Dysnomia — A Program for MEM analysis from X-Ray and Neutron Diffraction Data

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Version 1

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   K. Momma, T. Ikeda, A. A. Belik and F. Izumi, "Dysnomia, a computer program for maximum-entropy method (MEM) analysis and its performance in the MEM-based pattern fitting." *Powder Diffr.*, **28**, 184–193 (2013).

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Chapter 1

INTRODUCTION

The maximum entropy method (MEM) [1,2] is very useful to modify structural models adopted in Rietveld analysis and determine distributions of electron and nuclear (coherent-scattering length, b_c) densities from X-ray and neutron diffraction data, respectively [3]. The termination effect is less serious in MEM analysis than in Fourier/D synthesis because MEM is capable of estimating structure factors of high-Q reflections that have not been measured experimentally. In addition, after observed structure factors of overlapped reflections have been estimated on the basis of results of Rietveld analysis, subsequent MEM analysis more or less improves structure factors, which makes MEM very effective in the extraction of the maximum amount of structural information from powder diffraction data

Three-dimensional (3D) visualization of electron/nuclear densities resulting from diffraction data achieves a better understanding of the highly disordered structure, chemical bonding (X-ray diffraction), or anharmonic thermal motion. For example, diffusion paths of mobile chemical species in ionic conductors have been visualized in three dimensions from X-ray and neutron powder diffraction data by a sophisticated structure-refinement technique called MEM-based pattern fitting (MPF) [3–6]. MPF may be able to reveal even anharmonic thermal vibrations, which are very difficult to analyze from powder diffraction data because of many parameters to be refined by a nonlinear least-squares method.

Dysnomia [6–8] is a MEM analysis program succeeding PRIMA [3,9] which was put on the Internet in 2003 as part of a 3D visualization system VENUS. It was written from the ground up in the C++ language by introducing advances in MEM analysis from single-crystal and powder diffraction data. Since Dysnomia is the daemon of chaos in the Greek mythology, it will be suitable for the name of the program for MEM in which the information entropy, S, is maximized under some constraints.

Dysnomia provides the following features which were not supported in PRIMA:

1. linear combination of generalized F and G constraints,
2. weightings based on lattice-plane spacings.
3. two types of optimization algorithms (a variant of the Cambridge algorithm [10] and the limited-memory BFGS algorithm [11]) that converge to solutions close to the true maximum-entropy conditions,
4. automatic selection of fast Fourier transform (FFT) and discrete Fourier transform (DFT),
5. parallel processing using an API (application programming interface), OpenMP, for multi-platform shared-memory parallel programming,

Features 1–3 enable us to determine more or less better electron/nuclear densities with Dysnomia than with PRIMA. Thanks to features 4 and 5, Dysnomia runs faster and requires much less memory in large-sized caculations than PRIMA, which makes Dysnomia very suitable for its execution on standard personal computers equipped with multi-core CPUs.

This document outlines Dysnomia for those who are going to apply MEM to X-ray and neutron diffraction data measured by single-crystal and powder diffraction methods.

Chapter 2

ALGORITHM

2.1 The Fundamental Principle of MEM

The general principle of MEM analysis is to find the maximum of the ingformation entropy, S, under several constraints by iterative procedures. A few variations of the MEM formalism have hitherto been adopted in the literature [1, 12, 13]. Here, we will follow the formalism of Collins [1] based on Jaynes's expression of S [14].

In MEM analysis from X-ray and neutron diffraction data, electron and nuclear densities in the unit cell are represented by those in voxels (parallelepipeds) whose numbers along a, b, and c axes are N_a, N_b, and N_c, respectively; densities within a voxel is regarded as even. Let N ($= N_a N_b N_c$) be the total number of voxels in the unit cell, ρ_k the normalized density at position r_k in the 3D gridded space, τ_k the normalized density derived from prior information for r_k, and ρ_k^* the density at r_k. Then, S is computed by

$$S = -\sum_{k=1}^{N} \rho_k \ln\left(\frac{\rho_k}{\tau_k}\right) \tag{2.1}$$

with

$$\rho_k = \frac{\rho_k^*}{\sum_{k=1}^{N} \rho_k^*}. \tag{2.2}$$

S is maximized under constraints C by a method of undetermined Lagrange multipliers,

$$Q = S - \lambda C - \mu\left(\sum_{k=1}^{N} \rho_k - 1\right), \tag{2.3}$$

where Q is maximized through iterative computations with respect to ρ and two Lagrange multipliers, λ and μ.

2.2 Constraints

With Dysnomia, S in Eq. (2.1) is maximized by imposing a linear combination of generalized F and G constraints.

2.2.1 *F* constraint

Let N_F be the total number of reflections, $F_\mathrm{o}(\boldsymbol{h}_j)$ the observed structure factor, $F(\boldsymbol{h}_j)$ the calculated structure factor, and $\sigma(\boldsymbol{h}_j)$ the standard uncertainty of $|F_\mathrm{o}(\boldsymbol{h}_j)|$. The F constraint

used in MEM analysis from diffraction data is formulated as

$$C'_F = \sum_{j=1}^{N_F} |\Delta F_j|^2 - N_F, \tag{2.4}$$

where ΔF_j is the normalized residual for the structure factor:

$$\Delta F_j = \frac{F_{\rm o}(\boldsymbol{h}_j) - F(\boldsymbol{h}_j)}{\sigma(\boldsymbol{h}_j)}. \tag{2.5}$$

In the actual implementation of the F constraint in Dysnomia, C'_F is normalized with respect to N_F:

$$C_F = \frac{C'_F}{N_F} \tag{2.6}$$

$$= \frac{1}{N_F} \sum_{j=1}^{N_F} |\Delta F_j|^2 - 1. \tag{2.7}$$

2.2.2 *G* constraint

Information about overlapped reflections in powder diffraction data can be introduced into MEM analysis through the G constraint [15]:

$$C'_G = \sum_{j=1}^{N_G} \left| \frac{G_{{\rm o}j} - G_j}{\sigma_j} \right|^2 - N_G$$

$$= \sum_{j=1}^{N_G} |\Delta G_j|^2 - N_G \tag{2.8}$$

with

$$G_j = \left[\frac{\sum_{i=1}^{L_j} m_i \left| F(\boldsymbol{h}_i) \right|^2}{\sum_{i=1}^{L_j} m_i} \right]^{1/2}. \tag{2.9}$$

In Eqs. (2.8) and (2.9), N_G is the total number of groups comprising overlapped reflections, $G_{{\rm o}j}$ is the sum of the integrated intensities of overlapped reflections in group j, L_j is the number of overlapped reflections in group j, and m_i is the multiplicity of reflection i. Combination of C'_F and C'_G affords an integrated constraint, C_2:

$$C_2 = \frac{C'_F + C'_G}{N_F + N_G}. \tag{2.10}$$

2.2.3 Generalized constraint

The classical F and G constraints are based on χ^2 statistics, whose use assumes that experimental errors in $|F_{\rm o}(\boldsymbol{h}_j)|$'s are random with a Gaussian (normal) distribution. Though the use of χ^2 constraint is justified by the Gaussian distribution of errors, it is not a sufficient condition to ensure the Gaussian distribution of residuals between observed and estimated values. In the case of MEM analysis from diffraction data, some low-Q reflections tend to have very large $|\Delta F_j|$'s, which leads to a noisy distribution of electron or nuclear densities estimated by MEM. Such a

characteristic in MEM analysis from diffraction data was theoretically explained by Jauch [16]. To reduce such an undesirable tendency of MEM, Palatinus and van Smaalen [17] proposed to use higher order moments of ΔF_j as a constraint.

A probability distribution of a random variable x is characterized by the values of its central moments M_n. For the normalized Gaussian distribution, the central moments are defined as

$$M_n(\text{Gauss}) = \int_{-\infty}^{\infty} x^n (2\pi)^{-1/2} \exp\left(-x^2/2\right) \mathrm{d}x. \tag{2.11}$$

The moments of odd n are all zero while those of even n are

$$M_{2n}(\text{Gauss}) = \prod_{i=1}^{n} (2i-1). \tag{2.12}$$

In the case of N samples of the variable x, the central moments M_n can be computed by

$$M_n = \frac{1}{N} \sum_{i=1}^{N} x_i^n. \tag{2.13}$$

The generalized F constraint of order n is formulated as

$$C'_{Fn} = \frac{1}{M_n(\text{Gauss})} \sum_{j=1}^{N_F} |\Delta F_j|^n - N_F, \tag{2.14}$$

$$C_{Fn} = \frac{C'_{Fn}}{N_F}. \tag{2.15}$$

The classical F constraint corresponds to the generalized constraint of order 2, C_{F2}. The classical G constraint is also generalized as

$$C'_{Gn} = \frac{1}{M_n(\text{Gauss})} \sum_{j=1}^{N_F} |\Delta G_j|^n - N_G. \tag{2.16}$$

The generalized F and G constraints of order n, are combined to give a C_n constraint:

$$C_n = \frac{C'_{Fn} + C'_{Gn}}{N_F + N_G}. \tag{2.17}$$

2.2.4 Linear combination of generalized constraints with weightings

Dysnomia adopts a linear combination of the generalized F and G constraints with relative weights, λ_n ($n = 2, 4, 6, \ldots$):

$$C = \sum_n \lambda_n C_n \tag{2.18}$$

with

$$C_n = \frac{1}{(N_F + N_G) M_n(\text{Gauss})} \left[\sum_{j=1}^{N_F} w_j \left(|\Delta F_j|\right)^n + \sum_{j=1}^{G_F} w_j \left(|\Delta G_j|\right)^n \right] - C_{\mathrm{w}_n}, \tag{2.19}$$

where w_j is the weighting factor (see 2.3), and C_{w_n} is the criterion for convergence. When w_j is unity, the ideal constraint is $C_{\mathrm{w}_n} = 1$ for any even n. Such a rigorous constraint seems to be hardly satisfied in actual problems. Accordingly, Dysnomia always determines C_{w_n} automatically so as to satisfy Eq. (2.7) or (2.10) on use of the G constraint.

Information about central moments of the normalized residuals, ΔF_j and ΔG_j, is output to file *.out, for example,

```
C2  =  9.9992285E-01   ln(C2 ) =  -0.000077
C4  =  4.0802412E+00   ln(C4 ) =   1.406156
C6  =  2.8819103E+01   ln(C6 ) =   3.361038
C8  =  2.0165493E+02   ln(C8 ) =   5.306558
C10 =  1.2533774E+03   ln(C10) =   7.133597
C12 =  6.8066503E+03   ln(C12) =   8.825655
C14 =  3.2373854E+04   ln(C14) =  10.385106
C16 =  1.3593284E+05   ln(C16) =  11.819916
```

The first column, `C2`–`C16`, lists the central moments of order n for $|\Delta F_j|^n$ and $|\Delta G_j|^n$ normalized by those for Gaussian distribution. The second column, `ln(C2)`–`ln(C16)`, gives their natural logarithms.

If the distributions of ΔF_j and ΔG_j are Gaussian, values in the first column are all 1 while those in the second column are all 0. Normalized central moments larger than 1 imply that information in observed data is underestimated and not fully reconstructed by MEM. On the contrary, normalized central moments smaller than 1 imply the overestimation of data, which result in overfit to observed data.

In MEM analyses from X-ray diffraction data with traditional second-order constraints, the normalized central moments of order $n > 2$ are typically larger than 1, as shown in the above example. In such a case, increase λ_n of order 4 or higher to put restraints on them and bind them to the ideal value. The central moment of a higher order may be smaller than 1 depending on the type and quality of data, particularly when $N_F + N_G$ is relatively small. In such a case, set λ_n such that $\lambda_2 = 1$ and $\lambda_n = 0$ for $n > 2$, which corresponds to the traditional χ^2 constraint.

At any rate, be sure to check whether or not 3D distribution of electron/nuclear densities is physically and chemically reasonable with VESTA [18].

2.3 Weighting

Weighting in the F constraint on the basis of the lattice-plane spacing was first proposed by de Vries *et al* [19]. Its effectiveness was later confirmed by some other researchers including Hofmann *et al.* [20].

Let $\boldsymbol{s}_j$ be the reciprocal-lattice vector ($= h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$) for reflection j, x the real number for weighting, and d_j the lattice-plane spacing ($= 1/|\boldsymbol{s}_j|$). Then, the weighting factors, w_j, in Eq. (2.19) is given by

$$\begin{aligned} w_j &= \frac{1}{|\boldsymbol{s}_j|^x}\left[\sum_{i=1}^{N_F}\frac{1}{|\boldsymbol{s}_i|^x}\right] \\ &= \frac{1}{d_j^x}\left[\sum_{i=1}^{N_F}\frac{1}{d_i^x}\right]. \end{aligned} \tag{2.20}$$

If $x = 0$, no weight is imposed in the same way as with PRIMA [9].

This weighting scheme is suitable for X-ray diffraction where parts of low-Q reflections often have very large ΔF_j values. Values of around 2 are usually recommended in X-ray powder diffraction; x is increased as the quality of intensity data is improved. In the case of single-crystal X-ray diffraction, de Vries *et al.* [19] empirically found $x = 4$ to be optimum. On the other hand, this approach is not suited for the analysis of neutron diffraction data, where b_c values of constituent elements remain constant regardless Q, particularly those measured at low temperature. Therefore, x is usually set at 0 in neutron diffraction.

Ad-hoc weighting described above will be effective, particularly, in MEM analysis from X-ray diffraction data, where $\sigma_j(\boldsymbol{h}_j)$'s tend to be estimated at unreasonably large values for low-Q reflections.

2.4 Optimization algorithms

The following three types of MEM algorithms are implemented in Dysnomia:

1. 0th-order single pixel approximation (ZSPA) algorithm [21] .
2. Limited-memory Broyden–Fletcher–Goldfarb–Shanno (L-BFGS) algorithm [11].
3. A variant of the Cambridge algorithm [10].

Electron or nuclear densities determined with these algorithms are comparable to each other in most cases. However, solutions obtained with the ZSPA algorithm do not satisfy true maximum-entropy (MaxEnt) conditions whereas the Cambridge algorithm always converges to solutions close to the true MaxEnt ones [22]. The L-BFGS algorithm, which also converges to true MaxEnt conditions, is usually faster than our implementation of the Cambridge algorithm in Dysnomia. Therefore, the Cambridge algorithm in Dysnomia is now regarded as obsolete.

2.4.1 ZSPA algorithm

In the ZSPA algorithm, ρ_k in the $(i+1)$-th iteration is approximated by

$$\rho_k^{(i+1)} = \frac{\rho_k^{(i)}}{Z} \exp\left(-\lambda \cdot \frac{\partial C}{\partial \rho_k^{(i)}}\right) \tag{2.21}$$

with

$$Z = \sum_{k=1}^{N_\mathrm{v}} \exp\left(-\lambda \cdot \frac{\partial C}{\partial \rho_k^{(i)}}\right). \tag{2.22}$$

If ΔF_j's are kept close to Gaussian distribution during MEM iterations, the order of C_{F_n} in the (i)-th iteration is roughly equal to $(C_{F_2})^{n/2}$. Hence, on the substitution of Eq. (2.18) for C in Eq. (2.21), only the C_{F_n} constraint with the highest order takes effect practically at the beginning of MEM iterations. To overcome such a problem and make results obtained with the ZSPA algorithm comparable to those with the Cambridge algorithm, λ_n in Eq. (2.18) in the i-th iteration is adjusted in such a way as

$$\lambda_n^{(i)} = \frac{\lambda_n}{(C_{F_2})^{n/2-1}}. \tag{2.23}$$

2.4.2 Limited-memory BFGS algorithm

The L-BFGS method [11] is a variant of quasi-Newton algorithms, requiring significantly less memory than other quasi-Newton methods. Instead of storing a dense $n \times n$ approximation (n: the number of variables in the problem) to the inverse Hessian matrix, L-BFGS stores only a few vectors that represent the approximation implicitly. Let $d_k = H_k g_k$ be the search direction at k-th iteration, where H_k is the inverse Hessian matrix of the function, $Q(\rho)$, to be maximized, $g_k \equiv \nabla Q(\rho)$ is the gradient of Q, $s_k = \rho_{k+1} - \rho_k$, $y_k = g_{k+1} - g_k$, and $r_k = 1/y_k^T s_k$. Then, d_k is computed as follows:

$q = g_k$

For $(i = k-1;\ i >= k-m;\ i--)\{$

$\quad \alpha_i = r_i s_i^T q$

$\quad q = q - \alpha_i y_i$

$\}$

$H_k^0 = \dfrac{y_{k-1}^T s_{k-1}}{y_{k-1}^T y_{k-1}}$

$d = H_k^0 q$

For $(i = k-m;\ i <= k-1;\ i++)\{$

$\quad \beta_i = r_i y_i^T d$

$\quad d = d + s_i(\alpha_i - \beta_i)$

$\}$

The initial approximate of the inverse Hessian matrix, H_k^0, is represented as a diagonal matrix. The Lagrange multipliers, λ and μ in Eq. (2.3), cannot be optimized simultaneously with ρ during the L-BFGS iterations. Then, in the L-BFGS method, λ and μ are gradually changed, and L-BFGS optimizations are repeated until the two constraints, *i.e.*, Eqs. (2.2) and (2.18), are fulfilled to achieve convergence. The convergence of the L-BFGS algorithm is judged by

$$\sum_{k=1}^{N_\mathrm{V}} \rho_k \left(\frac{\partial Q}{\partial \rho_k} \right)^2 < \varepsilon, \tag{2.24}$$

where ε is a small threshold value, which is set at 2×10^{-4} by default.

2.4.3 Cambridge algorithm

The Cambridge algorithm adopts local quadratic approximation to Eq. (2.3). For simplicity, Dysnomia utilizes only the diagonal elements of the Laplacian, $\nabla^2 Q$, and approximate $Q(\rho+\Delta\rho)$ by

$$Q(\rho + \Delta\rho) = Q(\rho) + \Delta\rho \left(\frac{\partial Q}{\partial \rho} \right) + \frac{1}{2} \Delta\rho^2 \left(\frac{\partial^2 Q}{\partial \rho^2} \right). \tag{2.25}$$

Then, Q can be optimized by

$$\Delta\rho_k = - \left(\frac{\partial Q}{\partial \rho_k} \right) \left(\frac{\partial^2 Q}{\partial \rho_k^2} + \alpha \cdot \frac{\partial^2 S}{\partial \rho_k^2} \right)^{-1}, \tag{2.26}$$

where α (≥ 0) is the damping factor to ensure that $\rho + \Delta\rho$ remains in the trust region of the quadratic approximation [10]. Convergence is judged by comparing the gradient of Eq. (2.3) with a small threshold value, ε:

$$\frac{1}{N_\mathrm{v}} \sum_{k=1}^{N_\mathrm{V}} \left(\frac{\partial Q}{\partial \rho_k} \right)^2 < \varepsilon. \tag{2.27}$$

The Cambidge algorithm gives solutions close to the true maximum-entropy (MaxEnt) conditions whereas the ZSPA algorithms affords solutions far from the MaxEnt conditions [22].

2.5 Fourier transform algorithms

In MEM analysis, $F(\boldsymbol{h}_j)$'s are calculated by Fourier transform, which is very time-consuming, from electron or nuclear densities, with a result that the CPU time for MEM analysis generally depends on both N and N_F. FFT makes it possible to process huge amounts of data with very large values of N and N_F at high speed. Therefore, Dysnomia benefits MEM analyses of crystalline materials with large unit cells and low symmetry. Dysnomia is also very suitable for analyzing neutron diffraction data where nuclear densities tend to be confined in narrower spaces.

In Dysnomia, FFT is selected if

$$N_{\mathrm{a}} N_F n_{\mathrm{c}} > \frac{100N}{\ln N}, \tag{2.28}$$

where N_{a} is the total number of voxels in the asymmetric unit, and n_{c} is a factor to be selected depending on the presence or absence of an inversion center at the origin (centrosymmetric: 1, noncentrosymmetric: 2).

Parallel computation

For small-scale problems, a DFT routine making full use of multi-threaded parallel processing with the OpenMP technology is automatically selected to avoid overhead caused by FFT. Thus, in both FFT and DFT, the processing ability of Dysnomia increases in a nearly linear fashion with increasing number of CPU cores on the use of recent multi-core CPUs.

Chapter 3

ADJUSTMENT OF STANDARD UNCERTAINTIES

3.1 Powder Diffraction Data (*.fos)

In powder diffraction, $\sigma(\boldsymbol{h}_j)$'s are estimated on the basis of the law of propagation of errors in combination with counting statistics:

$$\sigma(\boldsymbol{h}_j) = \frac{|F_{\rm o}(\boldsymbol{h}_j)|}{2}\left\{\left[\frac{1}{EI_{\rm o}(\boldsymbol{h}_j)}\right]^2 + \left[\frac{\sigma(s)}{s}\right]^2\right\}^{\frac{1}{2}}, \tag{3.1}$$

where E is the factor to adjust $\sigma(\boldsymbol{h}_j)$, $I_{\rm o}(\boldsymbol{h}_j)$ is the observed integrated intensity, s is the scale factor, and $\sigma(s)$ is the standard uncertainty of s [6]. Both s and $\sigma(s)$ results from Rietveld analysis or whole-pattern fitting with RIETAN-FP. E is selected in such a way that electron- or nuclear-density distribution which is physically and chemically reasonable results from MEM analysis. Convenient bash scripts, MPF_multi.command, for automatic MPF analyses enable us to change E as specified in *.prf (see 4.2.2).

In the case of angle-dispersive-type powder diffraction where the step width, $\Delta 2\theta$, is usually constant, E is approximately equal to $1/\Delta 2\theta$ (unit: rad^{-1}), which is output as `E(SCIO)` in *.lst by RIETAN-FP[1] [23]. On the other hand, E depends on the step width, Δt, of the time-of-flight (TOF) in TOF neutron powder diffraction; a utility called Alchemy [24, 25] can be used to convert files output by GSAS and Fullprof into *.fos or *.mem (see 3.2).

3.2 Single-Crystal Data (*.mem)

The estimation of $\sigma(\boldsymbol{h}_j)$ is difficult even in single-crystal X-ray or neutron diffraction; $\sigma(\boldsymbol{h}_j)$'s are often underestimated or overestimated. With Dysnomia, $\sigma(\boldsymbol{h}_j)$'s can be changed with the adjustment factor, E, according to

$$\sigma'(\boldsymbol{h}_j) = \frac{\sigma(\boldsymbol{h}_j)}{\sqrt{E}} \tag{3.2}$$

without any conversion of $\sigma(\boldsymbol{h}_j)$'s in *.mem.

[1] http://fujioizumi.verse.jp/download/download_Eng.html

Chapter 4

INSTALLATION AND EXECUTION OF DYSNOMIA

4.1 Installation

Dysnomia runs on Windows, OS X, and Linux. For Windows and Linux, both 32 and 64 bit versions are available for download from the Web site of JP-Minerals.[1] URLs of their files are as follows:

Windows
http://www.geocities.jp/kmo_mma/crystal/download/Dysnomia.zip

OS X, 64 bit application
http://www.geocities.jp/kmo_mma/crystal/download/Dysnomia.dmg

Linux, 32 bit application
http://www.geocities.jp/kmo_mma/crystal/download/Dysnomia-i686.tar.bz2

Linux, 64 bit application
http://www.geocities.jp/kmo_mma/crystal/download/Dysnomia-x86_64.tar.bz2

To install Dysnomia for Windows, extract one of the zip files and move the resulting files to C:\Program Files\RIETAN_VENUS\. In the case of OS X, mount Dysnomia.dmg by double-clicking its icon and move all the files to folder /Applications/RIETAN_VENUS/. Both versions can be run in combination with a shell script, MPF_multi.command, written in bash for MPF. MPF_multi.command and its manual are included in distribution files of the RIETAN-FP–VENUS package.

4.2 How to Run Dysnomia

4.2.1 Interactive data entry followed by MEM analysis

Run Dysnomia by double-clicking its icon or entering the name of its executable binary file in a command line. Then, the program asks questions that must be answered by the user. In what follows, these questions are represented by boxed texts with gray background.

[1] http://jp-minerals.org

```
# The name of the MEM data set file, *.fos or *.mem.
```

Type the absolute path of an input file, for example, C:\users\user_name\sample\sample.fos (Windows).

```
# The type of the MEM data set file.
# 0. (a) X-ray diffraction data or (b) neutron diffraction data of a compound
#    containing no element with a negative bc value.
# 1. Neutron diffraction data of a compound containing at least one element
#    with a negative bc value.
```

This option is set for the backward compatibility of input files because the file format of *.mem is different depending on dataset types.

```
# From which densities will you start?
# 0. Uniform densities.
# 1. Restart from densities recorded in the 3D densities file (*.pgrid).
```

If you choose the second option, initial densities are input from *.pgrid. This option is useful when you restart MEM analysis after precedent iterations. Note that this option is different from the choice of prior density τ_k in Eq. (2.1) in strict sense, although on the use of ZSPA algorithm, use of non-uniform prior is approximated by restarting calculation from τ_k. For rigorous analyses using non-uniform prior, use L-BFGS or Cambridge algorithms and specify the prior data on the later question. MEM analysis can only be restarted from densities recorded in *.pgrid output by Dysnomia.

```
# Optimization algorithm.
# 0. 0th order single-pixel approximation (ZSPA).
# 1. The Limited-memory BFGS algorithm (L-BFGS).
# 2. The Cambridge algorithm (Obsolete).
```

Read 2.4 for details in the above two algorithms.

```
# Which initial Lagrangian multiplier will you use (LM_type)?
# 0. The value input by user.
# 1. The value calculated by Dysnomia.
# 2. The value written in the MEM data set file.
```

This question appears only on use of the ZSPA algorithm, and option 2 appears only when the format of the MEM dataset file is *.mem.

```
# The initial Lagrangian multiplier, lambda
```

This question is asked only when 0 is input in the previous question.

```
# A parameter x to impose weighting factors on the basis of
# lattice-plane spacing.
```

Parameter x is included in Eq. (2.20). Input $x = 0$ in classical MEM analysis where no weight is imposed in the F constraint. If $x > 0$, it is regarded as x in Eq. (2.20). As described in 2.3, typically $x = 0$ in neutron diffraction, $x = 1$–2 in X-ray powder diffraction, and $x = 4$ is optimum in single-crystal X-ray diffraction.

```
# The coefficient, t, to adjust the Lagrangian multiplier.
```

This question appears only on use of the ZSPA algorithm. Input a value between 0.05 and 0.1 for fast computation. If λ is too large, MEM iterations diverge and never reach the solution. If λ is too small, the convergence of the MEM equation is ensured whereas the computation time may increase considerably, with no convergence achieved on specification of a relatively small maximum number of cycles. The coefficient t allows us to find the best λ value automatically through multiplying λ by $1 + t$ in every cycle of MEM iterations until λ becomes too large to converge the MEM equation, which is different from the manner of changing λ in PRIMA [9].

```
# The coefficient, E, to adjust estimated standard uncertainty of
# structure factors.
```

For details in E, see 3.1 and 3.2.

```
# Will you save a feedback data file?
# 0. Yes (output only individual F data).
# 1. Yes (output all the F data including those for grouped reflections
#    and estimated for unobserved reflections).
# 2. No.
```

In MPF, option 1 is usually selected to include $F(\boldsymbol{h}_j)$'s of high-Q reflections whose profiles are partly lacking.

```
# Will you save a e(GAUSS) distribution data file?
# 0. Yes (raw data file, *_eps.raw).
# 1. No.
```

When option 0 is selected, a text file storing histogram of

$$\frac{|F_{\mathrm{o}}(\boldsymbol{h}_j)| - |F(\boldsymbol{h}_j)|}{\sigma(\boldsymbol{h}_j)}$$

will be output. See also section 5.2.

```
# Fractions of lambda for generalized constraints.
# (8 parameters; l_2, l_4, l_6, l_8, l_10, l_12, l_14, l_16)
```

Eight parameters, λ_n ($n = 2 - 16$), for the fractions of generalized constraints with orders of n (see 2.2.4).

```
# Which prior densities will you use?
# 0. Uniform densities.
# 1. Densities recorded in the 3D densities file (*_prior.pgrid).
```

This option appears only on the use of the L-BFGS and Cambridge algorithm. When option 1 is selected, τ_k in Eq. (2.1) will be read in from 3D densities file. To use non-uniform prior densities in the ZSPA algorithm, restart the calculation using a 3D data file (*.pgrid) storing prior densities.

```
# Will you save a preferences file?
# 0. No.
# 1. Yes (*.prf is output).
```

If *.prf is output, all the above parameters are stored in it and it can be reused as a template file for subsequent MEM analyses.

After answering all the questions, the conditions of MEM analysis are displayed in the screen. Before starting MEM iterations, Dysnomia asks the maximum number of iterations.

```
# Maximum number of cycles.
```

The iterations will continue until the convergence is achieved (CONSTR $\leq$ 1). When the convergence is reached, Dysnomia terminates after outputting CPU times.

4.2.2 Running Dysnomia to input *.prf

If the entire conditions of MEM calculations in `filename.prf` have already been input by modifying a template file with a text editor, Dysnomia can be executed in several different ways.

Let the name of *.prf be sample.prf. Then, Dysnomia can be run from the command line by typing

```
Dysnomia sample.prf
```

to read in sample.prf. When no environment variable PATH is set to a directory under which the program is placed, type the full path of the program, *e.g.*,

```
"C:\Program Files\RIETAN_VENUS\Dysnomia.exe" sample.prf
```

if Dysnomia.exe is stored in folder "C:\Program Files\RIETAN_VENUS\" on Windows. Of course, sample.prf has to be placed in the current folder in the above case. A simple batch file (Windows) or a shell script (OS X or Linux) where such a command is recorded would be more convenient.

The most practical and convenient way of carrying out MPF by Dysnomia is the use of MPF_multi.command because E in Eq. (3.1) can be automatically changed during a series of MPF analyses. For details in this bash script, read the manuals of MPF_multi.command, MPF_multi_Win.pdf (Windows) or MPF_multi_Mac.pdf (OS X), included in a distribution file, documents.zip.[2]

[2] http://fujioizumi.verse.jp/download/download_Eng.html

Chapter 5

INPUT AND OUTPUT FILES

5.1 Input Files

- *.mem: (a) Single-crystal data or (b) powder data where standard uncertainties of observed structure factors are given.
- *.fos: Powder data compatible with PRIMA [3].
- *.prf: An input file storing all the conditions of MEM calculations. This file keeps backward compatibility with PRIMA while some new parameters are added for new features in Dysnomia.

***.mem and *.fos**

A line to give values (`POP1`, `POP2`, `IPTYP`, `JPH`, `JPK`, and `JPL`) related to preferred orientation is currently a dummy one. Never analyze powder diffraction data where preferred orientation was observed.

Grid numbers along a, b, and c axes should be selected in such a way that symmetry elements such as mirrors, rotation axes, and inversion centers coincide with intersections of grid lines. In addition, the grid numbers must be appropriately set by considering lattice parameters, a, b, and c. On the use of FFT, the best performance is achieved when division number along each axis is represented as

$$2^p \times 3^q \times 4^r \times 5^s \times 7^t \times 11^u \times 13^v,$$

where p, q, r, s, t, u, and v are integers equal to or larger than 0. Any other integers are also allowed; the calculation time is proportional to $N \log N$ even for prime numbers of N.

Beware that the sum, T^-, of negative b_c's in the unit cell should be set at 0.0 even if the sample contains no element with a negative b_c value, *e.g.*, H, Li, Ti, or Mn.

In a solid solution where two or more elements occupy the same site, a special procedure is required for calculating the sum, T^+, of positive b_c's and/or the sum, T^-, of negative b_c's in the unit cell [26]. Suppose a virtual chemical species with an average coherent-scattering length, $\bar{b}_c$, calculated from the occupancies of the constituent elements. Then, add $\bar{b}_c$ multiplied by the number of the virtual chemical species in the unit cell to T^+ if $\bar{b}_c > 0$ or T^- if $\bar{b}_c < 0$.

With Alchemy [24], text files with the following two formats can be obtained from output files, *.lst, of GSAS:

***.fos**

Regardless of `ID(neg.)`, both positive and negative values of total scattering amplitudes are always input. If `ID(neg.)` = 0, the second amplitude must be 0.0 (dummy).

***.mem**

If `ID(neg.)` = 0, only a positive total scattering amplitude is input, followed by λ in the same line. If `ID(neg.)` = 1, both positive and negative values of total scattering amplitudes are input, followed by λ as well.

***.prf**

The content of *.prf storing various flags and specifications for MEM analysis is described in 4.2.1, and execution of Dysnomia and the subsequent input of *.prf in 4.2.2.

5.2 Output Files

***.out**

The standard output file of Dysnomia.

***.pgrid**

Three-dimensional voxel data storing electron or nuclear densities in a binary format. The content of thiis file can be visualized in three dimensions using VESTA [18] together with a crystal-structure model if necessary. Note that Dysnomia outputs no text files, *.den, storing 3D densities.

***.fba**

A list of structure factors calculated by Fourier transform from electron/nuclear densities resulting from MEM analysis. This file is used by RIETAN-FP [27] for whole-pattern fitting in MPF [3–5].

***.raw**

A text file storing histogram of the difference between the absolute $F_\mathrm{o}(\boldsymbol{h}_j)$ and $F(\boldsymbol{h}_j)$ values divided by the standard uncertainty, $\sigma(\boldsymbol{h}_j)$, of $|F_\mathrm{o}(\boldsymbol{h}_j)|$ to give a sample of the random variable with normalized Gaussian distribution, ϵ(Gauss) [17]:

$$\epsilon(\mathrm{Gauss}) = \frac{|F_\mathrm{o}(\boldsymbol{h}_j)| - |F(\boldsymbol{h}_j)|}{\sigma(\boldsymbol{h}_j)} \qquad (j = 1\text{–}N_F).$$

This file is useful for evaluating distribution of errors resulting from MEM analysis.

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