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What periodicities can be found in diffraction patterns of quasicrystals?

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The structure of quasicrystals is aperiodic. Their diffraction patterns, however, can be considered periodic. They are composed solely of series of peaks which exhibit a fully periodic arrangement in reciprocal space. Furthermore, the peak intensities in each series define the so-called 'envelope function'. A Fourier transform of the envelope function gives an average unit cell, whose definition is based on the statistical distribution of atomic coordinates in physical space. If such a distribution is lifted to higher-dimensional space, it becomes the so-called atomic surface – the most fundamental feature of higher-dimensional analysis.

1. Introduction

Quasicrystals were introduced to the physics of new materials in 1984 (Shechtman *et al.*, 1984; Levine & Steinhardt, 1984), two years after they were discovered by Dan Shechtman. His achievement was awarded with the Nobel Prize in Chemistry in 2011. One of the most prominent features of quasicrystals is their diffraction pattern. Although the structure of quasicrystals is aperiodic, their diffraction patterns contain sharp peaks, which proves that they have good long-range order. Additionally, the patterns exhibit point symmetries considered forbidden in classical crystallography (*e.g.* fivefold), because of their incompatibility with periodic (translational) long-range order. This is a first-hand proof of the aperiodicity of quasicrystalline structures. Conversely, the reverse reasoning, that is the structure aperiodicity leads to the pattern aperiodicity, is far from being true. In this paper it is demonstrated that the periodicities in the diffraction patterns of aperiodic structures carry important information about their structure. Two model structures will be analysed: a one-dimensional quasicrystal, the Fibonacci chain, and a two-dimensional quasicrystal represented by the Penrose tiling.

The structure of quasicrystals and modulated structures is often described in a higher-dimensional space. This approach allows one to restore periodicity at the expense of increasing the dimensionality of space used for the description. It leads also to derivation of a higher-dimensional reciprocal lattice allowing a full description of the diffraction pattern using multiple indices. The number of indices needed for such a description is equal to the rank of the higher-dimensional space. Higher-dimensional analysis is an excellent mathematical tool, but it turns atoms decorating the structure to stretched multidimensional objects called atomic surfaces. The atomic surface itself is a non-physical object defined in perpendicular space (also called internal or complementary space). Another description is based on statistical analysis of atomic positions in a physical space (Wolny, 1998*a*,*b*). It reduces the structure to the hypothetical unit cell (the so-called average unit cell, AUC). The individual atoms obtained in such a cell do not occupy specific positions but are continuously distributed over a certain range of positions with a specified probability. The relevant probability distributions can in principle be determined from the measured diffraction patterns and on that basis the decoration of structural units used in the modelling, such as decoration of two rhombuses of the Penrose tiling, can be derived. This approach has successfully been applied to structure refinement of a number of decagonal quasicrystals (Kozakowski & Wolny, 2010; Kuczera *et al.*, 2012).

In this paper, we go a step further with respect to the AUC approach. The basic structure solution is carried out in the scattering-vector space (Fourier space); using Fourier transform of the probability distributions in the AUC, one can define the envelopes of the diffraction peaks directly measured for particular scattering vectors. For this purpose, unique properties of the diffraction pattern are used, allowing for a smooth fit of the envelopes. Exact knowledge of the peaks' envelopes enables the crystal structure solution in the following step.

We use the following nomenclature in this paper: direct space is that where the structure is observed, reciprocal space that where the diffraction pattern is observed. Both direct space and reciprocal space in the higher-dimensional approach have two orthogonal sub-spaces: parallel and perpendicular. The parallel sub-space is sometimes called 'physical' or 'real'. We will use the term 'physical' as a synonym to 'parallel'. It is used to describe the sub-space in which the observations are

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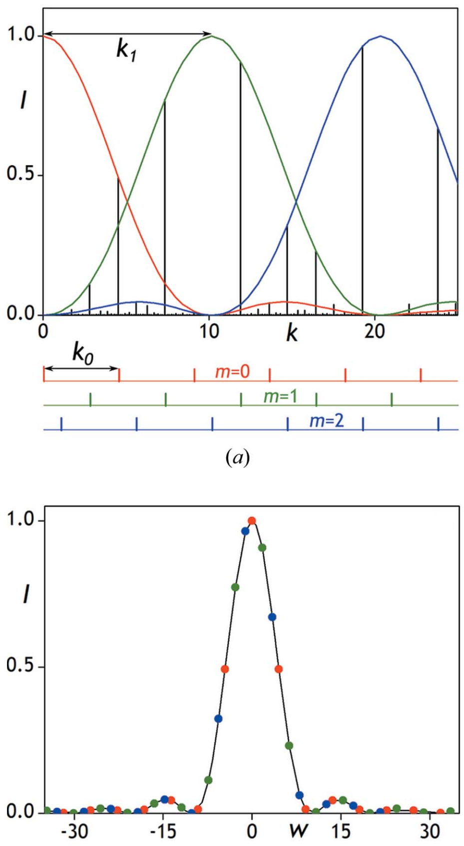
made (of the diffraction pattern or of the real atomic structure) and can refer to reciprocal or direct space.

2. Fibonacci chain

A Fibonacci chain can be generated by using the following algorithm: start the chain with an L segment and, subsequently, recursively replace the segments according to the following inflation rule: L → LS, S → L. The first few steps are: {L}, {LS}, {LSL}, {LSLLS}. The ratio of the number of L segments to the number of S segments converges to $\tau \simeq 1.618$ (golden ratio) as the sequence grows to infinity. If the length of the L (long) segment is τ, the length of the S (short) segment is 1, and the start point of each segment is decorated with an identical pseudo-atom (point), then an entirely aperiodic, infinite set of points is obtained. It is, at the same time, strictly deterministic (Senechal, 1995; Buczek *et al.*, 2005). Therefore, it is often chosen as an example of a one-dimensional quasicrystal. Its diffraction pattern is presented in Fig. 1(*a*). It contains only Bragg peaks, which are arranged in an aperiodic way. However, it is easy to notice that the aperiodic pattern is actually a superposition of an infinite number of periodic series of peaks. Three such series, marked with $m = 0$, 1 and 2, are highlighted in Fig. 1(*a*). The periodicity of each series is the same. In this case the period k_0 is related to the average distance between points in the chain, which is $a_0 \simeq 1.382$ and $k_0 = 2\pi/a_0 \simeq 4.547$. The shift between any two consecutive series is also constant and equal to $k_1 = k_0 5^{1/2} \simeq 10.17$. Based on these two facts, it can be deduced that it is possible to reach the position k of any peak by using only those two periods: k_1 and k_0 (by the formula $k = nk_0 + \Delta k_m$ with n, m being integers, where Δk_m is a constant shift related to k_1 for each series; for the first three series it reads $\Delta k_0 = 0$, $\Delta k_1 = k_1/(2+\tau) \simeq 2.81$, $\Delta k_2 = (3\tau - 4)k_1/5\tau \simeq 1.07$.



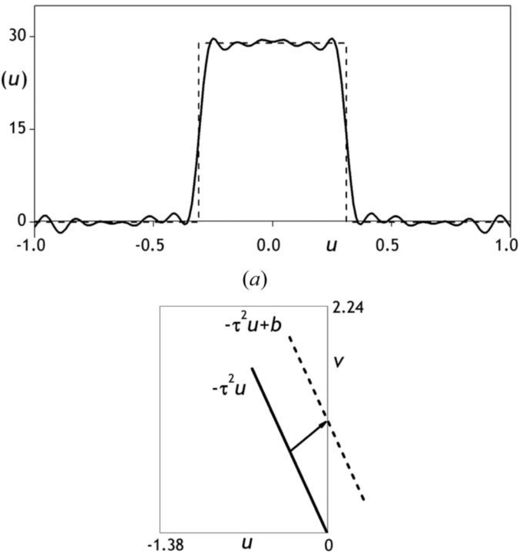
(*a*)

(*b*)

Figure 1
Diffraction pattern of the Fibonacci chain. (*a*) Three infinite periodic series of peaks (the envelopes of intensities and peak positions, with period k_0 and order index m) are highlighted. The pattern consists of an infinite number of such series. The shift between any two series is an integer multiple of k_1. (*b*) The envelope function running over the maxima of all peaks is the result of reducing the peaks' positions by the multiple of k_1: $w = k - mk_1$.

2.1. Envelope function

The pattern undergoes an interesting transformation when we take away the k_1 component from the peaks' coordinates. The result is presented in Fig. 1(*b*). The peak maxima form a curve called the 'envelope'. This curve, from the mathematical point of view, is the square of a Fourier transform of a uniform density function limited to a finite segment – such as the one shown in Fig. 2(*a*). The inverse Fourier transform of the unmodified diffraction pattern results in a Patterson map. It is a density–density correlation function, indicating the distribution of interatomic vectors. Similarly, the rectangular function discussed here also has an interpretation of a density function. In this case, however, it is a distribution of atomic positions modified in a way related to the modification applied to the original diffraction pattern. It is mathematically proved (Wolny, 1998*a*,*b*; Buczek *et al.*, 2005) that such a distribution



(*a*)

(*b*)

Figure 2
(*a*) The uniform distribution of atomic positions in the AUC obtained as a product of the inverse Fourier transform of the envelope function of the structure factor. The dotted line is the theoretical shape of the AUC for a Fibonacci chain. (*b*) The AUC is non-zero only along a line segment. This property is called the TAU2-scaling. If $P(u, v)$ is shifted to the points of symmetry of the reference frame, the parameter b determines the phase value (0 or π) of the satellite peaks.

can be obtained directly from the theoretical atomic positions by reducing the coordinates from their original values x to the reduced ones u, according to the equation $u = x \bmod (a_0)$. The distribution $P(u)$ is called the 'average unit cell' (AUC). A reverse problem can also be resolved. We can determine the AUC directly from the diffraction pattern and its envelope curve, and finally also get the atomic positions of the analysed structure. This is however not straightforward. The envelope obtained from an experimental pattern provides information only on the amplitude of the structure factor, which, in principle, is a complex number. The information on the phase is experimentally not accessible. For a centrosymmetric structure, however, the phase can be equal only to 0 or π. An interesting feature of the envelope function is that the phase changes its value every time the envelope function from Fig. 1(*b*) reaches zero. This simple rule allows us to obtain the distribution of atomic positions (Fig. 2*a*) without the need to fit the phase values iteratively.

The scattering vector k_1 introduced in the previous paragraph measures the distance between two series of periodic peaks. Usually, however, yet another scattering vector is used to index peak positions: $q_0 = k_0/\tau$ (Wolny, 1998*a*,*b*; Buczek *et al.*, 2005). This vector is called the 'modulation vector'. Vectors k_0 and q_0 can be used to point to the position of any peak: $k = n_1k_0 + n_2q_0$ with n_1 and n_2 being integer indices of the n_1-th main peak and the n_2-th satellite peak. The respective AUC, *i.e.* the $P(v)$ distribution, for the q_0 vector is determined in a way identical to k_0. This time the positions are measured with respect to the points of a reference frame with the period of $a_0\tau$. That is, for any point x, its reduced coordinate is calculated as $v = x \bmod (a_0\tau)$. A single distribution $P(u)$ or $P(v)$ allows one to calculate only periodic peaks at positions n_1k_0 or n_2q_0, respectively, by taking their Fourier transforms. To reconstruct the whole pattern, including aperiodic positions, the $P(u, v)$ distribution has to be determined (Wolny, 1998*b*; Kozakowski & Wolny, 2010). To construct this distribution the position of every atom must be expressed in a two-dimensional reference frame (u, v). It turns out that this distribution is non-zero only along a certain line, as shown in Fig. 2(*b*). The black line represents the region of non-zero probability. After a proper shift (dashed line in Fig. 2*b*) the equation of the line is $v = -\tau^2u + b$. The linear coefficient $(-\tau^2)$ is characteristic for all decagonal and icosahedral quasicrystals. It is called the 'TAU2-scaling'. A practical conclusion is that if the TAU2-scaling is observed in a pattern of the studied material, it is certain that the pattern belongs to one of the aforementioned quasicrystalline families and not, for instance, to twins or crystalline approximants. Furthermore, this relation significantly simplifies the derivation of the structure factor for quasicrystals. It enables the derivation to be carried out in the three-dimensional physical space only and not in the abstract five-dimensional or six-dimensional space required in the 'cut-and-project' approach (for higher-dimensional analysis see: de Wolff *et al.*, 1981; de Bruijn, 1981; Kramer & Neri, 1984; Duneau & Katz, 1985; Kalugin *et al.*, 1985; Bak, 1986; Levine & Steinhardt, 1986; Elser, 1986; Jaric, 1986; Hof, 1995, 1997; Cervellino & Steurer, 2002; Takakura *et al.*, 2001). Finally, since the structure factor for a peak is calculated as the mode of the Fourier transform, the TAU2-scaling gives an immediate result for the peak's phase: n_2q_0b – on condition, however, that $P(u)$ is symmetric.

2.2. Two periodicities

The diffraction pattern of the Fibonacci chain exhibits two characteristic periodicities: k_0 and k_1. It is convenient to introduce a two-dimensional space to fully understand the existence of these two periodicities. Periodicity k_1 leads to an infinite set of parallel and equidistant lines. Three representatives of this set are marked with red, olive and blue in Fig. 3. The periodicity k_0 manifests itself as an infinite periodic set of points (open circles along each of the lines in Fig. 3). If the inclination angle of the lines related to periodicity k_1 is properly chosen, the points related to the periodicity k_0 will form a square lattice as in Fig. 3. The diffraction pattern is observed in the physical space, also called the 'parallel space' ($k_\parallel$ in Fig. 3). Peak positions are obtained by projecting the periodic set of points from each line onto the physical space. Colours of the dots indicating the peak positions in the parallel space match the colour of the line from which they were projected. The projection direction is perpendicular to the parallel space. In this direction the so-called perpendicular space is spanned ($k_\perp$ in Fig. 3). The envelope function from Fig. 1(*b*) is placed in the perpendicular space (marked in magenta in Fig. 3). It is rescaled according to the following formula: $k_\perp = w/\tau^3$, where $w = k \bmod (k_1)$, and centred at each of the parallel lines related to the periodicity k_1. The intensity of a given peak is defined by the values of the respective envelope function at $k_\perp = 0$.

Two very characteristic features of the diffraction pattern of quasicrystals can be easily explained with this construction. The diffraction pattern is infinitely dense because the set of

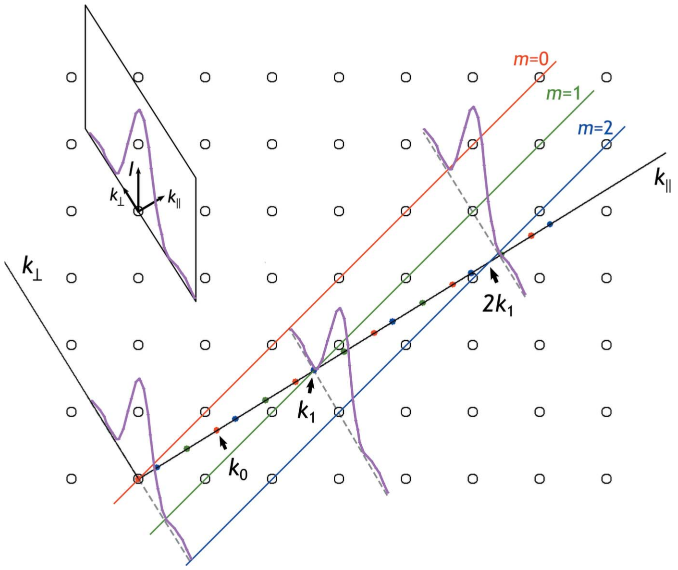


Figure 3
The diffraction pattern of the Fibonacci chain represented as a projection of two-dimensional square reciprocal lattice onto the physical space ($k_\parallel$).

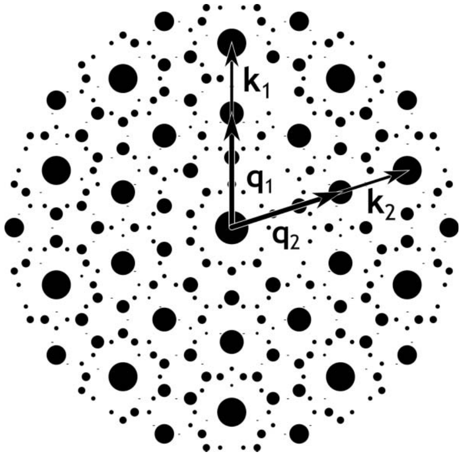


Figure 4
Diffraction pattern for the rhombic Penrose tiling. Arrows indicate basis vectors $\mathbf{k}_1, \mathbf{k}_2$ and $\mathbf{q}_1, \mathbf{q}_2$ used for the construction of the AUC.

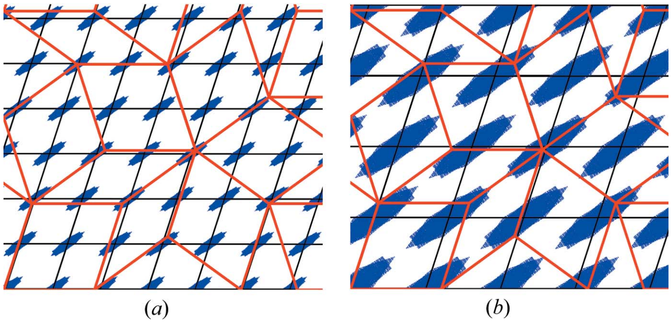
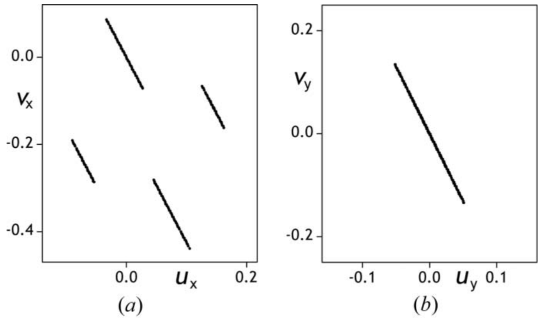

(*a*) (*b*)

Figure 5
The expanded AUC for rhombic Penrose tiling: (*a*) constructed for the basis vectors $\mathbf{k}_1 \simeq (0, 32.77)$, $\mathbf{k}_2 \simeq (31.16, 10.13)$ and (*b*) constructed for basis modulation vectors $\mathbf{q}_1 \simeq (0, 20.25)$, $\mathbf{q}_2 \simeq (19.26, 6.26)$. The set of basis vectors is indicated in Fig. 4. The blue area indicates the AUC shape (overlapped pentagons) and the red grid indicates the rhombic Penrose tiling.

lines related to the periodicity k_1 is infinite and the intensities of the peaks with a higher $k_\perp$ component are, in general, weaker because the envelope function decays asymptotically. After transformation to the direct space, the Fibonacci chain becomes the result of a projection of points from within the so-called projection strip. A square reciprocal-lattice transforms into a square lattice in the direct space and the Fourier transformation of the envelope function of the structure factor in the perpendicular space results in the so-called atomic surface. Such an approach, based on construction of a square lattice, is the foundation of the higher-dimensional approach – the primary tool for analysis of quasicrystalline structures.

The three methods described here, AUC, peak envelopes and higher-dimensional 'cut-and-project', are perfectly equivalent in the case of quasicrystals. There are, however, structures not considered to be quasicrystalline or crystalline (for instance the Thue–Morse chain), which require an infinite number of dimensions to be properly described by the higher-dimensional analysis. In such a case, the higher-dimensional analysis fails and only physical-space-based approaches prove to be useful in describing their structures (Wolny *et al.*, 2000). This remark pertains especially to the singular continuous component of the diffraction pattern. Here, the physical-space approaches allow us to assess the relationship between the peak intensities and the number of atoms involved in the beam scattering.



(*a*) (*b*)

Figure 6
TAU2-scaling of AUCs for the rhombic Penrose tiling shown in Fig. 5. Scaling relation for (*a*) (u_x,v_x) and (*b*) (u_y,v_y) coordinates.

3. Penrose tiling

An example of a two-dimensional quasiperiodic structure is the rhombic Penrose tiling (Penrose, 1974). Similarly to the Fibonacci chain being constructed with two segments – long and short – the rhombic Penrose tiling is constructed with two rhombuses called thick and thin. The atoms are placed at their vertices. A diffraction pattern of such a structure is presented in Fig. 4. To index all peaks one needs to choose two primary scattering vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, and two appropriate modulation vectors $\mathbf{q}_1$ and $\mathbf{q}_2$: $\mathbf{q}_i = \mathbf{k}_i/\tau$ (Kozakowski & Wolny, 2010; Dąbrowska *et al.*, 2005). As in the case of the Fibonacci chain, the position of a peak is an integer, linear combination of those four basis vectors. Consequently, the diffraction pattern is a set of strictly periodic series of diffraction peaks. The expanded AUC for rhombic Penrose tiling, sometimes also called the periodic average structure (Steurer & Haibach, 1999), determined for a pair of vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ is shown in Fig. 5(*a*). Every vertex of rhombic Penrose tiling is uniquely mapped on the expanded AUC. The same construction for vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ is shown in Fig. 5(*b*). A single AUC consists of four overlapping pentagons (two large and two small) which are the equivalents of pentagonal atomic surfaces in perpendicular space. The exact shape of the AUC distribution always depends on the choice of the scattering vectors for which the AUC is constructed.

It is worth emphasizing again that the AUC is periodic despite the aperiodicity of the Penrose tiling. The periodicity of the AUC is a result of the periodicity of diffraction peaks. A Fourier transform of the AUC gives information about one series of peaks. To obtain the full pattern, one needs to find a relationship between the AUCs built for vectors $\mathbf{k}_i$ and $\mathbf{q}_i$ (Fig. 6). It is, of course, the TAU2-scaling relationship as in the case of the Fibonacci chain.

4. Summary

A diffraction pattern can be decomposed into periodic series of peaks. This holds true for classical crystals, quasicrystals and modulated structures (with commensurate or incommensurate modulation). The periodicity observed in the scattering-vector space (reciprocal space) is used to construct a reference frame in the direct space. The atomic positions of a model structure reduced to one period of a reference frame form the average unit cell. If the ratio of periodicities of two AUCs is τ (the ratio of the scattering vectors, for which the AUCs were calculated, is $1/\tau$), then they are related to each other according to the so-called TAU2-scaling. The TAU2-scaling is a linear relationship between the non-zero density regions of the two AUCs with the linear coefficient equal to $(-\tau^2)$. This scaling is representative for all commonly observed quasicrystals and enables us to use it in a derivation of the structure factor for decagonal quasicrystals (if their structure can be described as a decorated rhombic Penrose tiling) and subsequently refine a number of quasicrystalline structures (Kuczera *et al.*, 2012).

The periodicity observed for diffraction peaks is a very general property of the diffraction pattern and is not limited only to quasicrystals. A series of peaks can be used to construct the envelope function, which, mathematically speaking, is a Fourier transform of the AUC. The AUC on the other hand, is a distribution of reduced atomic positions, *i.e.* atomic positions taken modulo the unit cell of the reference lattice. The phases of the peaks can be determined from the properties of the envelope function. Because this approach is general and well defined in a mathematical sense, it can be used in the refinement of different complex structures like proteins, for instance. It should be stressed again that the approach does not require the structure to be periodic, because the periodic series of diffraction peaks are a product of any Fourier transform calculated over a density function. The approach gives meaningful results not only for Bragg peaks but also for the singular continuous component (which scales in a fractal way with the number of scattering atoms), and continuous component (diffuse scattering), of a diffraction pattern. This universality leads to the conviction that by using it in a refinement process of any, not necessarily periodic, structures it will be possible to take advantage of the whole information stored in a diffraction pattern and not only in the Bragg peaks.

Using the method presented in this article, the envelopes of the diffraction peaks may be determined directly from the diffraction pattern without having to re-calculate the Fourier transforms iteratively, which is the case for the standard procedures during structure determination (*e.g.* Palatinus & Chapuis, 2007; Palatinus, 2013). The envelopes of diffraction peaks are modelled in the physical sub-space of the reciprocal space, the same in which the diffraction patterns are observed. Experimentally determined envelopes with the phase analysis and scaling relations lead to the probability distributions in the physical sub-space of the direct space obtained by a Fourier transform. Knowing these distributions allows us to determine the positions of atoms decorating the structural units of any tiling, periodic or aperiodic. All calculations are carried out in the experiment-related physical space, both direct and reciprocal, and do not require higher-dimensional analysis.

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