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Diffraction by aperiodic structures at high temperatures

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Abstract. This paper studies, in the Einstein model, the influence of thermal motion on diffraction by aperiodic structures. In particular, it shows that in a quasicrystal thermal motion reduces the intensity of the Bragg peaks by a Debye–Waller factor in the same way as in a crystal. The result applies to a large class of aperiodic structures.

1. Introduction

Since the discovery of quasicrystals [1] considerable attention has been paid to diffraction by various aperiodic structures (see, for example, [2–4], and references given below). Inelastic neutron scattering in icosahedral quasicrystals has been the subject of several recent experimental (see, for example, [5–7]) and theoretical (see, for example, [8]) studies. This paper studies the effect on the diffraction spectrum of thermal motion in the Einstein approximation of the solid. Thus, this work pertains primarily to x-ray diffraction at high temperatures. It will show rigorously that, in the Einstein approximation, the diffraction spectrum of a large class of (hypothetical, monatomic) quasicrystals is affected by thermal motion in the same way as that of a crystal.

More specifically, the problem studied is the following. Consider a countable set $X \subset \mathbb{R}^d$ and let μ be the measure

$$\mu := \sum_{x \in X} \delta_x \tag{1.1}$$

where δ_x denotes the delta function at x. The measure μ models an infinite system of identical atoms at positions given by X. The set X will only be assumed to satisfy a hard-core conditon and an ergodicity condition described below. Such generality is desirable because the precise atomic structure of quasicrystals is not known. The conditions on X are satisfied for the set of vertices of tilings obtained by the projection method [4] or by a primitive substitution [9, 10]. Thus they are for instance satisfied for the models studied in [11–20].

Diffraction by the set X is described by the Fourier transform $\hat{\gamma}$ (in the sense of tempered distributions) of the autocorrelation

$$\gamma = \lim_{L \to \infty} (2L)^{-1} \sum_{x,y \in X \cap [-L,L]^d} \delta_{x-y} \tag{1.2}$$

(cf [4]). Both $\hat{\gamma}$ and γ are positive measures on $\mathbb{R}^d$. The physical meaning of $\hat{\gamma}$ is that $\hat{\gamma}(q/\lambda)\,dq$ is proportional to the intensity of radiation of wavelength λ scattered per atom

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into the volume element dq around Q_0+q, where Q_0 is the direction of the incident beam. Delta functions in $\hat{\gamma}$ correspond to Bragg peaks in the diffraction spectrum.

Thermal motion is now modelled by displacing the atoms by independent identically distributed random variables η_x; if $X' = \{x+\eta_x \mid x \in X\}$ then $\mu' = \sum_{x\in X'} \delta_x$ represents (a realization of) the instantaneous positions of the atoms. It will be shown here that $\gamma_{\mu'}$, the autocorrelation of μ', is almost surely constant and is completely determined by γ_μ and the distribution of the random variables. There is no need to take an expectation with respect to the randomness; the system is 'self-averaging'. This is of interest because the frequency of thermal motion is much lower than that of x-ray radiation (cf [21, section 7.1.1]): the diffraction pattern is determined by μ' at every instant.

2. Preliminaries

This section recalls some facts about measures that will be needed and states the conditions on the set X. Among other things, those conditions imply that the limit (1.2) exists.

A measure μ on $\mathbb{R}^d$ is a linear functional on the space $\mathcal{K}$ of complex continuous functions on $\mathbb{R}^d$ of compact support with the property that for every compact subset K of $\mathbb{R}^d$ there is a constant a_K such that

$$|\mu(f)| \leqslant a_K \, \|f\|$$

for all $f \in \mathcal{K}$ with support in K; here $\|\cdot\|$ denotes the supremum norm. All measures encountered here will be positive: $\mu(f) \geqslant 0$ for all $f \geqslant 0$. The set of measures on $\mathbb{R}^d$ is given the vague topology: a sequence of measures $\{\mu_n\}$ converges to μ in the vague topology if $\lim_{n\to\infty} \mu_n(f) = \mu(f)$ for all $f \in \mathcal{K}$. For a general reference for measures as linear functionals, see [22].

For any function f, define $\check{f}$ by $\check{f}(x) := f(-x)$ and $\tilde{f}$ by $\tilde{f} := \overline{\check{f}}$, where the bar denotes complex conjugation. Similarly, for a measure μ, define $\check{\mu}$ by $\check{\mu}(f) := \mu(\check{f})$ and $\bar{\mu}$ by $\bar{\mu}(f) := \mu(\bar{f})$ and $\tilde{\mu}$ by $\tilde{\mu} := \bar{\check{\mu}}$. Recall that the convolution $\mu * \nu$ of two measures μ and ν is defined by $\mu * \nu(f) := \int \mu(\mathrm{d}x)\nu(\mathrm{d}y) f(x+y)$; it is welll defined if at least one of the two measures has compact support.

Denote the cube $[-L/2, L/2]^d$ by C_L. For an arbitrary measure ρ, let ρ_L denote its restriction to C_L, i.e. $\rho_L := 1_{C_L}\rho$. The autocorrelation γ_ρ of ρ is defined [4] as the vague limit of the measures $\gamma_\rho^L := L^{-d}\rho_L * \tilde{\rho}_L$, provided the limit exists. Note that this implies that for every compact set K there is a constant β_K such that

$$\gamma_\rho^L(K) \leqslant \beta_K \qquad \text{for all } L. \tag{2.1}$$

Since $\delta_x * \tilde{\delta}_y = \delta_{x-y}$, we see that $\gamma_\mu^L := (L)^{-d} \sum_{x,y\in X\cap C_L} \delta_{x-y}$ and that γ_μ is indeed given by (1.2). Note that for all X the autocorrelation γ_μ has a delta function at 0 with weight given by the density of X, the number of points per unit of volume.

The set X is required to satisfy two conditions. First, there is a minimium distance between points: there exists a δ such that $|x-y| > \delta$ for all $x, y \in X$. The second condition is an ergodicity condition, whose statement requires some definitions. Let $A \subset \mathbb{R}^d$ have a diameter smaller then $\delta/2$. An A-chain of length n ($n \geqslant 1$) is a sequence $(x_1, y_1), \ldots, (x_n, y_n)$ of n (ordered) pairs in $X \times X$ such that $x_i - y_i \in A$ and $y_i = x_{i+1}$ for all i. A pair $(x, y) \in X \times X$ such that $x - y \in A$ is called odd (even) if it has odd (even) index in the longest A-chain in which it occurs. The pairs in an A-chain of infinite length are called odd and even alternatingly, after one pair in the chain has arbitrarily been designated odd or even. (The small diameter of A ensures that chains cannot split.) Let $N_L^{\mathrm{o}}(A)$ ($N_L^{\mathrm{e}}(A)$) denote the number of odd (even) pairs $(x, y) \in X \times X$ in the cube C_L.

The second condition is that the frequencies $L^{-d}N_L^{\circ}(A)$ and $L^{-d}N_L^{\bullet}(A)$ exist as $L \to \infty$ for every translate $A = \{x \in \mathbb{R}^d \mid |x_i| < \delta'\} + a$ of a cube of side $\delta' < \delta/2\sqrt{d}$.

Both conditions are satisfied for the sets of vertices of tilings obtained from the projection method [4] and tilings defined by primitive substitutions (see, for example, [10]), because in these tilings the number of different (modulo translations) configurations of diameter less then R is finite for every R; moreover, each of these configurations occurs with a well defined frequency. Note, however, that the second condition can still be satisfied if the number of different configurations of diameter less then R is infinite. An example would be the set of vertices of a 'pinwheel tiling' of the plane [23].

3. Result

Theorem. Let γ_μ be the autocorrelation of $\mu = \sum_{x\in X}\delta_x$. Let $\{\eta_x\}_{x\in X}$ be independent, identically distributed random variables with common distribution ν and finite expectation, taking values in $\mathbb{R}^d$. Let $X' := \{x + \eta_x | x \in X\}$ and $\mu' := \sum_{x\in X'}\delta_x$. Then, with probability one, μ' has autocorrelation $\gamma_{\mu'}$ given by

$$\gamma_{\mu'} = \gamma_\mu * (\nu * \tilde{\nu}) + n_0(\delta_0 - \nu * \tilde{\nu}) \tag{3.1}$$

where $n_0 = \gamma_\mu(\{0\})$ is the density of X.

Proof. Note that it suffices to show that $\gamma_{\mu'}^L\phi \to \gamma_{\mu'}\phi$ with probability one as $L \to \infty$ for one $\phi \in \mathcal{K}$ because $\mathcal{K}$ is separable. Assume, without loss of generality, that the support of ϕ contains the origin.

For $l > 0$, let $\mathcal{P}_l$ be the partition of $\mathbb{R}^d$ by translates of the cube $\{x \in \mathbb{R}^d | -\frac{1}{2l} \leqslant x_i < \frac{1}{2l}\}$ centred around points of $\frac{1}{l}\mathbb{Z}^d$. Let $l > 2\sqrt{d}/\delta$, so that every cube in $\mathcal{P}_l$ contains at most one point of X. For every pair $(x, y) \in X \times X$, let $z_{x,y} \in \frac{1}{l}\mathbb{Z}^d$ be the centre of the cube in $\mathcal{P}_l$ containing $x - y$ and let $\zeta_{x,y} := \eta_x - \eta_y$.

Since ϕ is uniformly continuous, there is for every $\epsilon > 0$ an l' such that $l > l'$ implies that $|\phi(z') - \phi(z)| < \epsilon$ whenever z and z' lie in the same cube of $\mathcal{P}_l$. Then, for all L,

$$\left| L^{-d} \sum_{x,y\in X\cap C_L} \phi(x - y + \eta_x - \eta_y) - L^{-d} \sum_{x,y\in X\cap C_L} \phi(z_{x,y} + \zeta_{x,y}) \right|$$

$$\leqslant \epsilon L^{-d} \sum_{\substack{x,y\in X\cap C_L: \\ x-y\in \mathrm{supp}(\phi)}} 1 \leqslant K\epsilon$$

where the constant K depends on ϕ, but is independent of L (by (2.1)), ϵ and l. Clearly

$$\lim_{L\to\infty} L^{-d} \sum_{x,y\in X\cap C_L} \phi(z_{x,y}) = \sum_{z\in(1/l)\mathbb{Z}^d} \gamma_\mu(B_z)\phi(z)$$

where B_z is the cube in $\mathcal{P}_l$ centred around z. This equation defines a discrete measure σ^l that converges vaguely to γ_μ as $l \to \infty$. Now

$$L^{-d}\sum_{x,y\in X\cap C_L}\phi(z_{x,y}+\zeta_{x,y})=L^{-d}\sum_{x\in X\cap C_L}\phi(0)$$

$$+L^{-d}\sum_{z\in(1/l)\mathbb{Z}^d\setminus\{0\}}\left(\sum_{\substack{x,y\in X\cap C_L:\,z_{x,y}=z\\(x,y)\text{ odd}}}\phi(z+\zeta_{x,y})+\sum_{\substack{x,y\in X\cap C_L:\,z_{x,y}=z\\(x,y)\text{ even}}}\phi(z+\zeta_{x,y})\right).$$

The $\zeta_{x,y}$ are identically distributed random variables with distribution $\nu*\check{\nu}=\nu*\tilde{\nu}$. Moreover, the $\{\zeta_{x,y}\}_{\{(x,y)\,|\,z_{x,y}=z\}}$ in the 'odd' sum are independent, and so are those in the 'even' sum, because ζ_{x_1,x_2} and ζ_{x_3,z_4} are independent if and only if the pairs (x_1,x_2) and (x_3,x_4) have no point in common. Hence, if $z\neq 0$,

$$\lim_{L\to\infty}L^{-d}\sum_{\substack{x,y\in X\cap C_L:\,z_{x,y}=z\\(x,y)\text{ odd}}}\phi(z+\zeta_{x,y})=n_z^{\mathrm{o}}\int\phi(z+t)\nu*\tilde{\nu}(\mathrm{d}t)$$

with probability one by the strong law of large numbers, where n_z^{o} is the density of the pairs (x,y) that contribute to the sum; this density exists by the second condition on X. An analogous statement holds for the even pairs. Note that $n_z^{\mathrm{o}}+n_z^{\mathrm{e}}=\gamma_\mu(B_z)$.

Since the support of ϕ contains finitely many points of $\frac{1}{l}\mathbb{Z}^d$ it follows that

$$\lim_{L\to\infty}L^{-d}\sum_{x,y\in X\cap C_L}\phi(z_{x,y}+\zeta_{x,y})$$

$$=\gamma_\mu(B_0)\phi(0)+\sum_{z\in(1/l)\mathbb{Z}^d\setminus\{0\}}\gamma_\mu(B_z)\int\phi(z+t)\nu*\tilde{\nu}(\mathrm{d}t) \tag{3.2}$$

with probability one. Recall that γ_μ has a Dirac delta at 0; its weight is $n_0=\gamma_\mu(B_0)$ since l is so large that the diameter of B_0 is smaller than δ. Therefore the right-hand side of (3.2) can be written as

$$\left[\sigma^l*(\nu*\tilde{\nu})+(\delta_0-\nu*\tilde{\nu})n_0\right](\phi).$$

Since ϵ was arbitrary, letting $l\to\infty$ proves the theorem. □

Corollary. With probability one, $\hat{\gamma}_{\mu'}=\hat{\gamma}_\mu|\hat{\nu}|^2+n_0(1-|\hat{\nu}|^2)$. If $\hat{\gamma}_\mu$ is a purely discrete measure then, with probability one, the discrete part of $\hat{\gamma}_{\mu'}$ is given by $\hat{\gamma}_\mu|\hat{\nu}|^2$ and the continuous part by $n_0(1-|\hat{\nu}|^2)$.

4. Discussion

The corollary shows that 'switching on' the thermal motion has two effects on the diffraction spectrum. First, the Fourier transform of the original, 'static', autocorrelation is multiplied by $|\hat{\nu}|^2$. This is a function that is 1 at the origin and that tends to zero with yincreasing distance from the origin if ν is non-singular. The second effect is to add a continuous function, $n_0(1-|\hat{\nu}|^2)$, which describes diffuse scattering due to thermal motion.

If $\hat{\gamma}_\mu$ is purely discrete measure then one can regard X as the set of atomic positions of a monatomic crystal (if X is periodic) or of a hypothetical monatomic quasicrystal (if X is not periodic). Then $\hat{\gamma}_\mu|\hat{\nu}|^2$ is the discrete part of $\gamma_{\mu'}$: i.e. the weight of a delta function at q in $\hat{\gamma}_\mu$ is multiplied by a factor $|\hat{\nu}|^2(q)\leqslant 1$. Thus we see that $|\hat{\nu}|^2(q)$ is the Debye–Waller factor. But note that the theorem and the corollary make no assumption on γ_μ at all. They also hold when γ_μ has a continuous part, is absolutely continuous, or even purely singular continuous, as for instance in the model discussed in [14, 16].

The effects of thermal motion on the diffraction spectrum are well understood for crystals (see, e.g., [21, chapter 7]). They have first been studied by Debye [24], who considered a large but finite crystal and assumed that atoms moved independently in identical harmonic potentials. In our terminology, this amounts to taking for ν a Gaussian distribution. To get a time-independent spectrum Debye took the expectation over all configurations with respect to their thermal weights. He took the expection in Fourier space (i.e. the expectation of the scattered intensity) rather then in direct space. The integrals could be evaluated because the potential was harmonic. Often (see, e.g., [21, section 7.1.1]) the calculation of the expectation is simplified by the assumption that the displacements are small, an approximation that is 'quite rough' [21, p 189] in some situations.

What is new here is that the theorem is not restricted to periodic structures (i.e. crystals). But even for crystals our work differs from the standard treatment in its strictly probabilistic formulation and proof that allows us to consider arbitrary distributions ν and that dispenses with the need to take an expectation because of self-averaging in the infinite system. In addition, the displacements are by no means required to be small. For instance, the corollary shows that if $\hat{\gamma}_\mu$ is purely discrete and ν is the uniform distribution on a ball of radius R, then $\hat{\gamma}_{\mu'}$ has a discrete part for all $R > 0$.

It should be mentioned that the proof of the theorem can be generalized to systems with several atomic species (i.e. measures μ in which the delta functions have a weight indicating the atomic species) provided the second hypothesis on X is suitably strenghtened.

Finally, note that the first term in (3.1) is equal to the autocorrelation of $\mu * \nu$. Thus the corollary shows that the Dirac peaks of the system with thermal motion can be obtained from the 'time-averaged' structure $\mu * \nu$. This is often taken for granted in discussions of thermal motion in crystals (see, e.g., [25, section 7.3.4]).

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