence, x_i^1, such that $x_i^1(1) \to x^1 \in \mathbf{B}_1$ as $i \to \infty$. Again by the Bolanzo-Weierstrass theorem we may take a subsequence of x_i^1, call it x_i^2, such that $x_i^2(j) \to x^j \in \mathbf{B}_j$ for $j = 1, 2$ as $i \to \infty$. Continuing in this way we obtain subsequences x_i^m such that $x_i^m(j) \to x^j \in \mathbf{B}_j$ for $j = 1, ..., m$ as $i \to \infty$. Taking the diagonal subsequence x_m^m we have that $x_m^m(j) \to x^j \in \mathbf{B}_j$ for all j as $m \to \infty$. Note this gives rise to an allowed configuration $x = \{x^j |\, j \geq 1\}$ (that is, the hard core condition is satisfied by the collection of points $x^i, i \geq 1$). The fact that $x_m^m \to x$ in the metric on X follows simply. Q.E.D.

Consider the group of translations of $\mathbf{R}^3$ acting on X in the usual way: that is, every particle of a given configuration is translated by t; we denote this translation of x by $t(x)$ for all $x \in X$, $t \in \mathbf{R}^3$. Since X is compact and $\{t \,|\, t \in \mathbf{R}^3\}$ is a group of commuting homeomorphisms on X, there exists a Borel probability measure μ on X invariant under t for all $t \in \mathbf{R}^3$ (Markov-Kakutani theorem)[3]. We assume the action is ergodic, that is, $t(A) = A$ for all $t \in \mathbf{R}^3$ implies $\mu(A) = 0$ or 1. Let $L = L^2(X, \mu)$ be the Hilbert space of complex valued functions on X which are square integrable with respect to μ. Define the group of unitary operators $\{T^t \,|\, t \in \mathbf{R}^3\}$ on L by $[T^t(f)](x) = f[t(x)]$. Let $\delta(x) \in \mathbf{R}^3$ be any point in the configuration x closest to the origin, and for each $f : \mathbf{R}^3 \to \mathbf{R}$ define $\tilde{f}(x) = f[-\delta(x)]$. Take f to be any positive, real valued function on $\mathbf{R}^3$ such that: $supp(f) \subset B_0(\epsilon)$ (that is, f=0 outside a ball of radius ϵ centered at the origin), and $\int_{B_0(\epsilon)} f^2(s)ds = 1$. (For example, we may take f to be the constant function $1/vol[B_0(\epsilon)]$ on $B_0(\epsilon)$, 0 otherwise.) Furthermore suppose $\epsilon > 0$ is sufficiently small (e.g. $\epsilon < 1/2$) such that given any $x \in X$ there exists at most one point of x contained in $B_0(\epsilon)$. It then follows from the hard core condition that $\tilde{f}(x) = \sum_{j \geq 1} f[-\delta_j(x)]$, where $\delta_j(x)$ = position of j^{th} particle of x. Thus

$$T^s \tilde{f}(x) = \sum_{j \geq 1} f[s - \delta_j(x)]. \tag{1}$$

Consider the quantity:

$$< T^t \tilde{f}, \tilde{f} >= \int_X [T^t \tilde{f}(x)][\tilde{f}(x)] d\mu(x) \tag{2}$$

which by Birkhoff's pointwise ergodic theorem[4] satisfies, for μ - almost every $x \in X$,

$$< T^t \tilde{f}, \tilde{f} >= \lim_{V \to \mathbf{R}^3} \frac{1}{|V|} \int_V [T^{t+u} \tilde{f}(x)][T^u \tilde{f}(x)] du \tag{3}$$

and so,

$$< T^t \tilde{f}, \tilde{f} >= \lim_{V \to \mathbf{R}^3} \frac{1}{|V|} \int_V \sum_{j,k} f[t + u - \delta_j(x)] f[u - \delta_j(x)] du \tag{4}$$

Alternately, from Naimark's generalization of Stone's theorem[5] we know that

$$< T^t \tilde{f}, \tilde{f} >= \int_{\mathbf{R}^3} \exp(i 2\pi s \cdot t) \; d < E_s \tilde{f}, \tilde{f} > \tag{5}$$

where $E_s : L \to L$ is a spectral family of operators corresponding to the group of operators $\{T^t \,|\, t \in \mathbf{R}^3\}$. Now if we have N identical scatterers, centered at N points $\delta_j(x)$ in the configuration x of (4) which are in a volume V, each scatterer represented, not by a delta-function mass (or charge), but a mass (charge) distributed by a density $f[u - \delta_j(x)]$, they produce a total intensity I_N which satisfies (taking the inverse Fourier transform of equation 2.11 in Guinier)[1],

$$\int_V \sum_{j,k} f[t + u - \delta_j(x)] f[u - \delta_k(x)] du = \int_{\mathbf{R}^3} \exp(i 2\pi s \cdot t) \; I_N(s) ds \tag{6}$$

Comparing (4), (5) and (6) we have that:

$$\lim_{N \to \infty} \frac{I_N(s)}{N} ds = |V_0| \; d < E_s \tilde{f}, \tilde{f} > \tag{7}$$

where $|V_0| = V/N$ = average volume available to a scatterer. Alternately we have approximately:

$$I_N(s) ds \cong |V| \; d < E_s \tilde{f}, \tilde{f} > . \tag{8}$$

III. CONCLUDING REMARKS

It is perhaps useful to mention the observation motivating the application of ergodic theory to the study of the unit scattering power. Consideration of the quantity $< T^t\tilde{f}, \tilde{f} >$ was central to the above development and arose quite naturally in the context of averaging. By (4), $< T^t\tilde{f}, \tilde{f} >$ is related to the separation of scatterers- as can readily be seen in the case where f is uniformly supported over the ball of radius ϵ (that is, $f(u) = 1/vol[B_0(\epsilon)]$ for $u \in B_0(\epsilon)$, 0 otherwise). In this case when $x \in X$ is a lattice (as in the case of a simple crystal) and $t = \delta_j(x) - \delta_k(x)$ is a lattice vector, then $< T^t\tilde{f}, \tilde{f} >$ is the density of pairs separated by the vector t. If $t' \cong t$ (say $\|t' - t\| < 2\epsilon$) then $< T^{t'}\tilde{f}, \tilde{f} >$ will be nonzero, so indeed this quantity is related to the densities of pair separations.

It is hoped that the interplay between the two spectra will be of use to both crystallographers and ergodic theorists.

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