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Statistical Inference and Crystallite Size Distributions*

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Abstract

An information theory approach is devised in order to obtain crystallite size distributions from X-ray line broadening. The method is shown to be superior to those based on Fourier expansions, as illustrated by numerical examples and a realistic situation. The powder model of Warren and Averbach is considered, in which the sample is thought of as a 'column-like' structure of unit cells perpendicular to the diffraction plane. Errors in excess of 100% arise as a result of truncating the diffraction peak. It is shown that, with the present approach, the corresponding figure is reduced to 5%, which confirms the power of information theory, and makes this method especially convenient in those cases in which there are large overlaps between the tails of two diffraction peaks.

1. Introduction

Information theory (IT), after the pioneer work of Shannon (1948), has been extensively applied to a wide range of problems (see Brillouin, 1962; Alhassid & Levine, 1977, 1978, 1979; Levine, Steadman, Karp & Alhassid, 1978; Grandy, 1980; and references therein; Otero, Proto & Plastino, 1981). Statistical mechanics has received fruitful contributions from this standpoint (*e.g.* Jaynes, 1957, 1963, 1979; Katz, 1967). Some quantum problems have also been tackled within its framework (see, for instance, Otero, Plastino, Proto & Zannoli, 1982, 1984). Applications to crystallography should be mentioned as well (see Diamond, 1963; Tsoucaris, 1970; de Rango, Tsoucaris & Zelwer, 1974; Hosoya & Yokonami, 1967; Wilkins, Varghese & Lehmann, 1983; Piro, 1983; Bricogne, 1984).

It is the purpose of the present contribution to investigate to what extent IT concepts can be employed in order to determine, starting from diffraction experiments, crystallite sizes (CS). Recourse to Bienenstock's relationship (see Bienenstock, 1961, 1963), using the Fourier coefficients of the diffraction peaks (Bertaut, 1949; Warren & Averbach, 1950), is at present the main method for determining the CS distribution through powder diffraction. We shall attempt the formulation of an alternative method utilizing IT ideas in conjunction with the powder model of Warren & Averbach (1950).

In this model, the sample is thought of as a 'column-like' structure of unit cells perpendicular to the diffracting planes. Each column makes an independent contribution to the powder diffracting power. The column length is given by the number of cells, N, that characterizes it. The length distribution, $\gamma(N)$, is, however, unknown (in principle).

The paper is organized as follows: A brief overview of basic IT concepts is given in § 2.1, while their application for the present purposes is developed in § 2.2. Our formalism is illustrated in § 3 by reference to the simulation of two different experimental situations. Some results corresponding to an actual experimental situation are outlined in § 4. Some conclusions are drawn in § 5 and a rigorous presentation of the theoretical foundations of our approach can be found in the Appendix.

2. Formalism

2.1. *Some basic IT concepts*

We will present here a brief review of those IT aspects relevant for our present purposes. For a thorough discussion the reader is referred to Jaynes (1963, 1979) and Katz (1967). Within the IT framework, the density matrix $\tilde{\rho}$ is constructed according to a well defined prescription, starting from

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the knowledge of the expectation values of M operators $\hat{G}_i$:

$$\langle \hat{G}_i \rangle = g_i, \quad i = 1, 2, \ldots, M. \tag{2.1}$$

The statistical operator (or density matrix) $\hat{\rho}$ is then given by

$$\hat{\rho} = \exp\left(\lambda_0 - \sum_{i=1}^{M} \lambda_i \hat{G}_i\right), \tag{2.2}$$

in terms of $M+1$ lagrange multipliers λ_i, which are determined so as to fulfill the set of equalities (2.1), *i.e.*

$$\langle \hat{G}_i \rangle = \mathrm{tr}\,(\hat{\rho}\hat{G}_i) = g_i, \quad i = 1, 2, \ldots, M, \tag{2.3}$$

and the normalization condition

$$\mathrm{tr}\,\hat{\rho} = 1. \tag{2.4}$$

The operator constructed in this fashion maximizes the entropy

$$S(\hat{\rho}) = -k\,\mathrm{tr}\,\hat{\rho}\ln\hat{\rho}, \tag{2.5}$$

subject to the constraints (2.3) and (2.4) (k is Boltzmann's constant). The latter allows one to express the Lagrange multiplier λ_0 in terms of the M Lagrange multipliers $\lambda_1, \ldots, \lambda_M$:

$$\lambda_0(\lambda_1, \ldots, \lambda_M) = -\ln \mathrm{tr} \exp\left(-\sum_{i=1}^{M} \lambda_i \hat{G}_i\right), \tag{2.6}$$

while, from (2.3), we find

$$\partial\lambda_0/\partial\lambda_i = g_i, \quad i = 1, \ldots, M, \tag{2.7}$$

which provides us with a set of differential equations for the λ_i in terms of the 'input' information contained in the quantities g_i. Let us now consider an operator $\hat{O}_k$ that does not belong to the set $\{G_i\}$ discussed above. IT provides us with a statistical inference method that predicts its expectation value $\langle \hat{O}_k \rangle$ to be given by

$$\langle \hat{O}_k \rangle = \mathrm{tr}\,\hat{\rho}\hat{O}_k = \mathrm{tr}\left[\exp\left(\lambda_0 - \sum_{i=1}^{M} \lambda_i \hat{G}_i \hat{O}_k\right)\right]. \tag{2.8}$$

2.2. *Present approach*

In the classic paper of Warren & Averbach (1950) a method was developed for the determination of crystallite sizes in a powder sample by means of Fourier analysis of X-ray diffraction peaks. The basic idea of Warren & Averbach is that of depicting the sample as a column-like structure of unit cells perpendicular to the diffracting plane, in which each column makes an independent contribution to the powder diffracting pattern. In many-body language, this is a single-particle model, in which each column makes its 'single'-contribution to the measured intensity $I(\psi)$ corresponding to a given incident angle θ, where, for the case of 'oriented' samples,

$$\psi = \lambda^{-1} 2\pi d \sin\theta \tag{2.9}$$

(d is the interplanar spacing and λ the corresponding wavelength). Out of a column of N cells an interference function $G(N, \psi)$ arises (see James, 1954) of the form

$$G(N, \psi) = \sin^2(N\psi)/\sin^2\psi, \tag{2.10}$$

and the basic fact to be taken into account is that the intensity $I(\psi)$ observed at the angle ψ is proportional to the mean value of G at this angle. Correspondingly, $I(\psi)$ is to be written in the following fashion:

$$I(\psi) = K \sum_{N=1}^{\infty} \gamma(N) G(N, \psi), \tag{2.11}$$

K being a slowly varying function of angle, which usually can be considered a constant over the range of interest.

Our '*leit-motiv*' here is that of proposing a statistical inference method based upon IT in order to *predict* the distribution function $\gamma(N)$ on the basis of the measurement of the $I(\psi_i)$ for a small number of angles ψ_i. This inference method can be formulated in field-theoretical language, employing second quantization and other standard tools of the many-body theorist. This allows for great generality, with immediate applications to related problems. As not every reader has the time or the necessity to be bothered with abstract considerations not obviously relevant to the problem at hand, we shall consign this general treatment to the Appendix, and present here a more direct approach.

We shall try to approximate the unknown length distribution $\gamma(N)$ by means of a (classical) statistical function $\rho(N)$ (see Katz, 1967) constructed, *via* IT concepts, on the basis of the measurement of $I(\psi_i)$ for a judiciously chosen set of angles ψ_i. Consequently, we rewrite (2.11), for each angle ψ_i, in the following fashion

$$I(\psi_i) = K \sum_{N=1}^{\infty} \rho(N) G(N, \psi_i), \tag{2.12}$$

so that, by discretization of the intensity variation (this entails the selection of a finite set of M angles ψ_i) we generate M equations of the type (2.12). These are now to be interpreted, according to IT, as providing the 'input' [*cf.* (2.1)] necessary to build up the statistical function $\rho(N)$ in the form (see Katz, 1967)

$$\rho(N) = \exp(\lambda_0) \exp\left[-\sum_{j=1}^{M} \lambda_j G(N, \psi_j)\right], \tag{2.13}$$

$$-\lambda_0 = \ln\left\{\sum_{N=1}^{\infty} \exp\left[-\sum_{j=1}^{M} \lambda_j G(N, \psi_j)\right]\right\}. \tag{2.14}$$

The set of equations (2.7) holds both in the classical [statistical function $\rho(N)$] and in the quantum (density operator, density matrix ρ) cases. The set (2.7) is then immediately available and allows one to evaluate the λ_i, which in turn completely determines the statistical function ρ maximizing the statistical entropy. Summing up, on the basis of M measurements $I(\psi_i)$ we are able to construct the statistical function $\rho(N)$ and would, consequently, be in a position to predict the outcome of a measurement performed at angle ψ_{M+1}, say, not included in our initial data set

$$I(\psi_{M+1}) = K \sum_{N=1}^{\infty} \rho(N) G(N, \psi_{M+1})$$
$$= \exp(\lambda_0) K \sum_{N=1}^{\infty} \exp\left[-\sum_{j=1}^{M} \lambda_j G(N, \psi_j)\right] \times G(N, \psi_{M+1}). \quad (2.15)$$

If this prediction turns out to be right, that is, if it is experimentally verified *a posteriori*, then we may conclude that we have been able to obtain, by means of this statistical inference approach, a good representation of $\gamma(N)$. If predictions of the type (2.15) turn out, on the other hand, to be consistently wrong, this can only mean that some relevant information has been left out. The very experiments that prove our predictions (2.15) wrong supply new information, and with this information we may try again [for a 'better' $\rho(N)$ and so on]. If for a given selection of the initial input $I(\psi_i)$ we finally achieve a good representation of $\gamma(N)$, we will be in a position to determine the mean number of cells per column:

$$\langle N \rangle = \exp(\lambda_0) \sum_{N=1}^{\infty} \exp\left[-\sum_{j=1}^{M} \lambda_j G(N, \psi_j)\right] N$$
$$= \sum_{N=1}^{\infty} \rho(N) N. \quad (2.16)$$

It will be shown in § 3 that the proposed approach is of practical value, and that a small (judiciously chosen) number M of angles ψ_i allows for a good description of $\gamma(N)$.

3. Numerical examples

We shall illustrate the approach introduced in § 2.2 by numerical simulation of two different experimental situations.

3.1. *A Gaussian distribution*

Let us consider a diffraction peak characterized by a Gaussian distribution $\gamma(N)$:

$$\gamma^G(N) = \exp[-\sigma(N - N_0)^2] / \sum_N \exp[-\sigma(N - N_0)^2], \quad (3.1)$$

Table 1. *'Input': angles ψ_i, Lagrange multipliers λ_i, constant K and mean cell number $\langle N \rangle$ for the Gaussian distribution case of* § 3.1

M	ψ_i(rad)	λ_i	Approximate values	'Exact' values
1	$\psi_1 = \pi$	$\lambda_1 = 0{\cdot}033$	$K = 1079$	
			$\langle N \rangle = 3{\cdot}42$	
	$\psi_2 = 4{\cdot}04$			$K = 1151$
				$\langle N \rangle = 3{\cdot}55$
2	$\psi_1 = \pi$	$\lambda_1 = 0{\cdot}039$	$K = 1151$	
	$\psi_2 = 3{\cdot}48$	$\lambda_2 = -0{\cdot}109$	$\langle N \rangle = 3{\cdot}53$	
	$\psi_3 = 4{\cdot}04$			

The last angle in the second column is the one employed in order to adjust K. M denotes the number of Lagrange multipliers employed in building up $\hat{\rho}$.

where we take $N_0 = 3$, $\sigma = 0{\cdot}1$ and $K = 1151$. The 'true' mean number of cells per column arising in this case is $\langle N \rangle = 3{\cdot}55$. The 'diffraction peak' that (3.1) generates *via* (2.11) is depicted in Fig. 1(*a*).

In order to test our procedure we start by considering a statistical operator $\hat{\rho}$ of type (2.2) with $M = 1$ (the simplest possible case). The whole problem reduces itself here to that of determining a single Lagrange multiplier λ_1.

It is to be pointed out that the constant K in (2.11) is an arbitrary one, as, in measuring a diffraction peak, the corresponding intensity curve will always be multiplied by a constant factor determined by the experimental arrangement. As a bonus, our approach allows for the determination of K, as indicated below.

We determine λ_1 by numerically solving, for a selected angle ψ_1, the equation

$$I(\psi_1) = \exp(\lambda_0) K \sum_{N=1}^{\infty} \exp[-\lambda_1 G(N, \psi_1)] G(N, \psi_1), \quad (3.2)$$

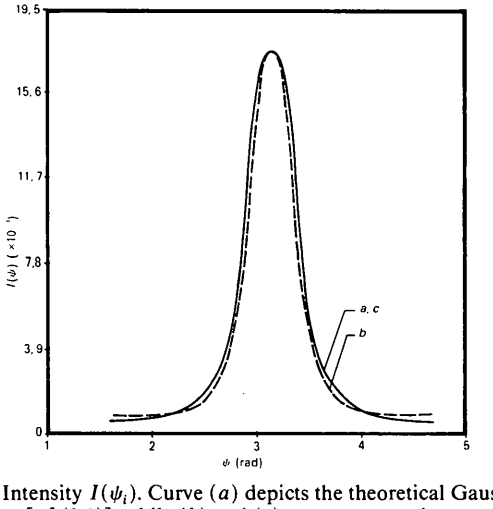

Fig. 1. Intensity $I(\psi_i)$. Curve (*a*) depicts the theoretical Gaussian pattern [*cf.* (3.1)], while (*b*) and (*c*) are our approximate results obtained by employing, respectively, one and two multipliers in building up the statistical operator $\hat{\rho}$.

where $I(\psi_1)$ is, of course, taken from our 'theoretical' experiment. It is apparent that we need another equation in order to fix K. By a judicious selection of another angle ψ_2 we achieve this goal, with the net result that we have to deal with a set of two coupled equations of the type (3.2), one for ψ_1 and the other for ψ_2. If we take here $\psi_1 = \pi$ and $\psi_2 = 4{\cdot}04$ rad (in order to try to reproduce both the peak and the tail of the distribution), we obtain the diffraction pattern given by curve (b) of Fig. 1, which is not too bad an approximation to the 'true' one. The values of $\langle N \rangle$ and K thus obtained are compared to the 'exact' ones in Table 1, and are also seen to resemble them closely.

If we work now with two Lagrange multipliers in order to improve our approach, we have to select three angles. The corresponding results are given in Fig. 1 and Table 1. In this case the approximate pattern is almost indistinguishable from the 'true' one. This can be confirmed by adding a third Lagrange multiplier: no noticeable improvements are obtained. The distributions $\gamma(N)$: exact, approximate (one multiplier) and approximate (two multipliers) are compared in Fig. 2. The improvement obtained by adding a second Lagrange multiplier is clearly seen.

3.2. *A normal-logarithmic distribution*

We consider now the case of a diffraction peak generated by

$$\gamma^L(N) = \exp\{-[(\ln N - \ln N_0)/\ln \sigma]^2/2\} \times \left[\sum_N \exp\{-[(\ln N - \ln N_0)/\ln \sigma]^2/2\}\right]^{-1}, \tag{3.3}$$

with $N_0 = 3$, $\sigma = 1{\cdot}3$, $K = 1542$ and $\langle N \rangle = 3{\cdot}33$. Fig. 3($a$) depicts the corresponding peak and Fig. 4(a) displays $\gamma^L(N)$. The curves that result in trying to represent the 'exact' (or 'true') results with our approach are labelled by the letters b, c, d and correspond to cases for which one employs, respectively, one, two and three Lagrange multipliers. The relevant figures are given in Table 2. It is seen that three multipliers are needed in order to obtain a satisfactory description.

Table 2. *'Input': angles ψ_i, Lagrange multipliers λ_i, constant K and mean cell number $\langle N \rangle$ for the normal-logarithm distribution case of* § 3.2

M	ψ_i(rad)	λ_i	Approximate values	'Exact' values
1	$\psi_1 = \pi$	$\lambda_1 = 0{\cdot}031$	$K = 1015$	
	$\psi_2 = 4{\cdot}04$		$\langle N \rangle = 3{\cdot}55$	
2	$\psi_1 = \pi$	$\lambda_1 = 0{\cdot}163$	$K = 1539$	$K = 1542$
	$\psi_2 = 3{\cdot}50$	$\lambda_2 = -0{\cdot}658$	$\langle N \rangle = 3{\cdot}31$	
	$\psi_3 = 4{\cdot}04$			$\langle N \rangle = 3{\cdot}33$
3	$\psi_1 = \pi$	$\lambda_1 = 0{\cdot}144$		
	$\psi_2 = 3{\cdot}50$	$\lambda_2 = -0{\cdot}641$	$K = 1541$	
	$\psi_3 = 4{\cdot}27$	$\lambda_3 = 0{\cdot}642$	$\langle N \rangle = 3{\cdot}32$	
	$\psi_4 = 4{\cdot}04$			

The last angle in the second column is the one employed in order to adjust K. M denotes the number of Lagrange multipliers employed in building up $\hat{\rho}$.

3.3. *Effects of a constant background*

Experimental diffraction patterns are affected by background effects that, in some circumstances, can be regarded as constant. In order to simulate such a constant background we added a constant B_T to the intensity peak generated by the Gaussian distribution of Fig. 1. Taking as data four points of the correspond-

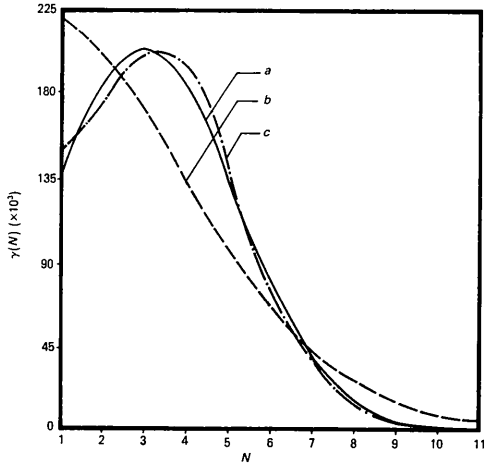

Fig. 2. Distributions $\gamma(N)$. Curve (a) is the one that generates the diffraction peak of Fig. 1(a) ('exact'), while (b) and (c) correspond to our approximate results obtained from a statistical operator $\hat{\rho}$ built up with one and two Lagrange multipliers, respectively.

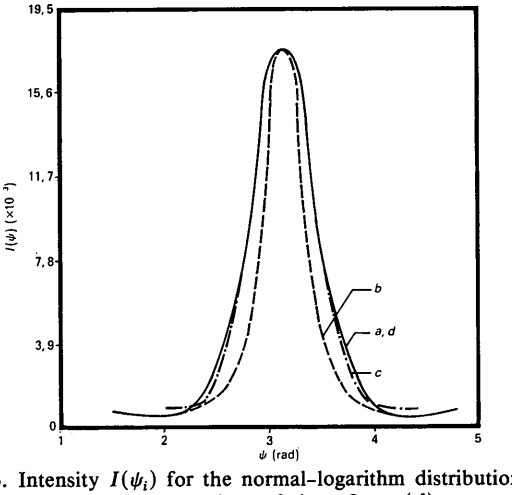

Fig. 3. Intensity $I(\psi_i)$ for the normal-logarithm distribution of § 3.2. Details are similar to those of Fig. 1. Curve (d) corresponds to an approximate result obtained with three Lagrange multipliers.

ing curve, the following set of equations was generated

$$I(\psi_i) = B_T + \exp(\lambda_0) \sum_{N=1}^{\infty} \exp[-\lambda_1 G(N, \psi_1) - \lambda_2 G(N, \psi_2)] G(N, \psi_i), \quad i = 1, 2, 3, 4, \quad (3.4)$$

with $\psi_1 = \pi$, $\psi_2 = 3{\cdot}48$ rad, $\psi_3 = 4{\cdot}26$ rad and $\psi_4 = 4{\cdot}04$ rad. A satisfactory agreement, similar to that of Fig. 2 (case *c*), was obtained. For $B_T = 200$ our method yielded $B_T^{app} = 197$.

4. A realistic situation

In § 3 we have dealt with 'ideal' numerically simulated experiments. This is the time-honoured procedure employed, in all branches of physics, to try new theoretical ideas. The reason for this approach is quite simple: one needs an 'exact' solution with which to compare. Simple-minded comparison of theoretical approaches with raw data can lead to serious errors of interpretation.

However, after such a test has been passed, comparison with experiment is the next step. Here we shall present a few results obtained by applying our method to a concrete experimental situation.

Fig. 5 displays the size distribution that we obtain by employing just three Lagrange multipliers, in the case of a montmorillonite sample for which the corresponding clay treatment is of special interest in view of its very small crystal size. The details of the corresponding experimental set-up as well as the treatment and results for a variety of samples will be published elsewhere.

Concluding remarks

The calculation of crystallite size distribution from X-ray line broadening by recourse to Fourier coefficients (see Bienenstock, 1961, 1963) is affected by errors that arise in truncating the diffraction peak. The careful study of Young, Gerdes & Wilson (1967) shows that a truncation of the order of 20% leads to size errors larger than 100%. With the present approach, the corresponding figure is of the order of a 5%, which obviously constitutes a sizeable improvement, and would make our method especially convenient in those cases in which there are larger overlaps between the tails of two diffraction peaks.

A salient aspect to be mentioned is that just a few Lagrange multipliers are needed in order to obtain a satisfactory description, which greatly simplifies the (non-linear) numerical problem one has to face. Even with just a single Lagrange multiplier the error in $\langle N \rangle$ is smaller than 7%. Our approach makes it quite easy to deal with a constant background. The so-called 'hook effect', which plagues the Fourier method whenever $\gamma(1)$ is not a negligible quantity, is totally absent here.

Summing-up, we believe that the statistical inference approach presented in this work may be regarded as a convenient tool for the calculation of crystallite size distributions.

APPENDIX

The method introduced in this paper can be rigorously founded by recourse to some elementary notions of field theory and linear algebra, which allow for immediate generalization to similar situations. We deal here with this type of approach, which, additionally, clearly exhibits the fact that there exists a

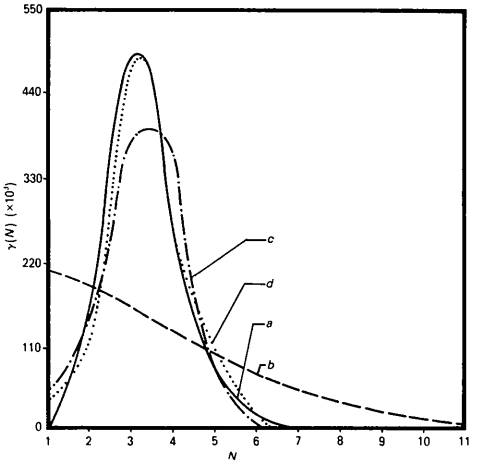

Fig. 4. Distributions $\gamma(N)$ for the normal-logarithm case. Details are similar to those of Fig. 2. Curve (*d*) corresponds to a case in which three Lagrange multipliers are employed.

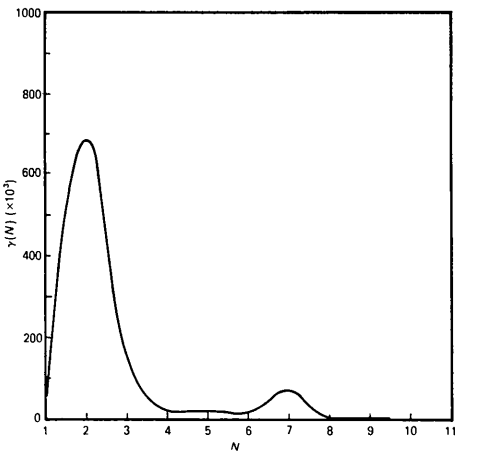

Fig. 5. Distribution $\gamma(N)$ for a montmorillonite sample corresponding to a reflection 001.

consistent *theory* behind (2.11)-(2.16) and not a mere numerical algorithm that just happens to work.

We start by introducing the diagonal matrix

$$[N]=\begin{pmatrix} 1 & 0 & 0 & \cdot & \cdot & \cdot & 0 & \cdot & \cdot & \cdot \\ 0 & 2 & 0 & \cdot & \cdot & \cdot & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & 3 & \cdot & \cdot & \cdot & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & n & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \quad (A.1)$$

such that its general element is $[N]_{ij}=i\delta_{ij}$. We call $|\nu\rangle$ the eigenvectors of $[N]$ and linear algebra tells us that there exists a linear operator $\hat{N}$ corresponding to $[N]$, whose eigenvectors are also the kets $|\nu\rangle$, such that

$$\hat{N}|\nu\rangle = n|\nu\rangle \quad (A.2)$$

$$\langle\nu|\nu'\rangle = \delta_{\nu,\nu'}. \quad (A.3)$$

Now field theory enters. If we associate with the integer number n *the number of cells per column*, $\hat{N}$ becomes a *number operator* and the states $|\nu\rangle$ span a (Fock) Hilbert space in which is represented the physics of our problem. Indeed, if we denote by ψ_i a variable that is unambiguously defined by subindex i, we are entitled to *define* new operators $\hat{G}_i$ by means of analytical applications over N. We choose them to be of the form

$$\hat{G}_i = \sin^2(\hat{N}\psi_i)/\sin^2\psi_i. \quad (A.4)$$

and it is immediately apparent that the basis $|\nu\rangle$ diagonalizes the $\hat{G}_i$. This can be seen by series expanding the numerator of (A.4)

$$\hat{G}_i = (1/2\sin^2\psi_i)\sum_{m=1}^{\infty}(-)^m(2\hat{N}\psi_i)^{2m}/(2m)!, \quad (A.5)$$

so that, obviously,

$$\hat{G}_i|\nu\rangle = (1/2\sin^2\psi_i)\sum_{m=1}^{\infty}(-)^m[(2n\psi_i)^{2m}/(2m)!]|\nu\rangle$$
$$= (\sin^2 n\psi_i/\sin^2\psi_i)|\nu\rangle. \quad (A.6)$$

Thus we find ourselves dealing with a set $\{\hat{G}_1,\ldots,\hat{G}_i,\ldots,\hat{G}_M,\hat{N}\}$ of mutually commuting operators, which are simultaneously diagonalized by the basis $|\nu\rangle$. The preceding considerations allow us now to cast the intensity corresponding to the angle ψ_i into quantum-statistical language [*cf.* (2.11)]:

$$I(\psi_i) = K\,\mathrm{tr}(\hat{\rho}\hat{G}_i) \quad (A.7)$$

and write down the statistical operator $\hat{\rho}$, according to the IT formalism, as the one that maximizes the statistical entropy subject to M constraints of the type (A.7)

$$\hat{\rho} = \exp(\lambda_0)\exp\left(-\sum_{j=1}^{M}\lambda_j\hat{G}_j\right), \quad (A.8)$$

$$\lambda_0 = -\ln\mathrm{tr}\exp\left(-\sum_{j=1}^{M}\lambda_j\hat{G}_j\right). \quad (A.9)$$

Evaluating traces by recourse to sums over the basis $|\nu\rangle$, we immediately obtain (2.12), (2.13) and (2.14). Moreover, (2.15) and (2.16) correspond to the *Predictions* that $\hat{\rho}$ enables one to make, that is

$$I(\psi_{M+1}) = K\,\mathrm{tr}(\hat{\rho}\hat{G}_{M+1}) \quad (A.10)$$

and

$$\langle\hat{N}\rangle = \mathrm{tr}(\hat{\rho}\hat{N}). \quad (A.11)$$

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