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The Use of Non-Local Constraints in Maximum-Entropy Electron Density Reconstruction

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Abstract

Different expressions of the maximum-entropy estimates of the electron density function, corresponding to different prior information are obtained. They show that no general-purpose configurational entropy of density maps exists. Some universal properties of the modellings are discussed. In particular, the meaning of super-resolution is clarified. The information of lower and upper bounds of the electron density is not in general strong enough to produce atomic maps. Atomicity is then introduced as non-local constraints and applied to the problem of phase extension using experimental data and low-resolution model phases. In all cases, the knowledge of phases up to 3·5-3 Å and observed moduli up to 1·5-1 Å allows an estimate of the electron density of roughly the same quality as the 1 Å map obtained from a Fourier summation to be produced.

Introduction

The foundations of the theory here developed were given in a previous paper: the criterion of maximal entropy was used to obtain an estimate of the electron density function on the basis of partial information. First a maximum-entropy probability distribution of maps was obtained, its functional form being a strict consequence of the type of constraints used. Next the electron density function was estimated using this maximum-entropy probability distribution (Navaza, 1985).

For the particular type of constraint considered the formulation corresponds exactly to a maximum-entropy algorithm using new forms of the configurational entropy of maps and gives rise to a modelling of the maximum-entropy estimate of the sought map.

In this paper a slightly different presentation is offered aiming to show that no underlying probability distribution of maps is in fact needed in order to apply the recipes of information theory, even if we can always think in terms of frequencies in an idealized experimental situation. However, the probabilistic interpretation offers a conceptually simpler frame in which the problem of object reconstruction can be discussed.

Different developments of maximum entropy have been proposed and the references can be found in the previous paper. More recent developments are those of Bricogne (1984), Livesey & Skilling (1985) and Semenovskaya, Khachaturyan & Khachaturyan (1985). It is not the aim of this paper to discuss the different formulations.

Different modellings corresponding to different prior information are obtained and applied to experimental data. The results clearly showed that in the *ab initio* problem most maximum-entropy algorithms give uninterpretable maps. Moreover it was also found that the model phases (the 'true' phases) are not even placed in a concave region in the space of phases.

The problem of phase extension is also considered. Good results are obtained when information on atomicity is introduced in the form of non-local constraints. From the experimentally observed moduli corresponding to 1 Å resolution and the model phases up to 3·5-3 Å, all the atoms were recovered for structures with different numbers of atoms in the unit cell.

Finally, a critical discussion of super-resolution is presented. It is shown that, in general, little or no extra resolution of peaks is to be expected when most of the maximum-entropy algorithms are used.

Information and feasible maps

Crystallographers are faced with the problem of reconstructing a certain function ρ, taking values at

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the different points r of the unit cell Ω, starting from a limited number of its Fourier coefficients F^{ob}.

ρ will be a dimensionless function representing for example the probability of the presence of electrons in the crystal (measured in arbitrary units) or the inverse Fourier transform of the scattering length for neutrons (also in arbitrary units) when scattered by the nuclei in the crystal.

Any diffraction experiment gives the moduli of a subset $\mathscr{L}$ of the whole set of Fourier coefficients of ρ:

$$F^{\text{ob}}(L)=1/V\int_{\Omega}\rho(r)\exp(2\pi iLr)\,\mathrm{d}^3r,\ L\in\mathscr{L}, \tag{1}$$

V being the volume of the unit cell Ω. In favourable cases the experiments can give information about the phases of some of the observed Fourier coefficients (*e.g.* isomorphous replacement methods).

The bare experimental information is then

$$\begin{cases} F^{\text{ob}}(H),\ H\in\mathscr{H} \\ |F^{\text{ob}}(K)|,\ K\in\mathscr{K} \\ \mathscr{H}\cup\mathscr{K}=\mathscr{L} \\ \text{periodicity of } \rho \\ \text{symmetry group of } \rho \text{ (the symmetry group of } \rho \\ \quad \text{is the group of symmetry operations which} \\ \quad \text{leave } \rho \text{ invariant).} \end{cases}$$

With this information the crystallographer usually performs an inverse Fourier transform

$$\tau(r)=\sum_{H\in\mathscr{H}}F^{\text{ob}}(H)\exp(-2\pi iHr), \tag{2}$$

which can be considered as an estimate of ρ, and tries to interpret it. This interpretation is done using information that comes from other fields, such as physics and chemistry.

This prior or non-experimental information typically consists of

$$\begin{cases} \text{bounds of } \rho\text{: } \rho_{\text{Min}}<\rho(r)<\rho_{\text{Max}},\ \text{for } r \text{ in } \Omega \\ \text{atomicity of } \rho \\ \text{stereochemistry.} \end{cases}$$

In the X-ray diffraction problem the prior lower bound is zero and the upper bound is given by quantum-mechanical atomic calculations, so that ρ is a positive function. In the case of neutron diffraction ρ can be positive as well as negative.

Atomicity means that ρ should present itself as the sum of almost non-overlapping peaks (after corrections for temperature effects), and stereochemistry imposes definite prescriptions for the distances and angles between these atomic peaks.

This prior informaton is by far the strongest one for the problem of reconstruction under consideration. For example, in the case of macromolecules, experimental data seldom extend much beyond 2·5 Å resolution. This means that the estimation cannot resolve features separated by less than about 2 Å, so that atoms cannot be resolved. It is only the non-experimental information that allows the crystallographer to build a model that makes physical sense. The estimation τ of ρ serves as a guide in the construction of such a model.

It is natural to look for a better estimation of ρ using experimental as well as non-experimental information. The degree of difficulty for some given information to be taken into account depends on the information itself and to a certain extent on the formalism employed. In this sense bounds of ρ will be 'easy' information whereas stereochemistry will be 'difficult' for us (except at the final stages of the reconstruction procedure).

Our procedure will consist in selecting some information, *assuming that this is all that is available.* Any map, say m, consistent with this information will be called a *feasible map.* There will be a lot of feasible maps so that we will not be able to consider or display all of them, but we will have no argument to prefer one more than any other.

We will then have to study the relevant features of the set $\mathscr{F}$ of all feasible maps in order to see whether the selected information can efficiently help us in the reconstruction of ρ. This will be done by using statistical procedures of analysis of data, computing average values of different functionals of the feasible maps. The averages will be computed by assigning the same weight to all feasible maps as, in keeping with the above assumption, it is the only unbiased assignment we can make. Average values with small associated mean-square fluctuations will be taken as good 'representatives' of $\mathscr{F}$.

Maximum-entropy estimates

The procedure just outlined can be formulated on the basis of information theory: the different averages will be calculated by assigning a probability value to each feasible map. Among all the admissible probability distributions we will choose the one that is the least committal with respect to missing information. To each probability law $P(m)$ we assign, *in a unique way,* a value that measures the lack of information associated with the law (Shannon & Weaver, 1949; Jaynes, 1968). This value is the entropy of $P(m)$ given by

$$H(P)=-1/\mu\int P(m)\ln[P(m)]\mathscr{D}_m, \tag{3}$$

μ being a parameter proportional to the number of degrees of freedom of the map, to be fixed at the end of the calculations. Here $\mathscr{D}_m$ is the element of measure in the space of maps, and $P(m)$ is the probability per unit measure. Our choice consists in selecting the probability law that makes H take its maximum value.

Expectation values computed with this law will be considered as estimates. These maximum-entropy estimates will be good 'representatives' of the whole set $\mathscr{F}$ of feasible maps if the mean-square fluctuations computed with the maximum-entropy probability law are small. In particular, the expectation value of the feasible maps will be the maximum-entropy estimate of ρ. Whether or not these estimates agree with the extra information *explicitly considered as not available*, they still represent the best estimates we could have made on the basis of the selected information. This form of statistical inference is called the maximum-entropy principle, MEP (Jaynes, 1957).

In the case under study this *criterion of maximal entropy* simply tells us that the maximum-entropy probability law is a uniform law. Conceptually the MEP is thus equivalent to the procedure previously outlined. Nevertheless it drastically simplifies the analysis if, as in most applications, information can be phrased in terms of average values.

We have so far assumed that the available information was strictly satisfied by each of the feasible maps. This led us to a uniform maximum-entropy probability distribution of maps. In view of the mathematical treatment we will also consider maps that will be consistent with only a subset of all the available information, the rest of it being satisfied 'on the average'. They will be called *admissible maps* and denoted by m as before. Their probability distribution determined by invoking the MEP will no longer be uniform.

Strict fitting of the information by each map corresponds, in statistical physics, to a microcanonical description of the set $\mathscr{F}$. It is well known that this description is not the most convenient one on mathematical grounds. Satisfaction of the information 'on the average' corresponds to a canonical description of the set $\mathscr{A}$ of admissible maps (obviously we have $\mathscr{F} < \mathscr{A}$). A number of pertinent results obtained in statistical physics (see, for example, Kubo, Ichimura, Usui & Hashitsume, 1978) concerning the equivalence between the different possible descriptions of 'statistical ensembles' can be extended to the problem here discussed.

In the microcanonical description one can also work with the set $\mathscr{A}$ but, in such a case, the probability law will be zero for maps not belonging to $\mathscr{F}$.

Selection of the information

No prior information

The simplest realistic case is that in which only the experimental information is considered as available. Infinitely many feasible maps can be constructed just by adding to τ (2) any number of extra terms corresponding to non-observed reflections and assigning arbitrary phase factors to the observed moduli for reflections in $\mathscr{K}$. If we call

$$F(L) = 1/V \int_{\Omega} m(r) \exp(2\pi i L r)\, \mathrm{d}^3 r, \tag{4}$$

the Fourier coefficient of m corresponding to the reciprocal vector L, a map belonging to $\mathscr{F}$ will be of the form

$$\begin{aligned} m(r) = \tau(r) + \sum_{K\in\mathscr{K}} |F^{\mathrm{ob}}(K)| \exp(i\varphi'_K - 2\pi i K r) \\ + \sum_{L'\notin\mathscr{L}} F(L') \exp(-2\pi i L' r), \end{aligned} \tag{5}$$

and the maximum-entropy probability distribution of maps $P_{\mathrm{ME}}(m)$,

$$P_{\mathrm{ME}}(m) = 1/W \text{ (a constant)}, \; m \in \mathscr{F}. \tag{6}$$

The maximum-entropy estimate of ρ is

$$\begin{aligned} \langle m(r)\rangle_{\mathrm{ME}} &= \int_{\mathscr{F}} P_{\mathrm{ME}}(m) m(r) \mathscr{D}_m \\ &= \tau(r) + \sum_{K\in\mathscr{K}} |F^{\mathrm{ob}}(K)| \exp(i\varphi_K - 2\pi i K r). \end{aligned} \tag{7}$$

This estimate depends on arbitrary phases φ_K associated with reflections in $\mathscr{K}$. This arbitrariness is a consequence of the fact that $\langle m\rangle_{\mathrm{ME}}$ given by (7) is a first-order approximation to the estimate of ρ. Higher-order corrections would lead us to definite predictions, as will be discussed later in one of the examples in the following section.

When the phases are experimentally accessible, we see that the maximum-entropy estimate of ρ coincides with τ. This widely used reconstruction procedure is very efficient when a reasonable number of Fourier coefficients are available.

Use of prior information

We can now try to incorporate some non-experimental information. The simplest case is when the bounds of ρ are used. In this case a feasible map will be defined by

$$m \in \mathscr{F} \text{ if } \begin{cases} \rho_{\mathrm{Min}} < m(r) < \rho_{\mathrm{Max}} \\ m \text{ has the correct periodicity} \\ \quad \text{and group symmetry} \\ F(H) - F^{\mathrm{ob}}(H) = 0,\; H \in \mathscr{H} \\ |F(K)| - |F^{\mathrm{ob}}(K)| = 0,\; K \in \mathscr{F}. \end{cases} \tag{8}$$

The ME estimate of ρ is now difficult to compute because analytical expressions for the feasible maps are not easily obtained.

The analysis is simplified if we adopt the alternative procedure of fitting some of the information 'on the average'. To this end we consider the set $\mathscr{A}$ of admissible maps defined by

$$m \in \mathscr{A} \text{ if } \begin{cases} \rho_{\mathrm{Min}} < m(r) < \rho_{\mathrm{Max}} \\ m \text{ has the observed periodicity} \\ \quad \text{and group symmetry,} \end{cases} \tag{9}$$

but now the Fourier coefficients of m do not necessarily fit the observed ones. We take the latter information to be satisfied 'on the average':

$$\begin{aligned} C_H &= \langle F(H)\rangle_{\mathrm{ME}} - F^{\mathrm{ob}}(H) = 0, \quad H \in \mathcal{H} \\ C_K &= |\langle F(K)\rangle_{\mathrm{ME}}| - |F^{\mathrm{ob}}(K)| = 0, \quad K \in \mathcal{K}. \end{aligned} \qquad (10)$$

Since Fourier transform and statistical average commute, (10) is equivalent to

$$\begin{aligned} &1/V \int_\Omega \langle m(r)\rangle_{\mathrm{ME}} \exp(2\pi i H r)\, \mathrm{d}^3 r - F^{\mathrm{ob}}(H) = 0, \\ &\hfill H \in \mathcal{H} \\ &|1/V \int_\Omega \langle m(r)\rangle_{\mathrm{ME}} \exp(2\pi i K r)\, \mathrm{d}^3 r| - |F^{\mathrm{ob}}(K)| = 0, \\ &\hfill K \in \mathcal{K}. \end{aligned} \qquad (11)$$

Information phrased in terms of average values will also be called constraints. We see that the particular constraints we have considered are of the very general type

$$C_a(\langle m\rangle_{\mathrm{ME}}) = 0, \qquad a = 1, \dots, A, \qquad (12)$$

i.e. they are functionals of the mean value of the maps. This estimate is in turn a functional of the ME probability distribution of maps, so that the constraints are in fact functionals of P_{ME},

$$C_a(\langle m\rangle_{\mathrm{ME}}) = D_a(P_{\mathrm{ME}}) = 0, \qquad a = 1, \dots, A. \qquad (13)$$

According to the MEP, P_{ME} will be determined by maximization of H taking into account the constraints D_a. This will be done by using the technique of Lagrange, which consists in maximizing

$$H(P) - \sum_{a=1}^{A} \lambda_a D_a(P), \qquad (14)$$

with respect to P, for fixed values of the λ_a's. This gives

$$P_{\mathrm{ME}}(m) = 1/Z \exp\left[-\mu/V \int_\Omega x(r) m(r)\, \mathrm{d}^3 r\right], \qquad (15)$$

where x is defined as the functional derivative

$$x(r) = \sum_{a=1}^{A} \lambda_a\, \delta C_a(\langle m\rangle_{\mathrm{ME}})/\delta\langle m(r)\rangle_{\mathrm{ME}}, \qquad (16)$$

and Z takes account of the normalization of P_{ME}:

$$\int_{\mathcal{A}} P_{ME}(m) \mathcal{D}_m = 1. \qquad (17)$$

The λ_a's are then determined so as to satisfy the constraints.

The mathematical treatment follows now a classical route. From the normalization condition we compute Z, the partition function, whose logarithm (divided by μ),

$$\begin{aligned} \Phi(x) &= 1/\mu \ln(Z) \\ &= 1/\mu \ln\left\{\int_{\mathcal{A}} \exp\left[-\mu/V \int_\Omega x(r) m(r)\, \mathrm{d}^3 r\right] \mathcal{D}_m\right\}, \end{aligned} \qquad (18)$$

will allow us to obtain all the relevant estimates. In particular,

$$\langle m(r)\rangle_{\mathrm{ME}} = -\delta\Phi(x)/\delta x(r). \qquad (19)$$

The mean-square fluctuation of the map is given by

$$\begin{aligned} \langle[\Delta m(r)]^2\rangle_{\mathrm{ME}} &= \langle[m(r) - \langle m(r)\rangle_{\mathrm{ME}}]^2\rangle_{\mathrm{ME}} \\ &= \delta^2\Phi(x)/\delta x(r)^2, \end{aligned} \qquad (20)$$

and the entropy corresponding to P_{ME} by

$$\begin{aligned} H(P_{\mathrm{ME}}) &= -1/\mu \langle \ln(P_{\mathrm{ME}})\rangle_{\mathrm{ME}} \\ &= \Phi(x) + 1/V \int_\Omega x(r) \langle m(r)\rangle_{\mathrm{ME}}\, \mathrm{d}^3 r. \end{aligned} \qquad (21)$$

The results so far obtained are independent of the particular forms the measure of integration $\mathcal{D}_m$ and the set of admissible maps $\mathcal{A}$ can take.

However, in most applications, and for practical reasons, the measure is assumed to be uniform, or at least factorizable (the precise meaning of this will be discussed in the next section), and the set of admissible maps is defined by giving the lower and upper bounds for the maps at the different points in Ω (one important exception is however the last example in the next section). In such a case (15) implies that the values of m at different points in Ω are statistically independent, so that $\Phi(x)$ is the integral over Ω of a function of x:

$$\Phi(x) = 1/V \int_\Omega \varphi[x(r)]\, \mathrm{d}^3 r. \qquad (22)$$

This fact allows us to write (19) and (20) as ordinary derivatives with respect to x:

$$\langle m\rangle_{\mathrm{ME}} = -\mathrm{d}\varphi/\mathrm{d}x \qquad (23)$$

and

$$\langle(\Delta m)^2\rangle_{\mathrm{ME}} = \langle(m - \langle m\rangle_{\mathrm{ME}})^2\rangle_{\mathrm{ME}} = \mathrm{d}^2\varphi/\mathrm{d}x^2 \geq 0. \qquad (24)$$

These last two equations imply that there is a local one-to-one relationship between $\langle m\rangle_{\mathrm{ME}}$ and x. As a consequence the entropy of P_{ME} will be given by an integral over Ω of a function of $\langle m\rangle_{\mathrm{ME}}$,

$$\begin{aligned} H(P_{\mathrm{ME}}) &= 1/V \int_\Omega [\varphi(x) - x\, \mathrm{d}\varphi/\mathrm{d}x]\, \mathrm{d}^3 r \\ &= 1/V \int_\Omega \sigma(x)\, \mathrm{d}^3 r \\ &= 1/V \int_\Omega h(\langle m(r)\rangle_{\mathrm{ME}})\, \mathrm{d}^3 r \\ &= S_{\mathrm{ME}}(\langle m\rangle_{\mathrm{ME}}). \end{aligned} \qquad (25)$$

We will call this last expression the configurational entropy of the map $\langle m\rangle_{\mathrm{ME}}$. It is worth noticing that the configurational entropy density h is also a local function of the estimated map $\langle m\rangle$.

The particular relationship between $\langle m\rangle_{\mathrm{ME}}$ and x can be considered as a 'modelling' of $\langle m\rangle_{\mathrm{ME}}$ (Collins, 1982). This modelling is intimately related to the configurational entropy. In fact it can easily be shown that the functional derivative of S_{ME} with respect to

$\langle m\rangle_{\rm ME}$ is the inverse of (19):

$$\delta S_{\rm ME}(\langle m\rangle_{\rm ME})/\delta\langle m(r)\rangle_{\rm ME}=x(r) \tag{26}$$

or, taking into account (25),

$$\mathrm{d}h(\langle m\rangle_{\rm ME})/\mathrm{d}\langle m\rangle_{\rm ME}=x. \tag{27}$$

The results (15)-(27) are of a very general character. They are valid whenever the constraints are expressed as functionals of the mean value of the maps. Another very important result is that the Fourier coefficients of the maps have a vanishingly small mean-square fluctuation (Navaza, 1985). They are thus good representatives of the set $\mathcal{F}$ of feasible maps (or of the admissible set $\mathcal{A}$).

We are now in a position to demonstrate a connection between our procedure to obtain the maximum-entropy estimate of ρ and the maximum-entropy method, MEM (see, for example, Livesey & Skilling, 1985). The MEM as used in crystallography amounts to obtaining a function f_M by maximization of a given functional of it under a certain number of constraints. If the functional is $S_{\rm ME}(f)$ given by (25) and the constraints $C_a(f)=0$, $a=1,\ldots,A$ as in (12), f_M is determined by maximization of

$$1/V\int_{\Omega} h[f(r)]\,\mathrm{d}^3r-\sum_{a=1}^{A}\lambda_a C_a(f). \tag{28}$$

It is easy to check that the solution f_M of this problem coincides with $\langle m\rangle_{\rm ME}$ given by (19) [or (23)].

Examples of modelling of $\langle m\rangle_{\rm ME}$

The modelling is entirely determined by the assumed information. Different information corresponds, in the above theory, to different sets of admissible maps, or different measures of integration, or different types of constraints, or any combination of them.

Different measures of integration

The measure we are here considering is that that simply tells us how the integrals have to be performed.

Sometimes the prior information can be satisfied by properly defining the measure $\mathcal{D}_m$ of integration. In the absence of any prior information the natural measure is the uniform one,

$$\mathcal{D}_m=\prod_{r\in\Omega}\mathrm{d}m(r), \tag{29}$$

i.e. we give the same 'weight' to different admissible maps.

Since we expect to recover atoms, an admissible map displaying atomicity should have a greater 'weight' than a flat one. As long as the measure of integration can be factorized in r the functional integrals can be easily calculated. For example, if we assume Gaussian atoms and make the weight proportional to the fraction of the volume of the unit cell at which ρ takes a given value, then

$$\rho=\exp(-ar^2), \tag{30}$$

$$\text{weight}\propto 4\pi r^2=-4\pi/a\ln(\rho),$$

so that

$$\mathcal{D}_m=\prod_{r\in\Omega}\ln[1/m(r)]\,\mathrm{d}m(r). \tag{31}$$

In this case the logarithm of the partition function is expressed in terms of the exponential-integral function. We see that the information of atomicity (in this very simplified version) amounts to giving a stronger weight to small values of the maps.

Different sets of admissible maps

Different modellings can be obtained by changing the set of admissible functions over which the functional integral defining Φ is carried out, as shown in the following examples. The measure (29) will be used and additive constants entering in the definition of $\Phi(x)$ will be ignored.

We will generalize the information (9) to the case in which $\rho_{\rm Min}$ and $\rho_{\rm Max}$ are both functions of r.

Putting

$$\begin{aligned}D(r)&=\tfrac{1}{2}[\rho_{\rm Max}(r)-\rho_{\rm Min}(r)],\\ M(r)&=\tfrac{1}{2}[\rho_{\rm Max}(r)+\rho_{\rm Min}(r)],\end{aligned} \tag{32}$$

the logarithm of the partition function is

$$\begin{aligned}\Phi(x)=1/V\int_{\Omega}&(\ln\{\sinh[x(r)D(r)]/x(r)D(r)\}\\ &-x(r)M(r))\,\mathrm{d}^3r,\end{aligned} \tag{33}$$

and the modelling is

$$\begin{aligned}\langle m(r)\rangle_{\rm ME}=M(r)+D(r)\{&1/x(r)D(r)\\ &-1/\tanh[x(r)D(r)]\}.\end{aligned} \tag{34}$$

This modelling can be used when dealing with neutron diffraction data, in which case $\rho_{\rm Min}$ can be negative, and also to introduce the information concerning the solvent region in a macromolecular structure, or the ordered portion in a disordered structure.

Particular cases of the above general formulae are the following:

(*a*) $\rho_{\rm Min}(r)=0$, $\rho_{\rm Max}(r)=1$

The modelling is

$$\langle m(r)\rangle_{\rm ME}=\tfrac{1}{2}+\tfrac{1}{2}\{1/[x(r)/2]-1/\tanh[x(r)/2]\}. \tag{35}$$

This function, as well as the corresponding configurational entropy density h, is shown in Fig. 1.

This modelling corresponds to the simplest realistic case in the crystallographic reconstruction of ρ (Navaza, 1985).

(*b*) $\rho_{\rm Min}(r)=-1$, $\rho_{\rm Max}(r)=1$

Now the modelling is

$$\langle m(r)\rangle_{\mathrm{ME}} = 1/x(r) - 1/\tanh\,[x(r)]. \qquad (36)$$

It can be used when only realness of the admissible maps is assumed. In such cases the bounds are kept fixed and the constraints scaled according to the assumed actual bounds. If these are very large, say $\rho_{\mathrm{Max}} \gg 1$, $\langle m\rangle_{\mathrm{ME}}$ will be small, of order $1/\rho_{\mathrm{Max}}$. Then (36) tells us that x will also be small,

$$\langle m\rangle_{\mathrm{ME}} = -x/3, \qquad (37)$$

and the configurational entropy, to the same order of approximation,

$$S_{\mathrm{ME}} = -\tfrac{3}{2} V \int_{\Omega} \langle m(r)\rangle^2_{\mathrm{ME}}\, \mathrm{d}^3 r. \qquad (38)$$

When the constraints are given by (10) the ME estimate of ρ is given by (7). We can now understand the origin of the arbitrary phases entering in (7). In fact, the configurational entropy is precisely

$$S_{\mathrm{ME}} = -\tfrac{3}{2} \sum_{L\in\mathscr{L}} |F^{\mathrm{ob}}(L)|^2, \qquad (39)$$

because of Parseval's theorem. This expression does not depend on the phases of the Fourier coefficients. The arbitrariness in question disappears when terms of higher order in $1/\rho_{\mathrm{Max}}$ are included.

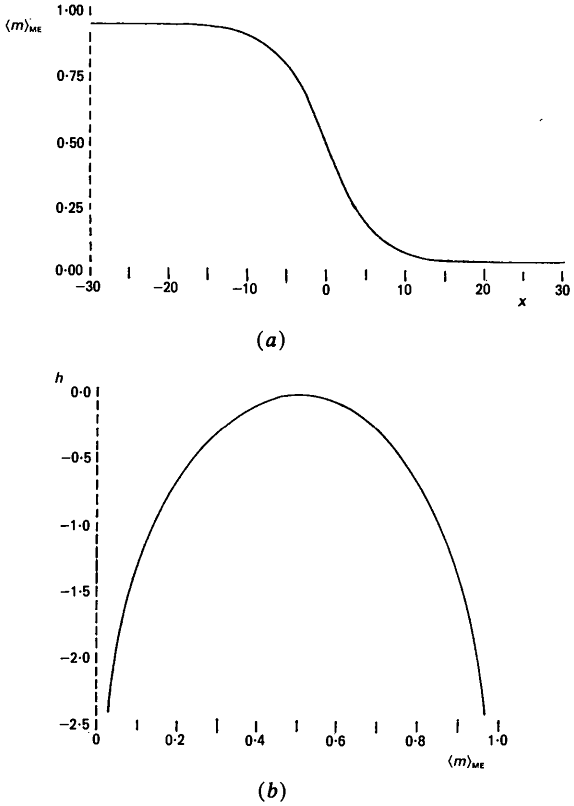


Fig. 1. (a) Maximum-entropy estimate $\langle m\rangle_{\mathrm{ME}}$ as a function of x (equation 35). (b) Configurational entropy density h as a function of $\langle m\rangle_{\mathrm{ME}}$ for modelling (35).

Different types of constraints

The preceding examples assumed constraints of the general type (12), *i.e.* functionals of the mean value of the maps. It may happen that such a type of constraint is not appropriate to deal with some particular information. For example, if we want to use the information of atomicity in the very approximate form

$$m(r)^2 - m(r) = 0, \quad \text{for } r \text{ in } \Omega, \qquad (40)$$

the constraints

$$\langle m(r)\rangle^2_{\mathrm{ME}} - \langle m(r)\rangle_{\mathrm{ME}} = 0, \quad \text{for } r \text{ in } \Omega, \qquad (41)$$

are too rigid, the solution being $\langle m(r)\rangle_{\mathrm{ME}} = 0$ or 1. This solution does not make full physical sense because the information is not exact. Instead, if we try to satisfy (40) 'on the average',

$$\langle m(r)^2 - m(r)\rangle_{\mathrm{ME}} = 0, \quad \text{for } r \text{ in } \Omega, \qquad (42)$$

(41) will no longer be satisfied. Constraints like these are of the general type

$$Q_b(\langle m^2\rangle_{\mathrm{ME}}, \langle m\rangle_{\mathrm{ME}}) = 0, \qquad b = 1,\dots, B. \qquad (43)$$

A remarkable result is that, even if the assumed information is quite different, a modelling similar to (35) is obtained. Here we will simply outline the steps leading to this result. The information assumed is:

$$\begin{cases} \text{information (9) with } \rho_{\mathrm{Min}} = -\infty \text{ and } \rho_{\mathrm{Max}} = \infty \\ \text{constraints of type (12) as before} \\ \text{constraints (42).} \end{cases}$$

Since now we have an infinite number of constraints (42) we have to introduce a density of Lagrangian multipliers w and maximize

$$H(P) - \sum_{a=1}^{A} \lambda_a D_a(P) - 1/V \int_{\Omega} w(r)\langle m(r)^2 - m(r)\rangle\, \mathrm{d}^3 r. \qquad (44)$$

with respect to P. This gives

$$P_{\mathrm{ME}}(m) = 1/Z \exp\,(-\mu/V \int_{\Omega} \{w(r) m(r)^2 + [x(r) - w(r)] m(r)\}\, \mathrm{d}^3 r), \qquad (45)$$

with x defined by (16) as before. The logarithm of Z (divided by μ) is now a functional of w and x,

$$\Phi(w, x) = 1/V \int_{\Omega} \{[1 - x(r)/w(r)]^2 w(r)/4 - \tfrac{1}{2} \ln\,[w(r)]\}\, \mathrm{d}^3 r, \qquad (46)$$

from which estimates can be computed by functional derivation. In particular,

$$-\delta\Phi/\delta w(r) = \langle m(r)^2 - m(r)\rangle_{\mathrm{ME}} = [\tfrac{1}{2} w(r)^2][2w(r) + x(r)^2 - w(r)^2] = 0, \qquad (47)$$

because of (42). This defines w as a function of x:

$$w(r) = 1 + [1 + x(r)^2]^{1/2} \tag{48}$$

[the negative root of (47) is ruled out because of convergence conditions for the functional integral defining Φ]. This last equation and

$$-\delta\Phi/\delta x(r) = \langle m(r)\rangle_{\rm ME} = \tfrac{1}{2}[1 - x(r)/w(r)] \tag{49}$$

give the modelling

$$\langle m(r)\rangle_{\rm ME} = \tfrac{1}{2}(1 - x(r)/\{1 + [1 + x(r)^2]^{1/2}\}). \tag{50}$$

It is interesting to notice that the mean value of the maps is always positive and bounded by 1, even if such information was not employed at all.

Configurational entropy generating relationships

The maximum-entropy probability distribution of maps $P_{\rm ME}$ (15), together with the definition of the admissible set and its associated measure of integration, uniquely determines the logarithm of the partition function which, in turn, defines the modelling, the mean-square fluctuation and the configurational entropy. According to formulae (23)-(25) there are definite relationships between these last three quantities.

Instead of starting from $P_{\rm ME}$ one can, on physical or mathematical grounds, make assumptions about the above relationships and the estimated map. This will, in general, allow us to determine $\varphi(x)$ using (23)-(25) which we will write as

$$\mathrm{d}\langle m\rangle/\mathrm{d}x = -\langle(\Delta m)^2\rangle \tag{51}$$

and

$$\mathrm{d}\sigma/\mathrm{d}x = -x\langle(\Delta m)^2\rangle. \tag{52}$$

Two cases will be discussed here:

(*a*) Assuming the mean-square fluctuation to be proportional to the symmetric function of the estimated map

$$\langle(\Delta m)^2\rangle \propto \langle m\rangle(1 - \langle m\rangle) \geq 0, \tag{53}$$

we obtain, using (51),

$$\langle m\rangle = [1 + \exp(x)]^{-1}. \tag{54}$$

This modelling corresponds to the Fermi-Dirac configurational entropy density

$$h(\langle m\rangle) = -\langle m\rangle \ln(\langle m\rangle) - (1 - \langle m\rangle)\ln(1 - \langle m\rangle). \tag{55}$$

In this case it is possible to find a law $P_{\rm ME}$ leading to (54) (Navaza, 1985). It corresponds to a formulation in which atomicity is explicitly introduced and provides a link between the algebraic theory of inequalities and statistical estimation. In fact the mean-square fluctuation of any estimated Fourier coefficient is given by the integral of (53), which goes to zero when a sufficient number of E's are given as information.

(*b*) Assuming the configurational entropy density to be proportional to the mean-square fluctuation of the maps

$$\sigma(x) \propto \langle(\Delta m)^2\rangle, \tag{56}$$

we obtain, using (52) and assuming $0 \leq \langle m\rangle \leq 1$,

$$\langle m\rangle = (2\pi)^{-1/2} \int\limits_x^\infty \exp(-t^2/2)\,\mathrm{d}t = \mathrm{erfc}(x). \tag{57}$$

This modelling is shown in Fig. 2. We did not succeed in finding a physically sound law $P_{\rm ME}$ from which (57) could be obtained.

Despite the many different modellings we have obtained, corresponding to different sets of information, there are some universal properties that make them very similar. In fact, x is defined up to a scale constant and, if the integral of $\langle m\rangle$ over Ω is given as constraint, up to an additive constant too. Moreover, *all* modellings are monotonically decreasing functions of x because of (24). The only essential feature that distinguishes one from the other is the presence or absence of built-in upper bounds.

For bounded modellings, the choice of the arbitrary additive and scale constants in x can be used to match the inflexion points and slopes of the different modellings. These uniform modellings differ now in asymptotic behaviour and height at the inflexion point. In this sense the only essential difference between (35) and (57) is that they approach the bounds as $1/|x|$ and $\exp(-x^2)$ respectively.

The universal character of the modelling will allow us critically to discuss super-resolution reported in the literature.

Other considerations

As already pointed out, (15)-(21) are independent of the particular forms of the measure of integration and of the admissible set. We will here study a particular case in which this fact is clearly shown.

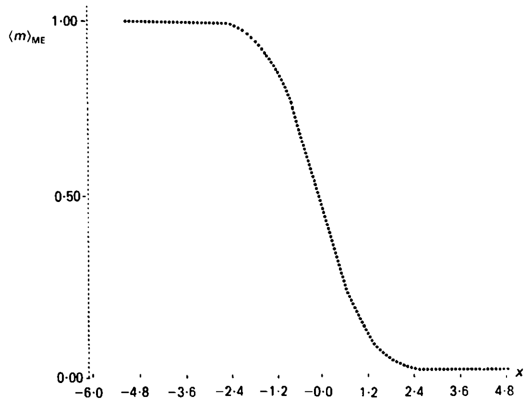


Fig. 2. $\langle m\rangle_{\rm ME} = \mathrm{erfc}(x)$ (equation 57).

Let us consider a crystal consisting of A equal units (atoms or fragments of molecules), the unit being completely characterized by the density function $d(r)$ (the origin of r being at the center of gravity of the unit). The Fourier coefficients of d will be denoted by $E(L)$, $L \in \mathcal{L}$.

One admissible map is now defined as the superposition of A functions obtained from $d(r)$ by arbitrary translations

$$m(r) = \sum_{a=1}^{A} d(r - R_a). \tag{58}$$

Each map is then characterized by the A parameters R_a. The Fourier transform of (58) gives

$$F(L) = E(L) \sum_{a=1}^{A} \exp(2\pi i L R_a). \tag{59}$$

The maximum-entropy probability distribution of maps (15) is now given by

$$\begin{aligned} P_{\mathrm{ME}}(m) &= 1/Z \prod_{a=1}^{A} \exp\left[-\mu/V \int_{\Omega} x(r)\, d(r-R_a)\, \mathrm{d}^3 r\right] \\ &= 1/Z \prod_{a=1}^{A} \exp[-y(R_a)] \end{aligned} \tag{60}$$

with

$$y(R) = \mu/V \int_{\Omega} x(r) d(r-R)\, \mathrm{d}^3 r. \tag{61}$$

The average map can be obtained directly from this equation. Using the normalization condition (17), assuming that the different translated units can overlap and that all translations are equally suitable (*i.e.* uniformly distributed in the unit cell), one obtains

$$\begin{aligned} \langle F(L)\rangle_{\mathrm{ME}} &= E(L)A/V \\ &\times \int_{\Omega} \exp(2\pi i L R) \exp[y(R)]\, \mathrm{d}^3 R. \end{aligned} \tag{62}$$

It can easily be seen that, when the units are the atoms themselves and the extra available information consists of (10), this formulation corresponds exactly to a maximum-entropy algorithm using the configurational entropy $-\langle m\rangle \ln(\langle m\rangle/e)$.

For arbitrary units $d(r)$ the formulation corresponds to a generalization of the translation function used in crystallography. A generalization of the rotation function can be done along the same lines.

Some numerical results

The information used in the examples considered here consisted of (9) and (10). In particular,

$$C_H = \langle F(H)\rangle_{\mathrm{ME}} - F^{\mathrm{ob}}(H) = 0, \quad H \in \mathcal{H}, \tag{63}$$

are complex. Even if we can always work with real and imaginary parts (as was assumed in the preceding analysis), it is simpler to keep the complex form and use both C_H and C_{-H} to obtain a real expression, because of Friedel's law. We will assume in the following that H and $-H$ are in $\mathcal{H}$, and K and $-K$ in $\mathcal{K}$, and the same for the associated Larangian multipliers.

The function x is in this case

$$\begin{aligned} x(r) &= \sum_{H \in \mathcal{H}} \lambda_H\, \delta C_H / \delta\langle m(r)\rangle_{\mathrm{ME}} \\ &\quad + \sum_{K \in \mathcal{K}} \nu_K\, \delta C_K / \delta\langle m(r)\rangle_{\mathrm{ME}} \\ &= \sum_{L \in \mathcal{L}} \lambda_L \exp(-2\pi i L r), \end{aligned} \tag{64}$$

the ν_K's being real numbers and

$$\lambda_L = \begin{cases} \lambda_H, & H \in \mathcal{H} \\ \nu_K \exp(i\varphi_K), & K \in \mathcal{K}, \end{cases} \tag{65}$$

where φ_K is the phase of $\langle F(K)\rangle_{\mathrm{ME}}$.

The numerical methods used to determine the λ_L's in order to satisfy the constraints were explained in the previous paper. The method was first applied to the structure of prostaglandin (De Titta, Langs, Edmonds & Duax, 1980). Three cases were considered ($\emptyset$ denotes the empty set):

(a) $\mathcal{H} \neq \emptyset$, $\mathcal{K} = \emptyset$

Most of the atomic positions were recovered when the phases corresponding to the 25 independent greatest E's were used. The Hessian matrix of the configurational entropy considered as a function of the phases had high negative diagonal terms but roughly half of its eigenvalues with the wrong sign. This means that the true phases are, individually, near the top of a very sharp maximum whereas, as a whole, they are not even placed in a concave region. Two configurational entropies were used in this calculation: a Fermi–Dirac entropy, which is the appropriate one when working with E's instead of F's, and $-\langle m\rangle \ln(\langle m\rangle/e)$.

(b) *Ab initio*, $\mathcal{H} = \emptyset$, $\mathcal{K} \neq \emptyset$

An uninterpretable estimation of ρ was obtained corresponding to a *local maximum* of the configurational entropy (Alzari & Navaza, 1983). Up to a maximum of forty E's were used in the calculations.

(c) $\mathcal{H} \neq \emptyset$, $\mathcal{K} \neq \emptyset$

When a certain number of phases were assumed as known, corresponding to 3 Å resolution (37 independent phases), and the moduli to 1 Å resolution (about 1000 reflections), the structure could be recovered by inspection although the estimated map was not an atomic one. All the modellings of the preceding section, compatible with the assumed information, were used in the tests. The results were qualitatively the same, irrespective of the particular modelling chosen.

Cases (b) and (c) were tried with other structures having a greater number of atoms. As a general rule, when all moduli and phases were used to a resolution of 1·5–1 Å, the estimated maps displayed atomicity and super-resolution. In case (*c*) recognition of the structure became more difficult as the number of atoms was increased.

Atomicity in terms of non-local constraints

A common feature of all the modellings discussed in the preceding sections is the local character of the relationship between $\langle m\rangle$ and x. By local we mean that the value of $\langle m\rangle$ at a given point r in Ω is determined by the value of x at the same point.

The origin of this property is the type of constraint assumed [(12), but also (42)] and the domain of admissible maps. It is very difficult to change them, keeping the mathematics at a tractable level.

Non-locality can also be introduced in the form of constraints of type (12). In this case the modelling is not changed but x is now a function of $\langle m\rangle$. This was already the case of formula (64) where x was a complicated non-local functional of $\langle m\rangle$ through the phases φ_K. The results of the preceding section clearly show that this form of non-locality is not sufficient to obtain either atomic maps or reliable phases.

Better results are obtained when Sayre's equations are used as constraints of type (12) (Navaza, Castellano & Tsoucaris, 1983). They are formulated as

$$\langle m(r)\rangle_{\mathrm{ME}}-1/V\int_{\Omega} g(r-r')\langle m(r)\rangle^2_{\mathrm{ME}}\,\mathrm{d}^3r=0,\ r \text{ in } \Omega, \tag{66}$$

or their Fourier transform

$$D_S=\langle F(S)\rangle_{\mathrm{ME}}-\theta(S)F^{\mathrm{sq}}(S)=0,\ S\in\mathscr{S}, \tag{67}$$

$\mathscr{S}$ being the set of all the reciprocal vectors. θ is the Fourier transform of g and

$$F^{\mathrm{sq}}(S)=1/V\int_{\Omega}\langle m(r)\rangle^2_{\mathrm{ME}}\exp(2\pi iSr)\,\mathrm{d}^3r. \tag{68}$$

The important feature in (66) is that it compares the value of $\langle m\rangle$ at point r with those of $\langle m\rangle^2$ at all points in a neighbourhood of r, whose extent is determined by the function g (typically 1 Å). The effect of these non-local constraints is then to model $\langle m\rangle$ according to g. Since (66) is independent of the experimental data any power of $\langle m\rangle$ may be used. However, the original choice of Sayre is that that leads to the least number of calculations.

We introduce one complex Lagrangian multiplier μ_S for each constraint D_S and compute x (16). Calling x_0 the function (64) that takes account of information (10), we have

$$\begin{aligned} x(r)&=x_0(r)+\sum_{S\in\mathscr{S}}\mu_S\,\delta D_S/\delta\langle m(r)\rangle_{\mathrm{ME}}\\ &=\sum_{L\in\mathscr{L}}\lambda_L\exp(-2\pi iLr)+\sum_{S\in\mathscr{S}}\mu_S\exp(-2\pi iSr)\\ &\quad-2\langle m\rangle_{\mathrm{ME}}\sum_{S\in\mathscr{S}}\theta(S)\mu_S\exp(-2\pi iSr). \end{aligned} \tag{69}$$

This formula is valid even if $\mathscr{S}$ is a finite subset of reciprocal vectors. In particular, we can choose $\mathscr{S}=\mathscr{L}$,

$$x(r)=\alpha(r)+\beta(r)\langle m(r)\rangle_{\mathrm{ME}}, \tag{70}$$

with

$$\begin{aligned}\alpha(r)&=\sum_{L\in\mathscr{L}}(\lambda_L+\mu_L)\exp(-2\pi iLr)\\ &=\sum_{L\in\mathscr{L}}a_L\exp(-2\pi iLr)\end{aligned} \tag{71}$$

and

$$\begin{aligned}\beta(r)&=\sum_{L\in\mathscr{L}}\theta(L)\mu_L\exp(-2\pi iLr)\\ &=\sum_{L\in\mathscr{L}}b_L\exp(-2\pi iLr)\end{aligned} \tag{72}$$

[$\theta(L)$ is different from zero in any finite set $\mathscr{L}$].

The modelling together with (70) gives parametrically, with x as parameter, $\langle m\rangle_{\mathrm{ME}}$ as a local function of α and β.

For given α and β (70) is a linear function of x and $\langle m\rangle_{\mathrm{ME}}$. The intersections of this line with the modelling give all the possible values of $\langle m\rangle_{\mathrm{ME}}$. It is easy to check that for bounded modellings there is always at least one and a maximum of three intersections.

We will not discuss here the possible procedures of determination of the a's and b's in order to satisfy the constraints. Instead we will give the arguments we used to simplify (70).

As already stated in the preceding section, when moduli and phases are used to 1 Å resolution the estimated map displays atomicity and super-resolution. This means that atomicity is qualitatively compatible with an x function having a spectrum limited to 1 Å resolution. We have then used x as given by (64) with all the complex λ's considered as free parameters and minimized the function

$$\sum_{H\in\mathscr{H}}|C_H|^2+\sum_{K\in\mathscr{K}}C_K^2+\sum_{L\in\mathscr{L}}|D_L|^2 \tag{73}$$

with respect to them. The modelling used was $\langle m\rangle_{\mathrm{ME}}=\mathrm{erfc}\,(x)$. Four structures were used as tests:

prostaglandin, $C_{20}H_{32}O_{35}$, $Z=1$, $P1$;

loganin, $C_{17}H_{26}O_{10}$, $Z=4$, $P2_12_12_1$ (Jones, Sheldrick, Glusenkamp & Tietze, 1980);

alamethacin, $C_{28}H_{42}O_7N_4$, $Z=2$, $P2_1$ (Smith, undated);

ergocalciferol, $C_{28}H_{44}O_7$, $Z=8$, $P2_12_12_1$ (Hull, Leban, Main, White & Woolfson, 1976).

For all the structures the $\langle m\rangle_{\mathrm{ME}}$ showed all the atoms at almost their right positions when the *model* phases to 3 Å resolution and the *observed* moduli to 1 Å resolution were used (see Figs. 3–6).

Some preliminary results on insulin seem to confirm that these results will also hold in the case of macromolecules (de Rango & Navaza, 1984). A full account of the tests performed on insulin will be given elsewhere.

In the case of prostaglandin the same procedure was used but with model phases to 3·5 Å and the same good results were obtained (Fig. 3).

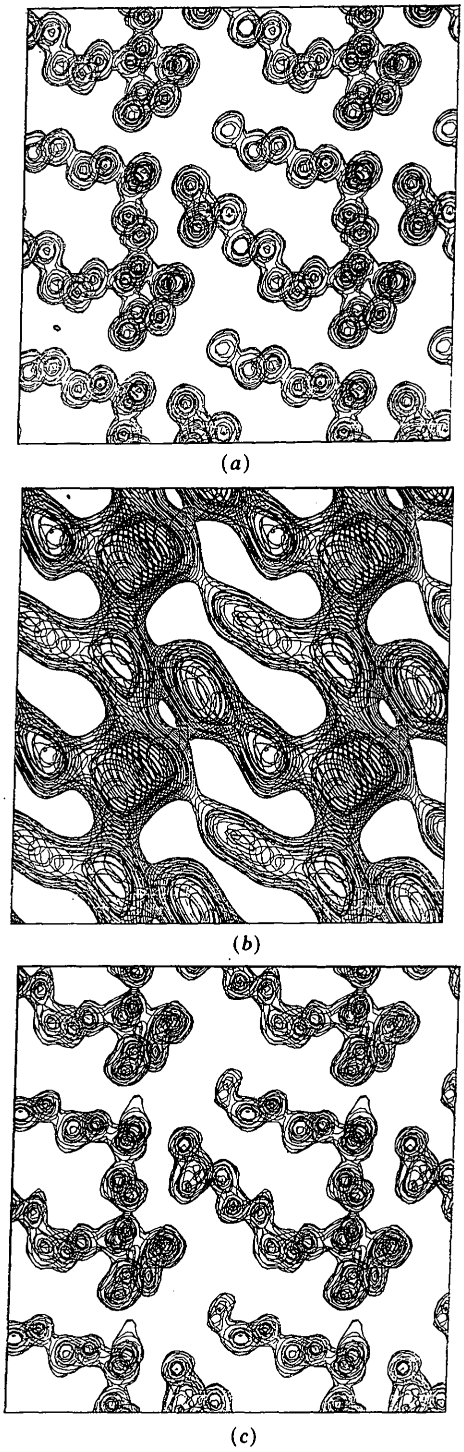

(a)
(b)
(c)

Fig. 3. (a) Projection of the electron density function of prostaglandin (1 Å resolution Fourier series). (b) Projection of the electron density function of prostaglandin (3·5 Å resolution Fourier series). (c) $\langle m\rangle_{\mathrm{ME}}$ based on the observed structure factor amplitudes to 1 Å resolution and model phases to 3·5 Å resolution (23 independent phases).

The nature of maximum-entropy estimations

We will discuss the case most often found in the literature of constraints (10). The ME probability of maps (15), when expressed in terms of the Fourier coefficients of the admissible maps, gives

$$P_{\mathrm{ME}}(m)=1/Z\exp\Big[-\mu\sum_{L\in\mathscr{L}}\lambda_L^*F(L)\Big]. \qquad (74)$$

We see that the law only depends on the Fourier coefficients associated with the available experimental information. It is then maximally noncommittal with respect to missing information.

Since the λ's are determined so as to satisfy (10), the ME estimate of ρ is

$$\begin{aligned}\langle m(r)\rangle_{\mathrm{ME}}=&\sum_{H\in\mathscr{H}}F^{\mathrm{ob}}(H)\exp(-2\pi iHr)\\&+\sum_{K\in\mathscr{K}}|F^{\mathrm{ob}}(K)|\\&\times\exp(i\langle\varphi_K\rangle_{\mathrm{ME}})\exp(-2\pi iKr)\\&+\sum_{L'\notin\mathscr{L}}\langle F(L')\rangle_{\mathrm{ME}}\exp(-2\pi iL'r): \qquad (75)\end{aligned}$$

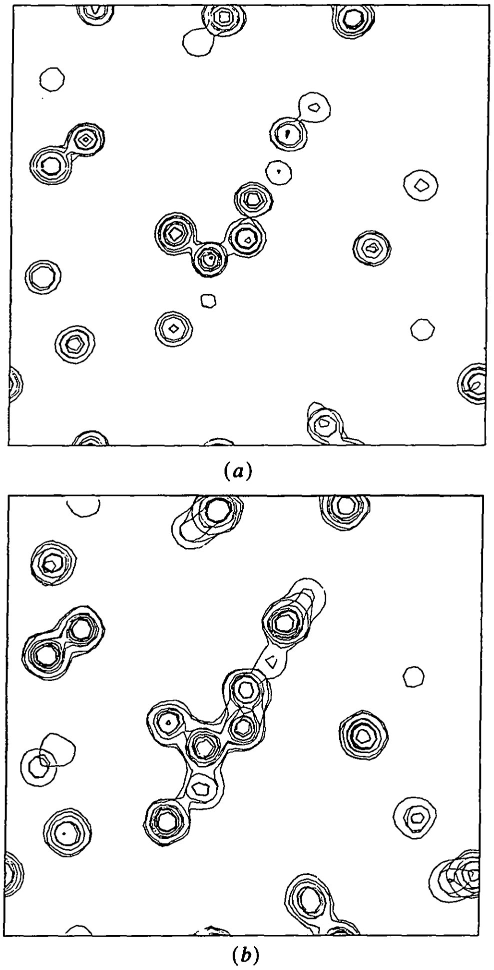

(a)
(b)

Fig. 4. (a) Section of the electron density function of loganin (1 Å resolution Fourier series). (b) Same section of $\langle m\rangle_{\mathrm{ME}}$ based on the observed structure factor amplitudes to 1 Å resolution and model phases to 3 Å resolution.

what is not given as information is averaged using the law P_{ME}. The extra terms $L' \notin \mathcal{L}$ are to take into account the prior information [(9), (32) or (42)] and give rise to super-resolution. It is precisely this prior information that determines the modelling, so that super-resolution is modelling dependent.

Notwithstanding, owing to some universal properties of modelling discussed in a preceding section, it is possible to understand qualitatively the amount and the sense of the super-resolution one can expect in a given reconstruction problem, irrespective of the particular local modelling chosen.

We recall the two fundamental properties:

(*a*) $x(r)$ has the resolution of the experimentally available Fourier coefficients of ρ;

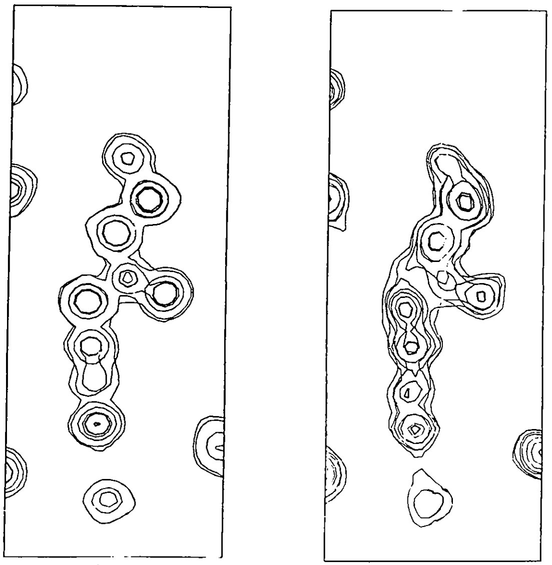
(*b*) the modelling is a monotonically decreasing function of x.

These two properties imply that $\langle m \rangle_{\mathrm{ME}}$ has much the same *spatial* resolution as the experimental Fourier coefficients, in the sense that it is difficult to resolve features that a Fourier series of this same experimental resolution does not resolve.

Some modellings can give very sharp peaks, which in turn give high-resolution Fourier coefficients, but they will not, usually, give peaks at distances closer than the minimal compatible with the experimental resolution.

The point we are here discussing is the following: what features can a trigonometric summation (Fourier series) with coefficients up to a given resolution show? To answer this question let us start with the one-dimensional case

$$y(x) = \sum_{n=-N}^{N} c_n \exp(-2\pi i n x) = \sum_{n=-N}^{N} c_n z^n, \qquad (76)$$



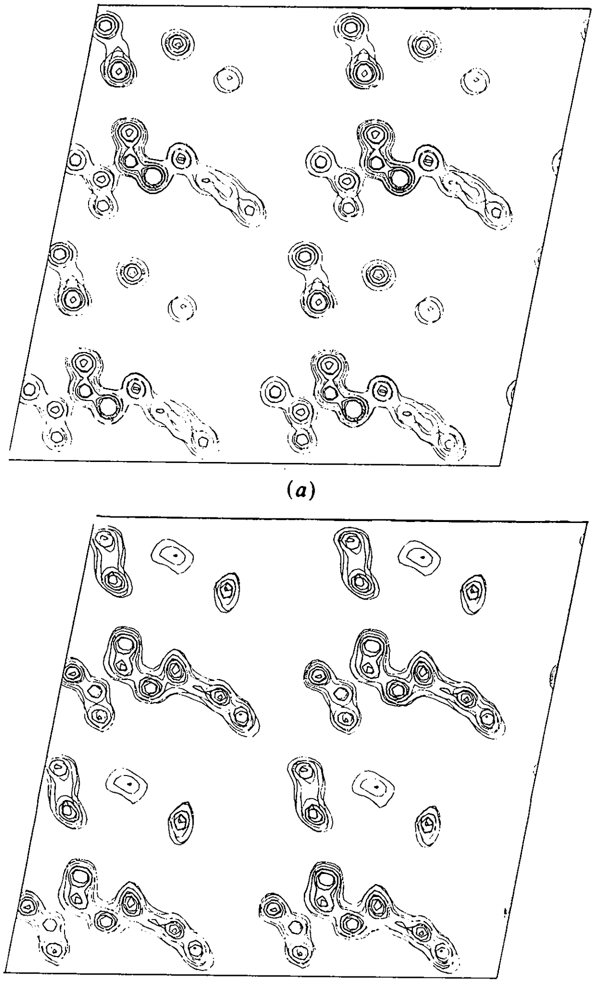
(*a*) (*b*)

Fig. 5. (*a*) Section of the electron density function of alamethacin (1 Å resolution Fourier series). (*b*) Same section of $\langle m \rangle_{\mathrm{ME}}$ based on the observed structure factor amplitudes to 1 Å resolution and model phases to 3 Å resolution.

with $z = \exp(-2\pi i x)$ in the unit circle of the complex plane. The derivative of $y(x)$,

$$\mathrm{d}y(x)/\mathrm{d}x = -2\pi i \sum_{n=-N}^{N} n c_n z^{n-1}, \qquad (77)$$

has at most $2N$ zeros in the unit circle, hence $2N$ zeros for $0 \le x \le 1$. This implies that $y(x)$ presents at most N peaks so that any local MEM procedure using the information of Fourier coefficients up to the index N will never show more than N peaks. In principle, nothing prevents some of them being infinitely close, but crystallographic experience tells us that the closest distance that can be resolved is of the order of the resolution of the Fourier coefficients. This has full statistical sense because the interatomic distances between neighbouring atoms is always of the same order of magnitude so that there is no reason that two neighbouring peaks be shown instead of any others. Similar conclusions, although not so categori-



(*a*)

(*b*)

Fig. 6. (*a*) Section of the electron density function of ergocalciferol (1 Å resolution Fourier series). (*b*) Same section of $\langle m \rangle_{\mathrm{ME}}$ based on the observed structure factor amplitudes to 1 Å resolution and model phases to 3 Å resolution.

cal, can be drawn in the three-dimensional case [using, for example, the formalism developed by Navaza & Silva (1979)].

These conclusions do not mean that $\langle \hat{m} \rangle_{\rm ME}$ is equivalent to the traditional inverse Fourier reconstruction τ (when phases are available), because τ is not x, even if they have the same number of terms corresponding to the same reciprocal vectors. It just clarifies the sense of super-resolution and puts limits to the confidence we can give to phases and Fourier coefficients estimated by any local MEM procedure that only uses experimental data as constraints.

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An Examination of the Relationship of the $\Delta\omega$, $\Delta 2\theta$ Intensity Distribution to Crystal Substructure (Mosaic Distribution) and Shape

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Abstract

The basic $\Delta\omega$, $\Delta 2\theta$ technique for examining single-crystal Bragg reflections [Mathieson (1982). *Acta Cryst.* **A38**, 378-387] has recently been improved [Mathieson & Stevenson (1984). *Aust. J. Phys.* **37**, 657-665], by using a simple experimental modification which reduces the source component to a minor (angular) role, thereby making the extraction (deconvolution) of the remaining components more accurate. The application of this new technique in the determination of reflectivity (rocking) curves for imperfect crystals has been demonstrated [Mathieson & Stevenson (1985). *Acta Cryst.* **A41**, 290-296]. In the present case, the examination of individual reflections from a small single crystal of $\mathrm{CuInSe_2}$ reveals that the improved technique is capable (i) of identifying, by its locus extension in $\Delta\omega$, $\Delta 2\theta$ space, diffraction from one side of the specimen crystal to the other (in the diffraction plane), even for a crystal of average dimension ~0·06 mm, and (ii) of estimating the reflectivity curve for different parts of the crystal. A series of model cases is discussed, to clarify the interpretation of observed two-dimensional intensity distributions. While considered here in relation to a small crystal, this technique is applicable to extended-plate crystals (in transmission mode) by a selected-area procedure.

1. Introduction

In a recent series of papers, Mathieson (1982) being the first, Mathieson has demonstrated the advantages of the two-dimensional $\Delta\omega$, $\Delta 2\theta$ method for examining single-crystal Bragg reflections, relative to the conventional $\Delta\omega$ profile method. The one-dimensional intensity profile obtained in the conventional procedure represents the convolution of a number of components such as the mosaic spread, μ, the source size, σ, the wavelength distribution, λ, the specimen crystal size (Mathieson, 1984*a*), c, and, most importantly, the wide aperture in front of the detector, A. The $\Delta\omega$, $\Delta 2\theta$ technique, involving the introduction of a narrow aperture in front of the detector and the consequent extension to a second measurement parameter, results, in effect, in a form of partial deconvolution, with the individual major components being readily identified by their characteristic loci in $\Delta\omega$, $\Delta 2\theta$ space.

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