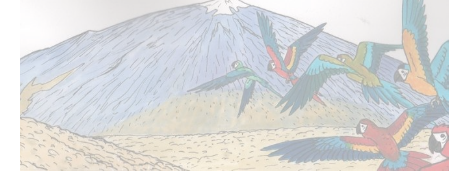
The “incoherent approximation”
The “phonon expansion”

Estimate S(q,ω) from nearly nothing ?

E. Farhi, ILL.



Background - Old stuff !

- Most inelastic neutron scattering fundamental theory was written in the 50'-70':

  → Sears, Sjölander, Egelstaff, van Hove, Squires, Oskotskii, Sköld, Carpenter, Schober ...

- Nothing really new since then.

- Remains in the text books, old software is deprecated. Not used much these days.
- Let's recap these concepts...

NEUTRONS FOR SOCIETY

The "generalised" density of states

- The generalised density of states (gDOS) formalism states that it is possible to write an "effective" density of states from a complex material made of *d* species with "partial" vDOS g_d:

$$\frac{\sigma}{m} G(\omega) = \sum_d \frac{\sigma_d}{m_d} g_d(\omega)$$

- It is often named "neutron weighted density of states"

- The gDOS (meas. average) is ***NOT*** the vDOS.

- *Reminder*: $g(\omega)$ density of modes in $[\omega, \omega + d\omega]$

Density of states estimate

- Carpenter/Bellisent/Egelstaff:

$$g(\omega) \approx \lim_{Q \to 0} \frac{\omega}{(n(\omega)+1) Q^2} S_{inc}(Q,\omega) \approx \lim_{Q \to 0} \frac{\omega^2}{Q^2} S_{inc}(Q,\omega)$$

Cons: Measurement never reaches Q→0, and only use the smallest angle data (low statistics).

- Bredov/Oskotskii:

$$g(\omega) \approx \frac{\omega \int Q\, S(Q,\omega)\, e^{2W(Q)}\, dQ}{[Q_{max}^4 - Q_{min}^4][n(\omega)+1]}$$

Pros: Use the whole data set, integrated over the instrument dynamic range (higher statistics).

iFit: ‘dos’ method for Sqw2D

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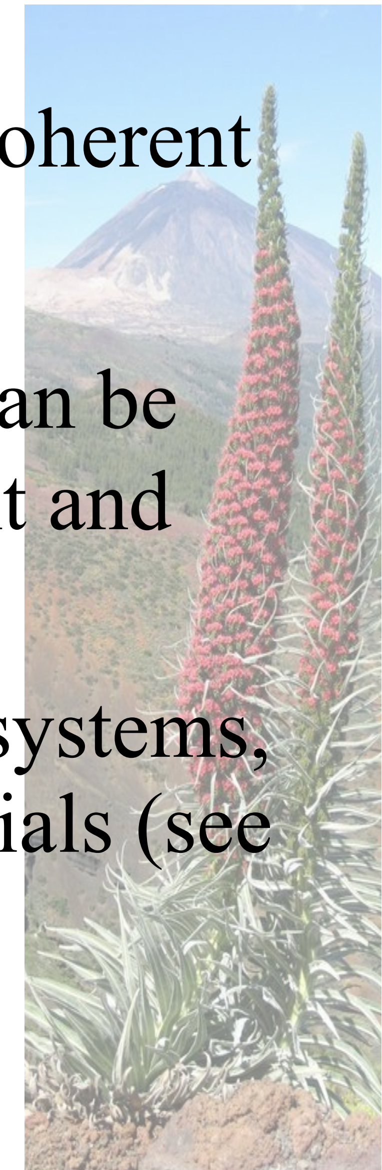
The "incoherent approximation"



- The integrated $\int dQ$ or $d\theta$ incoherent and coherent contributions are roughly equal (apart σ).
- **Consequence**: the density of states $g(\omega)$ can be obtained equally from coherent, incoherent and total scattering. Better use "Bredov".
- **Limitation**: Exact for cubic monoatomic systems, can be extended to isotropic density materials (see gDOS).
- See: Oskotskii (1967)

NEUTRONS FOR SOCIETY

Scattering law, harmonic

- The scattering law can be written:

$$S(\vec{Q},\omega) = \sum_{\kappa,\kappa'} b_\kappa b^*_{\kappa'} S_{\kappa,\kappa'}(\vec{Q},\omega)$$

σ

with partials:

$$S_{\kappa,\kappa'}(\vec{Q},\omega) = \frac{1}{2\pi\hbar} \sum_{j\in\{j_\kappa\},j'\in\{j_{\kappa'}\}} \int_{-\infty}^{\infty} \mathrm{d}t \langle \mathrm{e}^{-\mathrm{i}\vec{Q}\cdot\vec{\mathbf{R}}_{j'}(t=0)} \mathrm{e}^{\mathrm{i}\vec{Q}\cdot\vec{\mathbf{R}}_j(t)} \rangle \mathrm{e}^{-\mathrm{i}\omega t}$$

autocorrelation of displacements

- Writing $\boldsymbol{R}=\boldsymbol{R}_0+\boldsymbol{u}$, we can expand S.

Equil. Small displ. (harmonic)

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Scattering law, harmonic

$$S_{\kappa,\kappa'}(\vec{Q},\omega) = \frac{1}{2\pi N\hbar} \sum_{j\in\{j_\kappa\},j'\in\{j_{\kappa'}\}} \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{e}^{-\mathrm{i}\vec{Q}\cdot(\vec{R}^0_{j'}-\vec{R}^0_j)} \mathrm{e}^{-W_{j'}(\vec{Q})} \mathrm{e}^{-W_j(\vec{Q})} \mathrm{e}^{\aleph_{j',j}(\vec{Q},t)}$$

Structure

Average motions

Dynamics

- Debye-Waller function $2W_j(\vec{Q}) = \langle(\vec{Q}\cdot\vec{u}_j)^2\rangle$
- Motion correlations: $\aleph_{j',j}(\vec{Q},t) = \langle(\vec{Q}\cdot\vec{u}_{j'})(\vec{Q}\cdot\vec{u}_j(t))\rangle$

DON'T PANIC (yet)

NEUTRONS FOR SOCIETY

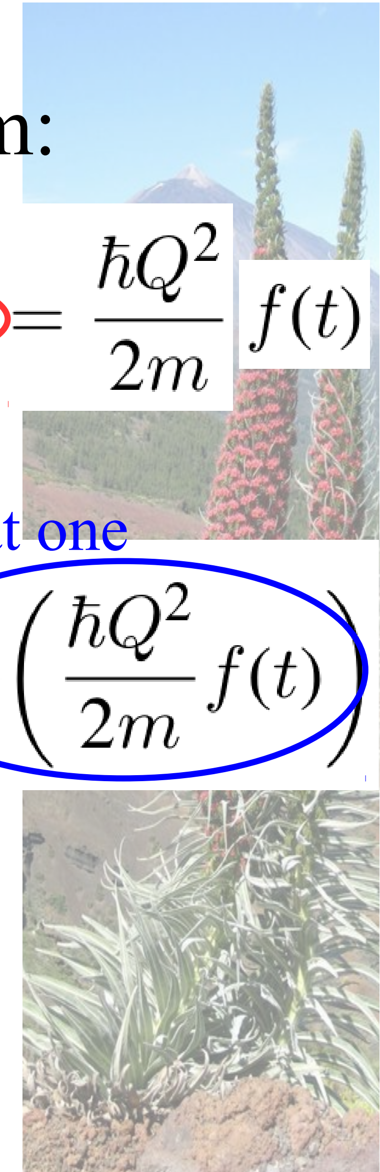
Scattered intensity (interlude)

- Of course, the scattered intensity (differential cross section) is as usual:

$$\frac{\mathrm{d}^2\sigma_{\vec{k}_i \rightarrow \vec{k}_f}}{\mathrm{d}\Omega\,\mathrm{d}E_f} = \frac{k_f}{k_i} S(\vec{Q},\omega)$$

- Monoatomic system: $S(Q,\omega) = \sigma\, S_{k,k}(Q,\omega)$
- We usually only consider the 1st term in $\aleph$.

S(Q,w) harmonic isotropic incoherent



- For a harmonic isotropic incoherent system:

$$\aleph_{j,j}(\vec{Q},t) = \frac{\hbar Q^2}{2m} \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{g(\omega)}{\omega} \cdot (n(\omega)+1) \cdot \exp(\mathrm{i}\omega t) = \frac{\hbar Q^2}{2m} f(t)$$

f(t)

- And:

Look at that one

$$S(\vec{Q},\omega) = \frac{\sigma_{\mathrm{inc}}}{4\pi} \frac{N}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}t e^{-\mathrm{i}\omega t} \exp(-2W(\vec{Q})) \cdot \exp\left(\frac{\hbar Q^2}{2m} f(t)\right)$$

Average motions

- See: Sjölander (1958)

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The "phonon expansion"

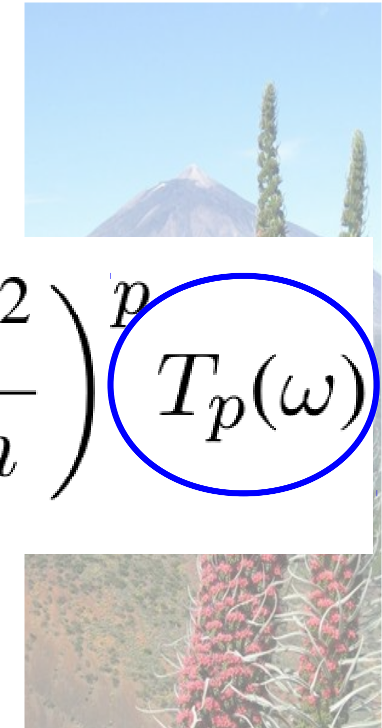
- We develop the last *exp[f(t)]* term in Taylor series → "**phonon expansion**"

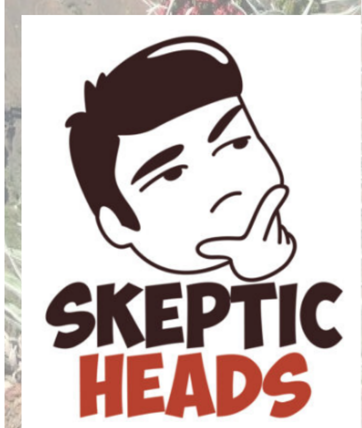
$$S(\vec{Q},\omega) = \frac{\sigma_{\mathrm{inc}}}{4\pi} N \exp\left(-2W(Q)\right) \sum_{p=0}^{\infty} \frac{1}{p!} \left(\frac{\hbar Q^2}{2m}\right)^p T_p(\omega)$$

T_p obtained recursively

$$T_1(\omega) = \frac{g(\omega)}{2\hbar\omega}\left(\coth\left(\frac{\hbar\omega}{2kT}\right)+1\right)$$

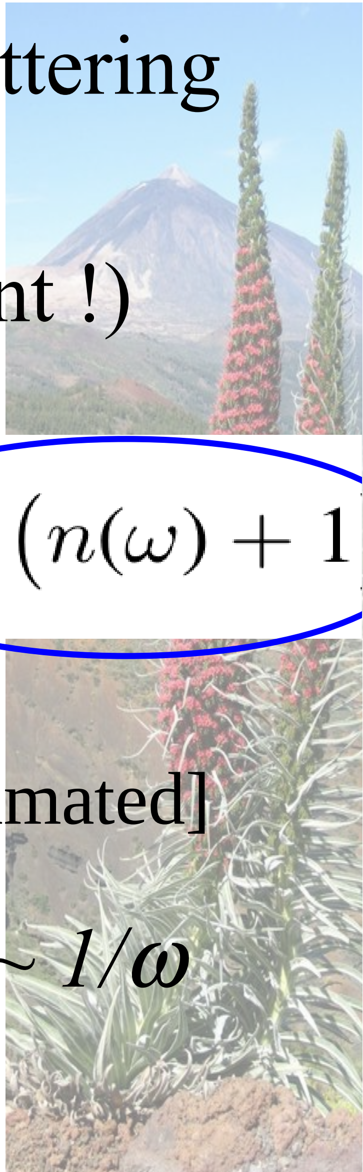
$$T_p(\omega) = T_1(\omega) * T_{p-1}(\omega)$$





- The "phonon" terminology comes from the fact that initially, the partial $S_{K,K'}$ includes both coherent and incoherent processes, and the high order terms correspond to **multi-phonons**.
- Phonons in an incoherent scatterer is somewhat odd.

Let's keep calm



- The *p=0* term is the Elastic Incoherent Scattering Function (EISF) → DW.
- The *p=1* term is the one-phonon (incoherent !) response:

$$S_{(p=1)}(\vec{Q},\omega) = \frac{N}{8\pi} Q^2 \frac{\sigma_{\text{inc}}}{m} \exp\left(-2W(\vec{Q})\right) \frac{g(\omega)}{\omega}\left(n(\omega)+1\right)$$

$T_1(\omega)$

- $2W(Q) = hQ^2/2m \int T_1(\omega)\, d\omega$ [often over estimated]
- For $Q \rightarrow 0$, Debye-Waller → 1. As $n(\omega)+1 \sim 1/\omega$ we get an estimate of $g(\omega)$ from $S(Q,\omega)$:

$$\lim_{Q\to 0} S(Q,\omega) \approx \frac{Q^2}{\omega^2} g(\omega)$$

[Bellissent-Funel 1991]

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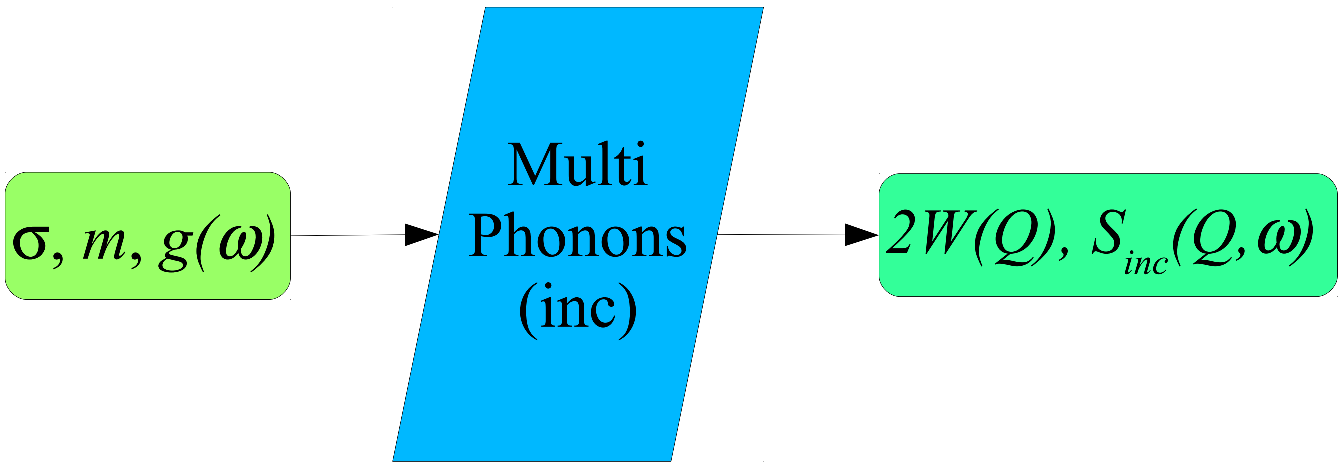
How to use this…

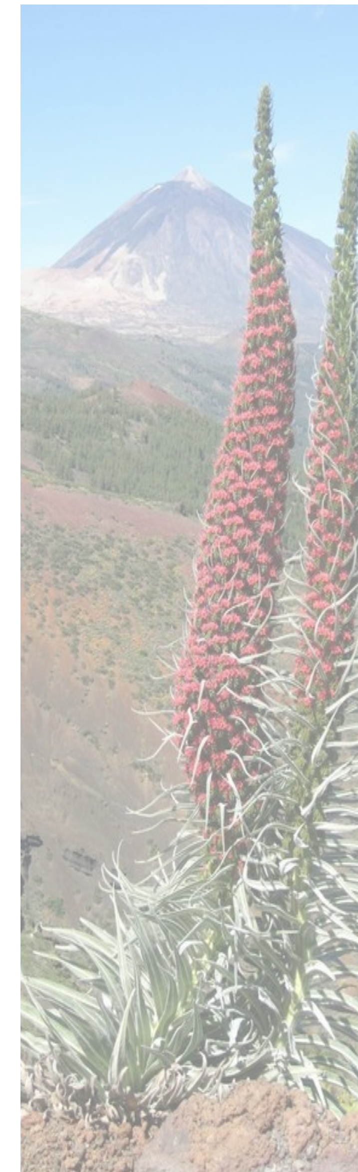
Input: σ, *m*, *g(ω)* , [optional: DW]

Output: Debye-Waller estimate $2W(Q)$, $S_{inc}(Q,\omega)$

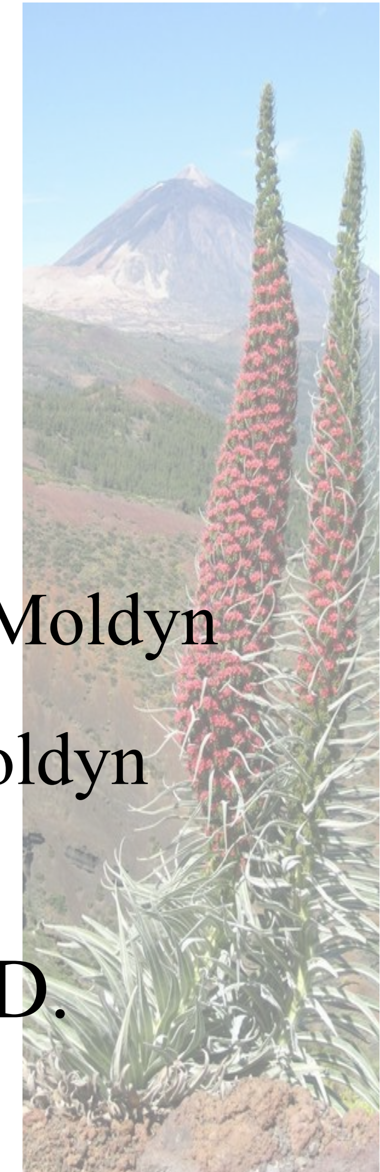


iFit: ‘incoherent’ method for vDOS

Older code 1D: MUPHOCOR, LAMP



Does it work ?



- Monoatomic isotropic material: *l*-Al
- Can simulate liquid dynamics using DFT:
  - 200 atoms in a box, PAW PBE
  - 12000 MD steps of 3fs, T=1300 K $\rightarrow \boldsymbol{R}(t)$
  - Compute $S_{inc}(q,\omega)$ $S_{coh}(q,\omega)$ using MDANSE/nMoldyn
  - Compute the vDOS $g(\omega)$ using MDANSE/nMoldyn
- Compute the incoherent from the vDOS and compare with the 'true' $S_{inc}(q,\omega)$ from the MD.

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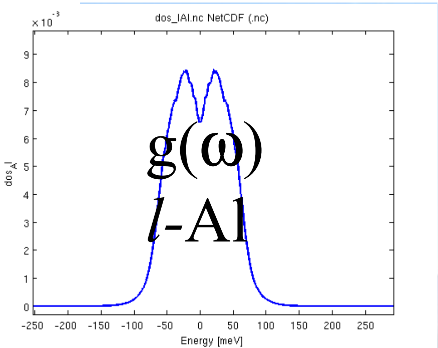
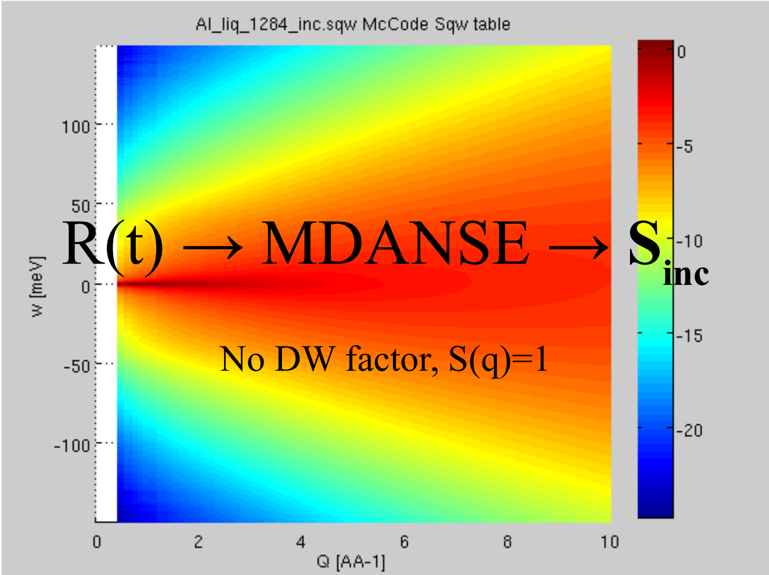
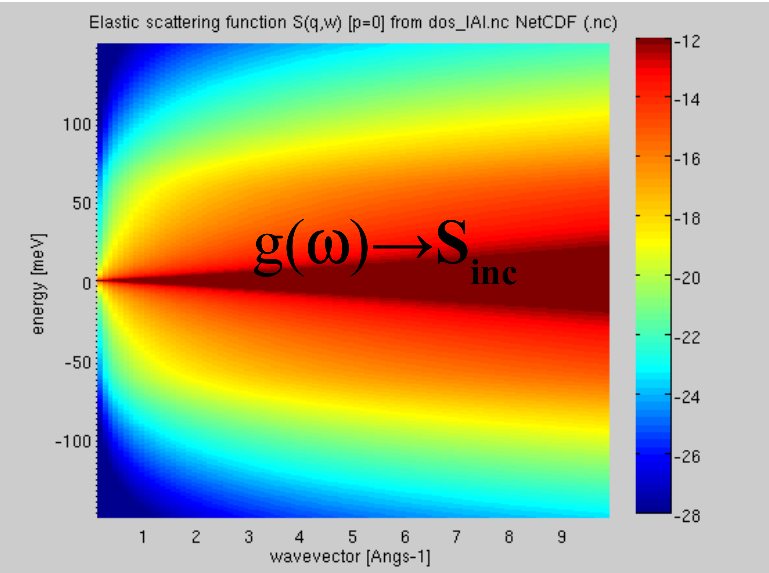
Incoherent liq-Al: approximation

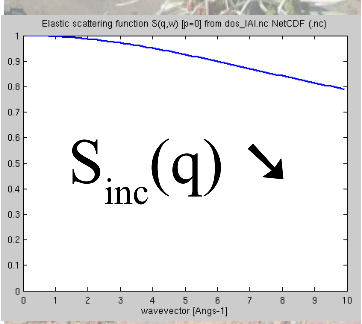
- ***R(t)* → *MDANSE* → $S_{inc}(Q,w)$**
- ***R(t)* → MDANSE → g(ω)**
- iFit:
  - g=iData_vDOS('dos-lAl.nc');
  - Sinc=plus(**incoherent**(g,'T',1300,**'DW'**,**0.01**, 'm',27));





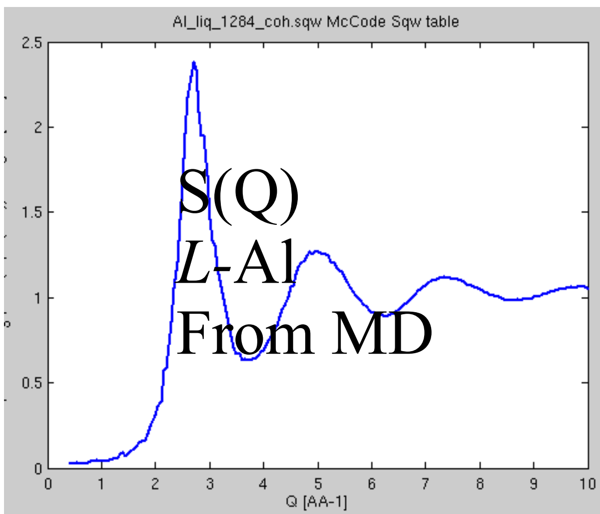
Not perfect, but ...





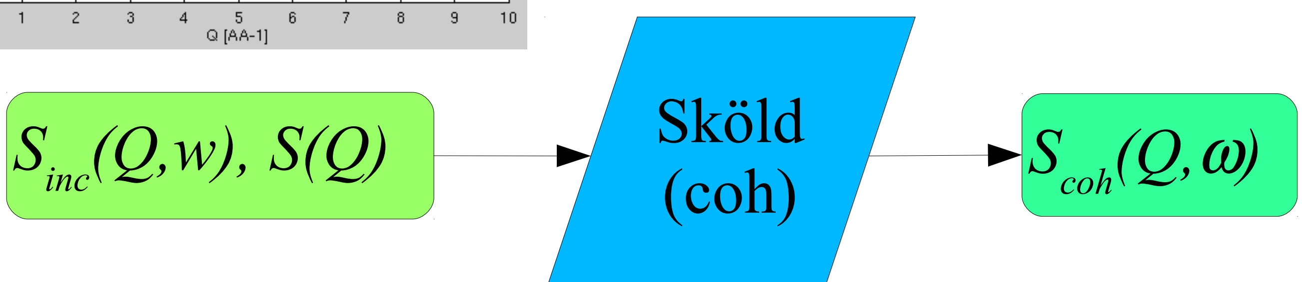
What about the coherent ?

- *Al* is a coherent scatterer
- Phenomenological guess [Sköld 1967]

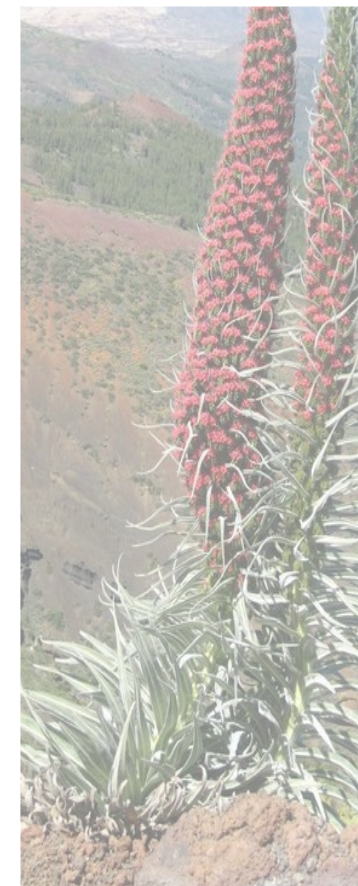


$$S_{coh}(Q,\omega)=S(Q)\,S_{inc}\left(\frac{Q}{\sqrt{S(Q)}},\omega\right)$$

Structure is 'forced' in.

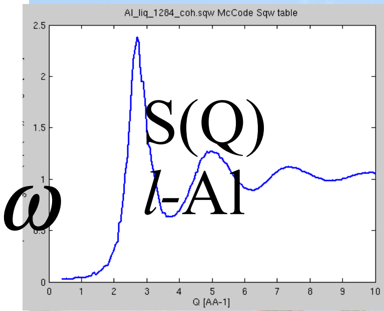


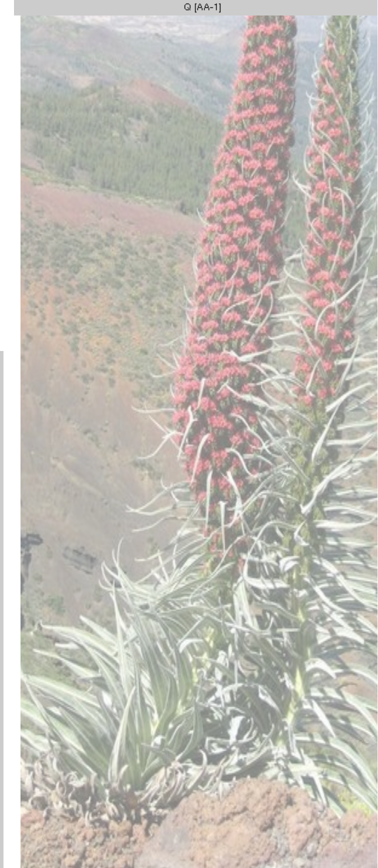
iFit: 'coherent' method for Sqw2D

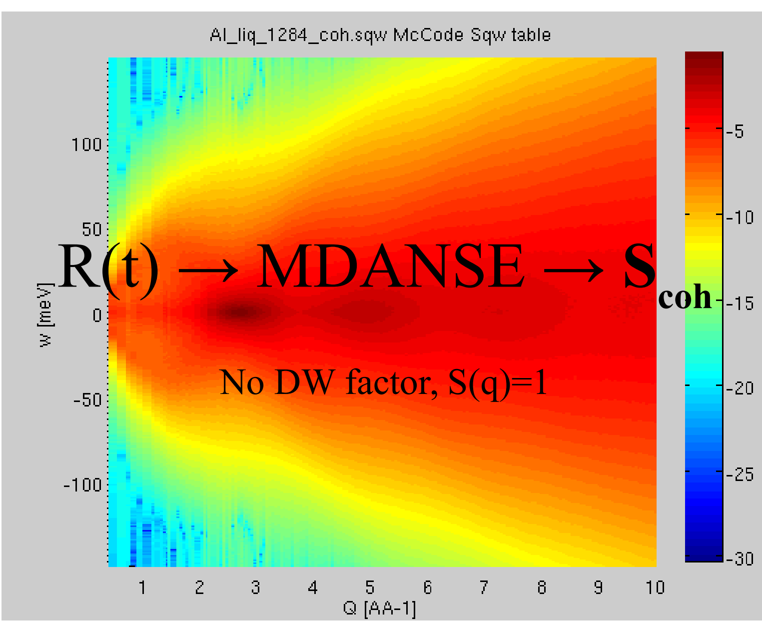


Coherent liq-Al: approximation

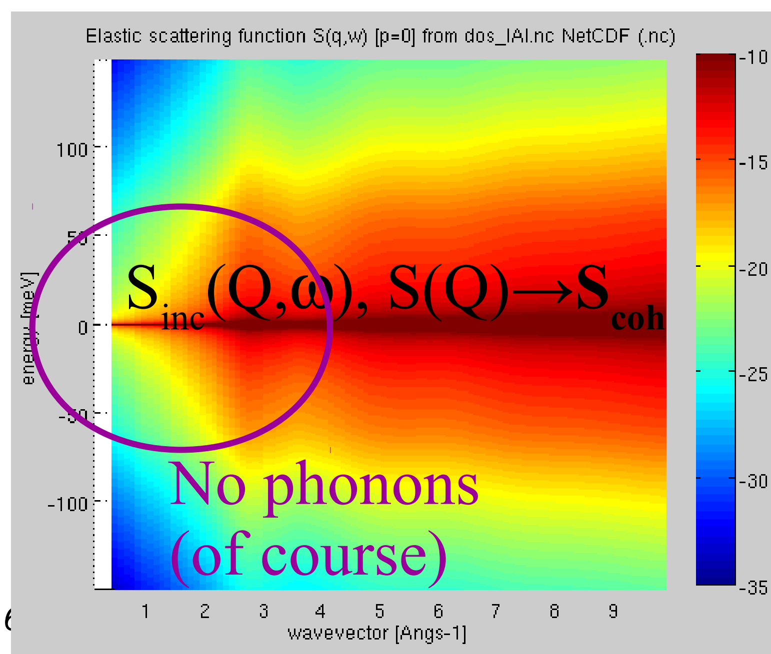
- $\boldsymbol{R}(\mathrm{t}) \rightarrow$ MDANSE $\rightarrow S_{coh}(Q,w)$
- $\boldsymbol{R}(t) \rightarrow$ MDANSE $\rightarrow S(Q)$ or $\int S_{coh}(Q,\omega)\, d\omega$
- iFit:
  - Sq=iData('Sq-lAl.nc');
  - Scoh=**coherent**(Sinc, Sq);







Not perfect, but ...



Partial summary

- If we have an estimate for the vDOS, we can compute the S_{inc} with a reasonable agreement.
  - This is the foundation for NJOY/LEAPR. $g(\omega)$ can be estimated from neutron ToF experiment, MD and lattice dynamics (solids). Search literature !
- If in addition we have an estimate for the structure $S(Q)$, we can also get S_{coh}.

WARNING: Not perfect, but we get it from very limited information.

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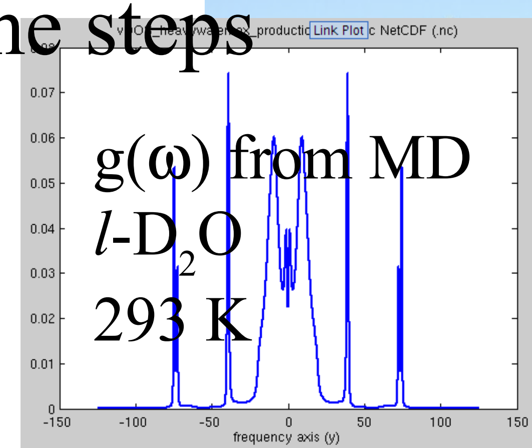
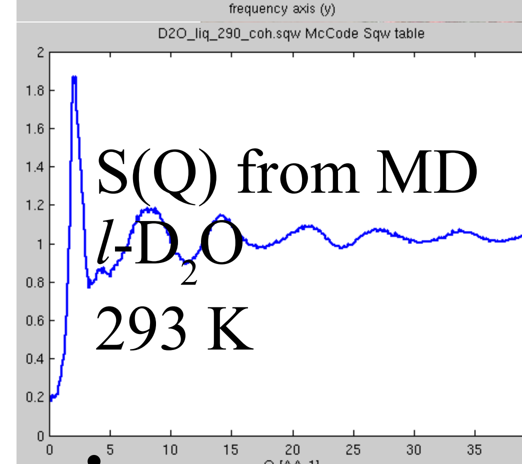
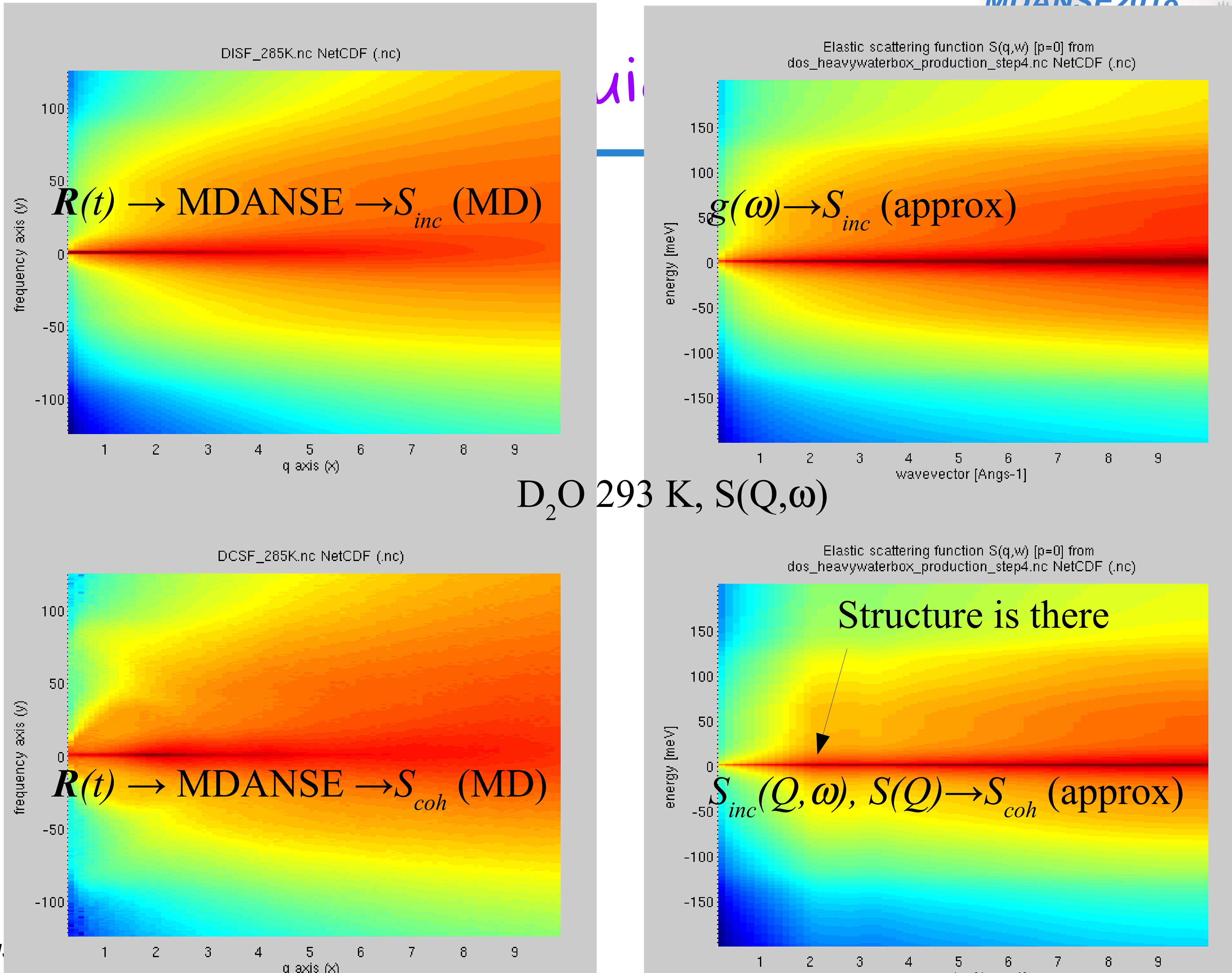
More complex: water (liquid)

- GROMACS 4000 D_2O, MD 2500 time steps
- $\boldsymbol{R}(t)$→MDANSE→$g(\omega)$→S_{inc}
- Compare with S_{inc} from MD
- Get $S(Q)$ from MD
- Estimate S_{coh} from [S_{inc} and $S(Q)$]





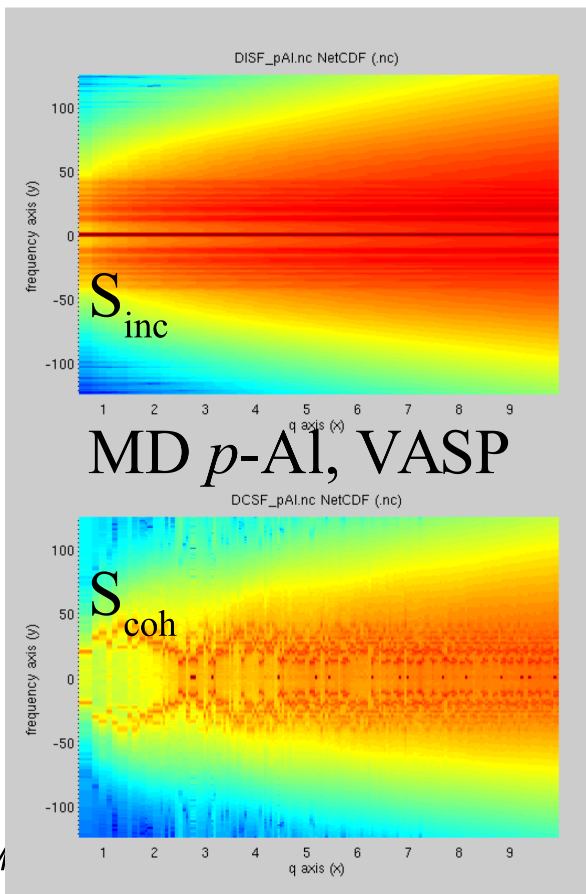
- WARNING: not exact: **non monoatomic**

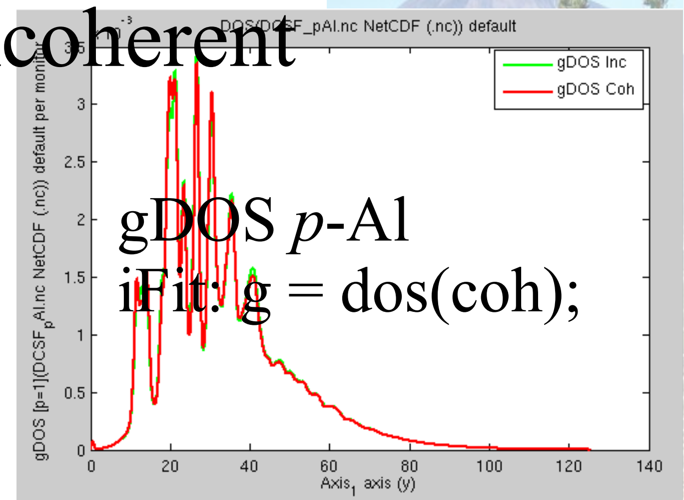

DISF_285K.nc NetCDF (.nc)
frequency axis (y)
q axis (x)
$R(t) \rightarrow$ MDANSE $\rightarrow S_{inc}$ (MD)
Elastic scattering function S(q,w) [p=0] from dos_heavywaterbox_production_step4.nc NetCDF (.nc)
energy [meV]
wavevector [Angs-1]
$g(\omega) \rightarrow S_{inc}$ (approx)
DCSF_285K.nc NetCDF (.nc)
frequency axis (y)
q axis (x)
$R(t) \rightarrow$ MDANSE $\rightarrow S_{coh}$ (MD)
Elastic scattering function S(q,w) [p=0] from dos_heavywaterbox_production_step4.nc NetCDF (.nc)
energy [meV]
Structure is there
$S_{inc}(Q,\omega)$, $S(Q) \rightarrow S_{coh}$ (approx)

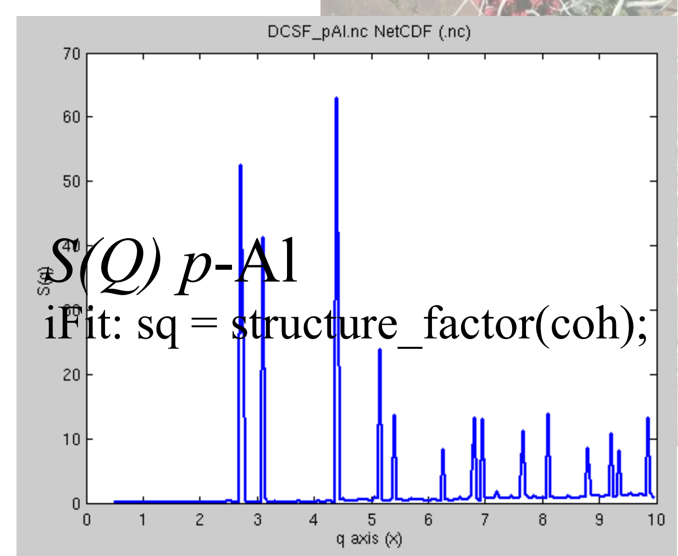
D_2O 293 K, S(Q,ω)

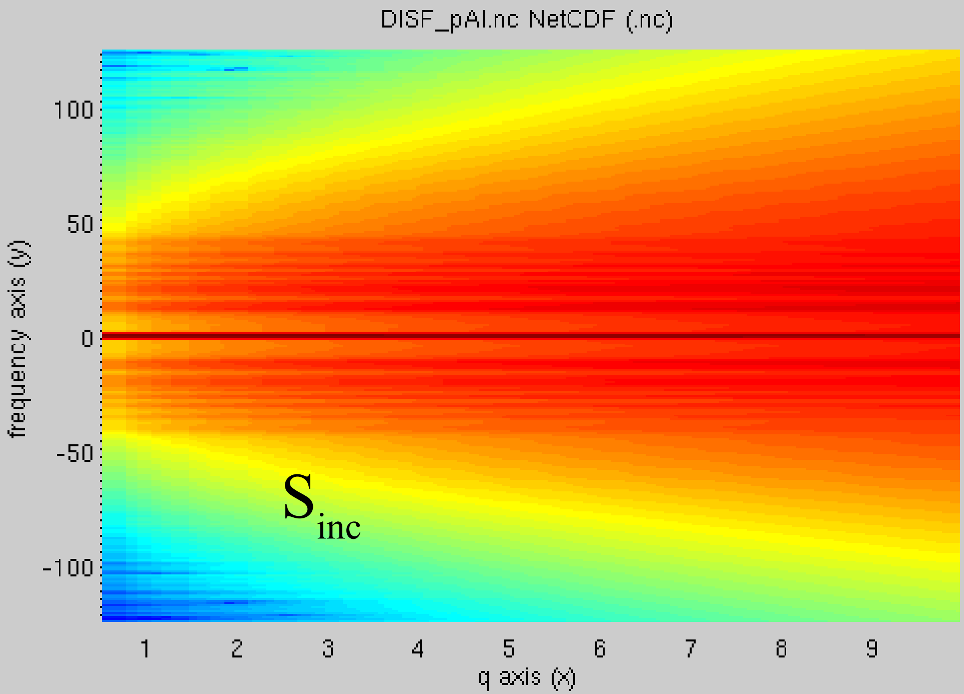
Powders (solid, isotropic)

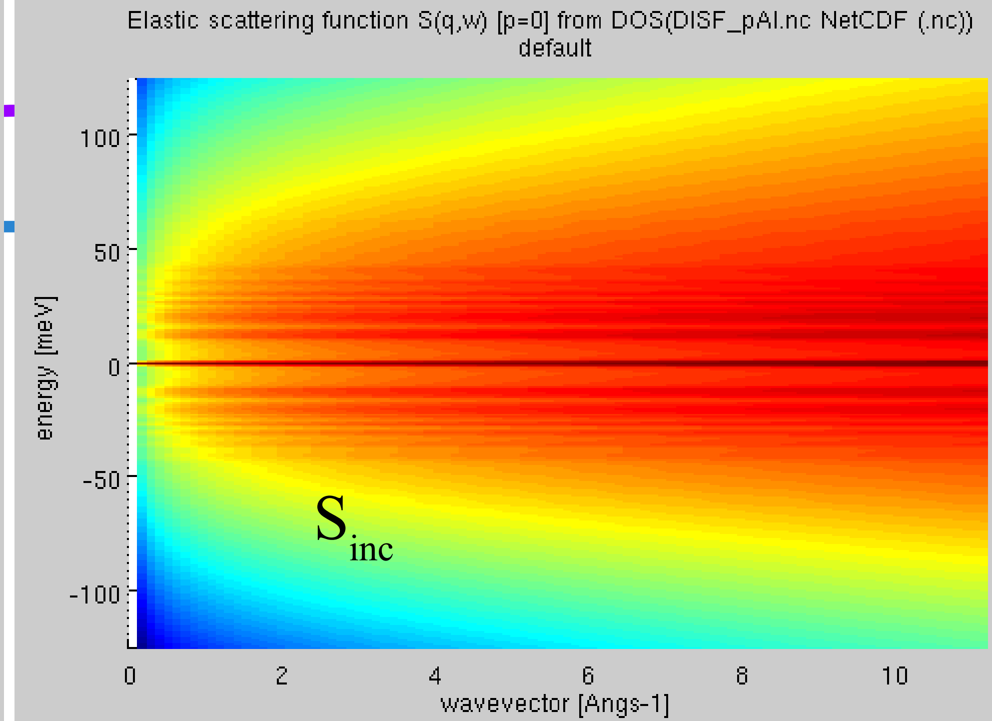
- VASP 200 Al atoms, PAW PBE. MD 300 K.
- Check for gDOS: coherent and incoherent estimates are equal (Bredov).





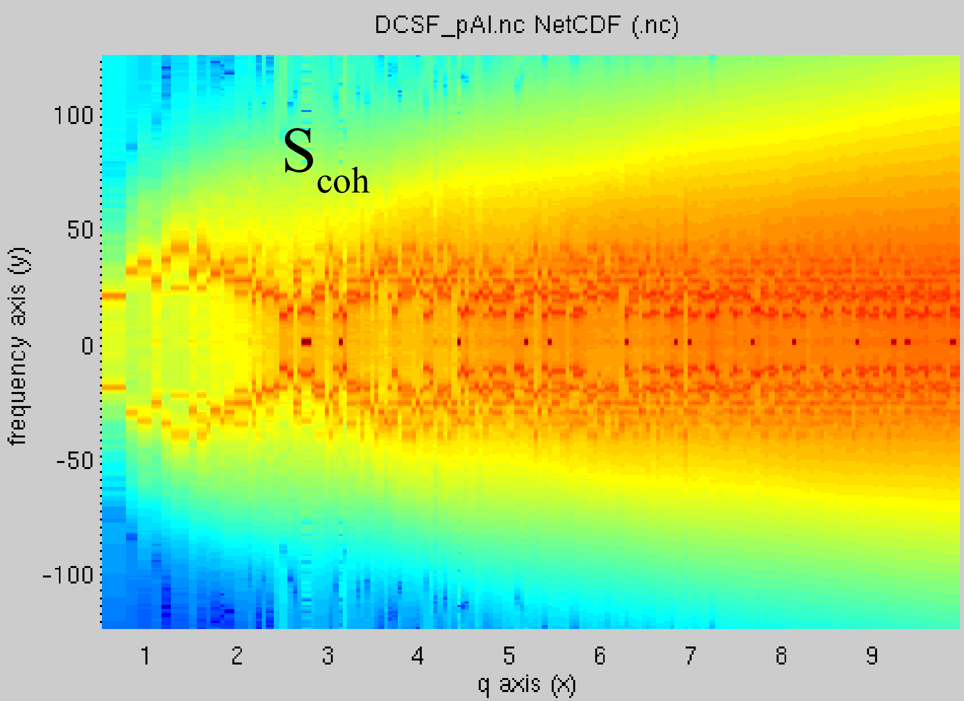


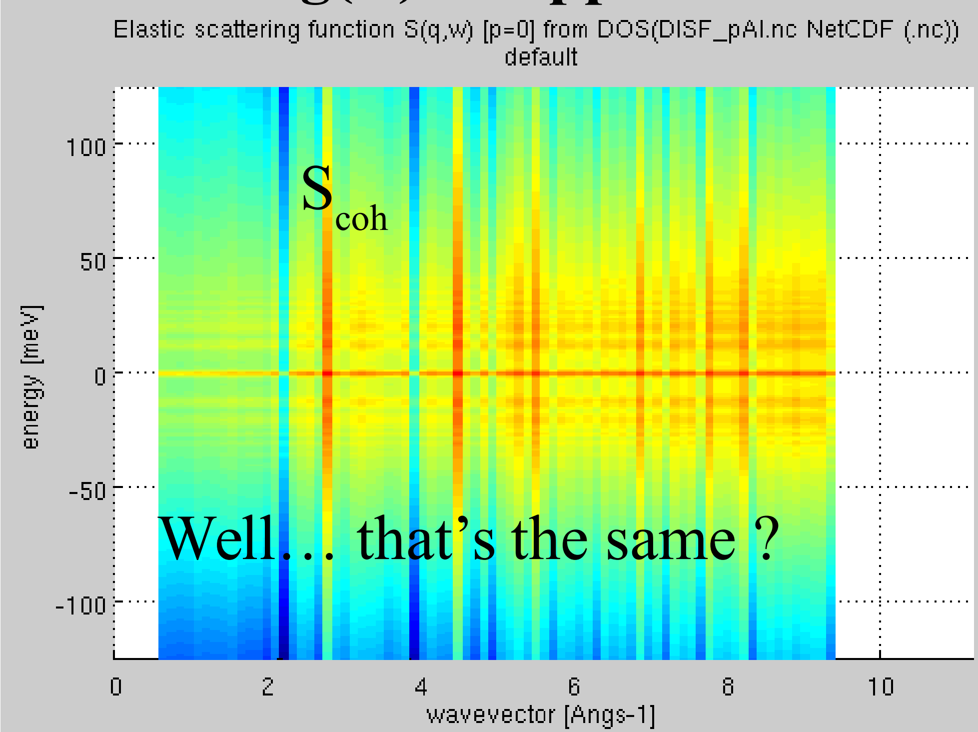




MD *p*-Al, VASP

g(ω) → approx





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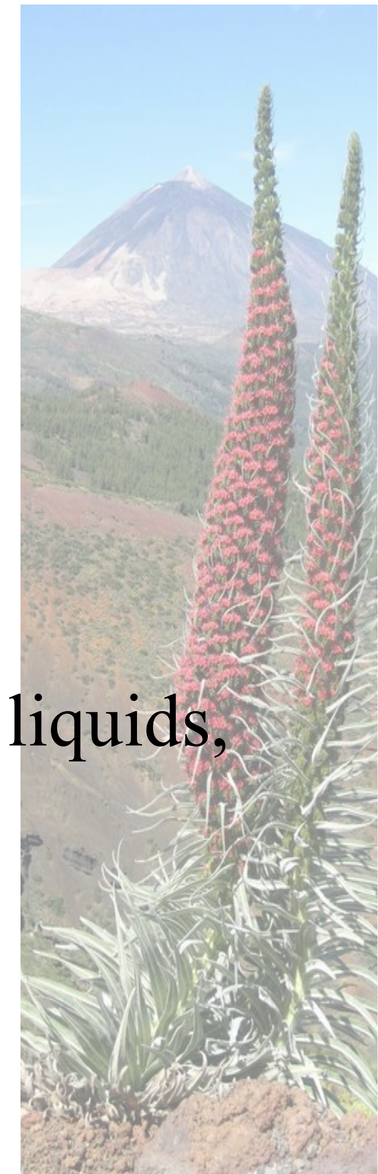
Validity: Pros



- Pros:
  - Requires minimal info: $g(\omega)$, $S(q)$
  - Very fast to compute.
  - Applicable to any isotropic material.
  - Not meant to be exact (strong hypothesis).
  - Acceptable results when nothing else exists: liquids, amorphous, powders, gases

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Validity: Cons

- Cons:
  - Does not reconstruct low Q dynamics (phonons, …).
  - Structure is forced in, but does not satisfy De Gennes narrowing (narrow at Bragg peaks).
  - Incoherent estimate better than coherent one.
  - Would require partial g(ω) and S(Q) per atom to improve accuracy.
  - Assumes cross terms $S_{KK'}$ are null.

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Applicability

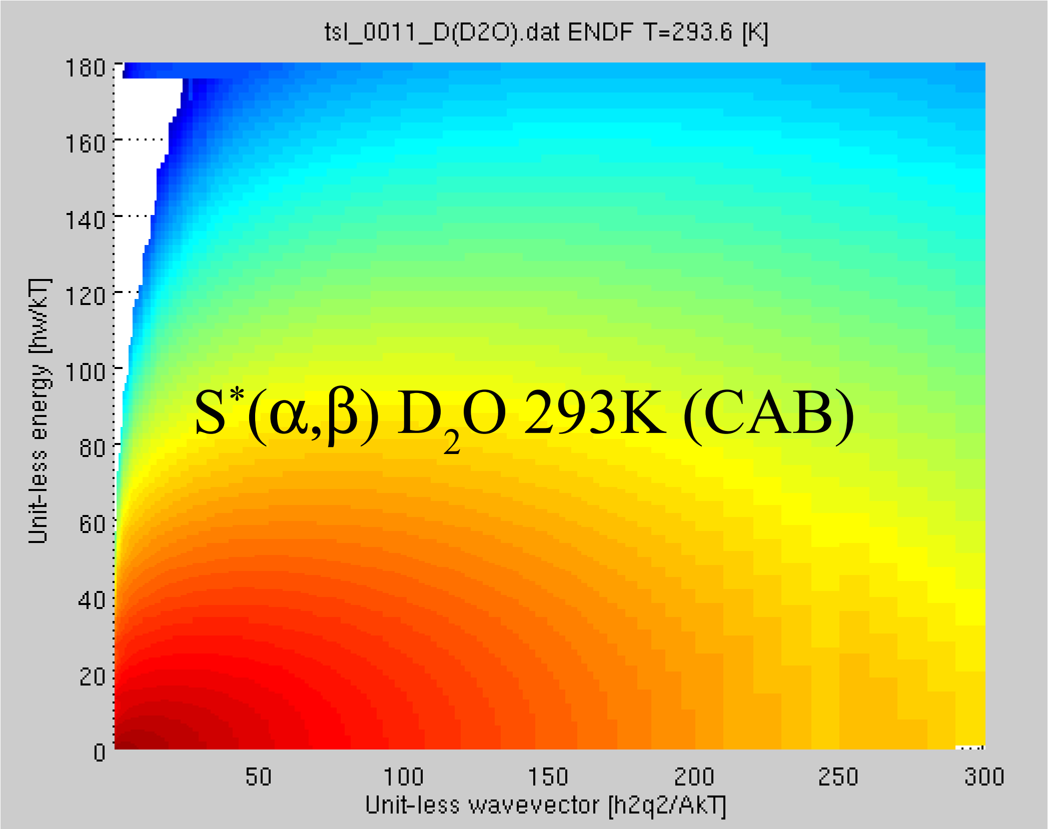
- Experiments: total = coh+inc
- Can estimate incoherent quite well, to e.g. help subtract ‘background’ and better estimate the coherent part.
- Can build $S(q,\omega)$ estimates from very little info.

Nuclear data bases

- Some of this is in NJOY/LEAPR module
  - Incoherent “phonon-expansion”
  - Coherent [Sköld] estimate only used for D_2O
  - Contribution is in m^{-p} / $!p$, usually p=5-10 is enough.
  - All materials, including coherent scatterers are assumed incoherent.
  - $S(\alpha{=}h^2Q^2/2mkT, \beta{=}{-}h\omega/kT) \sim S(Q,\omega)/Q$ depends on T, whereas $S(Q,\omega)$ mostly changes around phase transitions (except for Bose factor).
  - Material descriptions in ENDF are few.

Nuclear data bases: D_2O $S(\alpha,\beta)$

- Get Bariloche "D in D_2O" ENDF TSL-0011.
- iFit: sab=iData('tsl_0011_D(D2O).zip'); sab=sab(1); *% 293 K*



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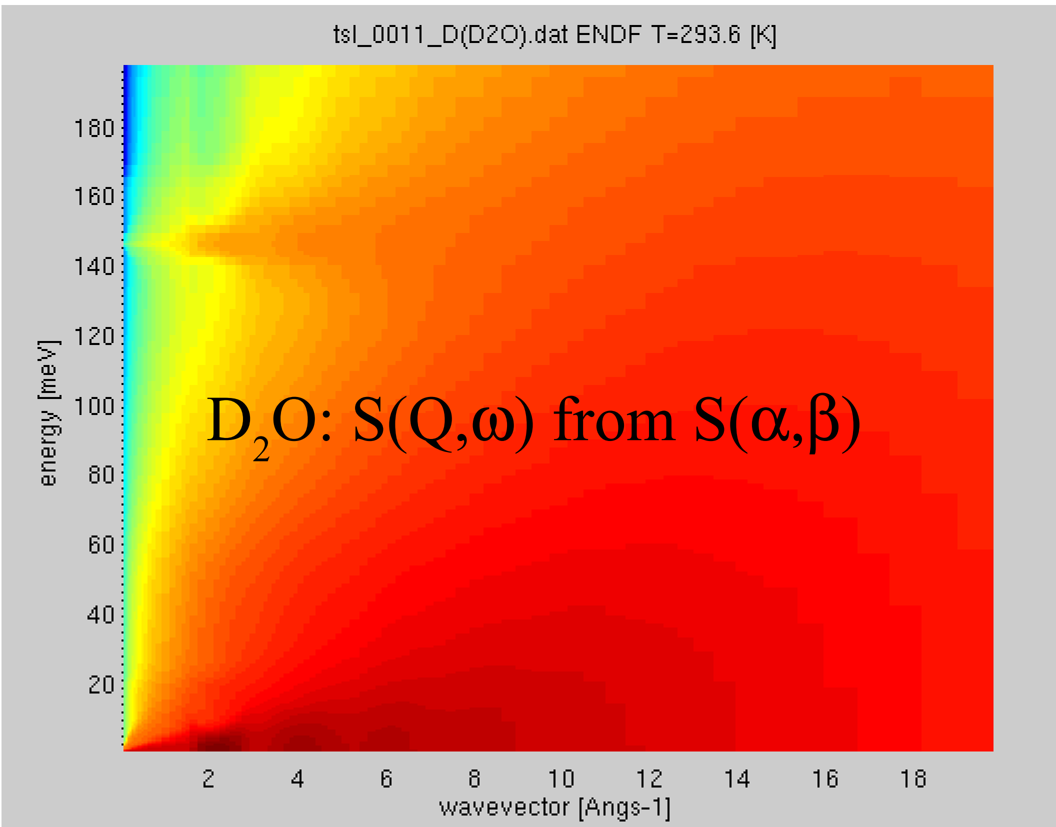
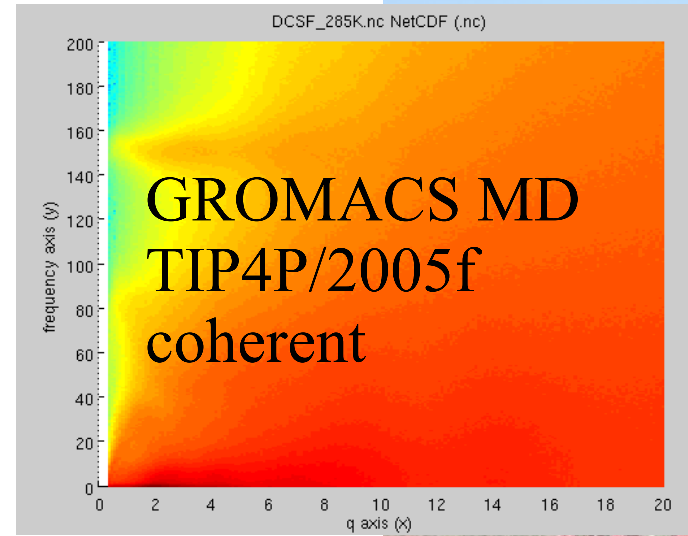
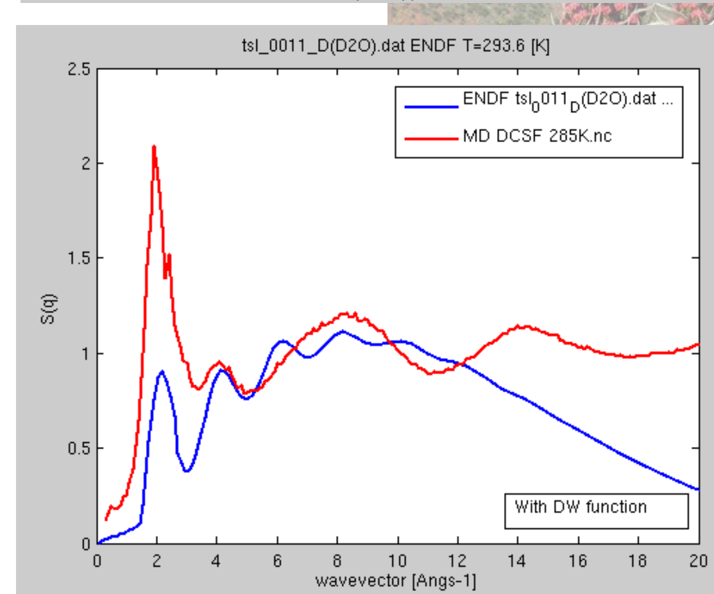
ENDF D_2O S(q,w)







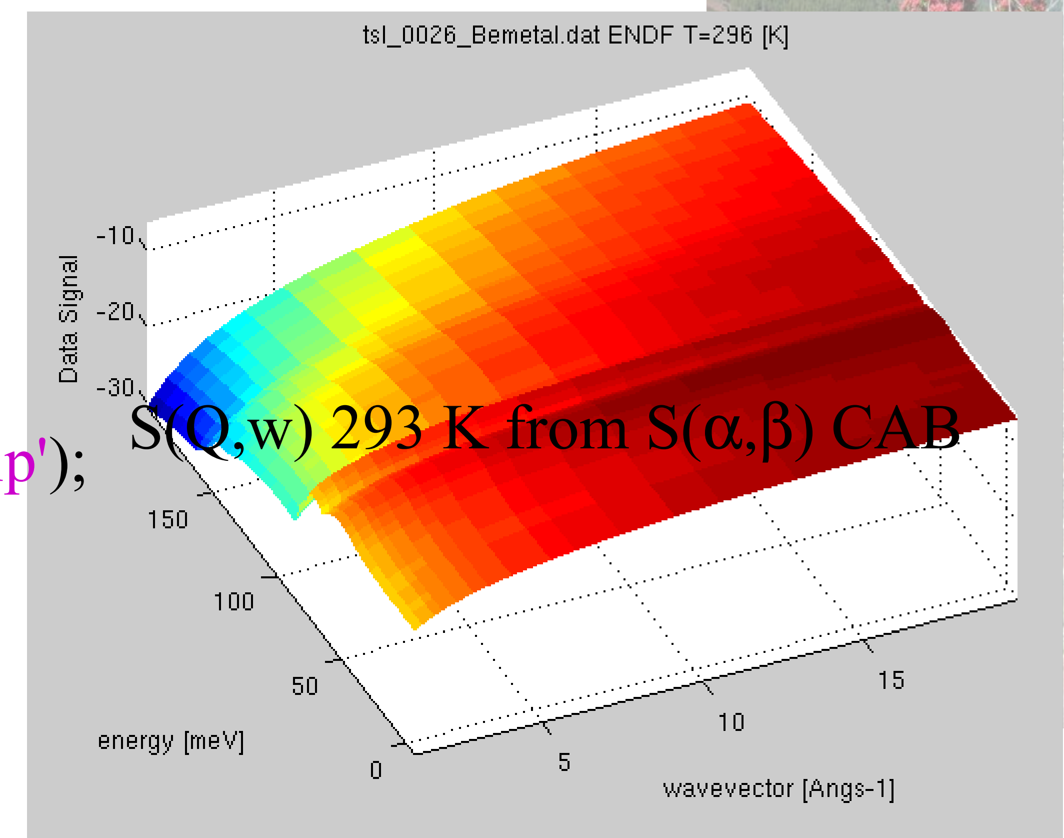
iFit: sqw = Sqw(sab);

CAB model is fair.

ENDF Be metal

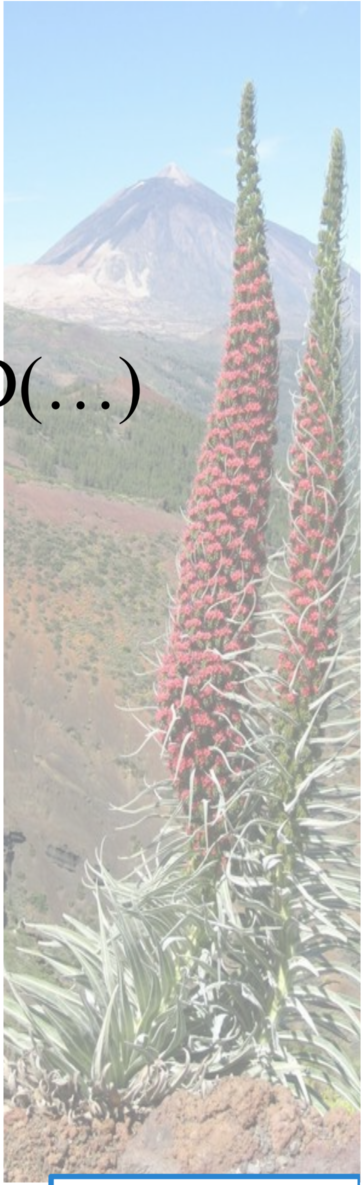
- ENDF Be does not contain any structure. Fully incoherent, but this is in fact a pure coherent scatterer.
- Some vibrational bands, but there should be phonons…
- iFit:

- iFit:
  - Be=iData(‘tsl_0026_Bemetal.zip');
  - Be=Be(9); % 293 K
  - Sqw = Sqw(iData_Sab(Be));



Using all this in iFit

- Load a data set: blah = iData(file);
- Make it a vDOS or Sab or Sqw2D
  - iData_vDOS(..) iData_Sab(…) iData_Sqw2D(…)
- Compute:
  - vdos=dos(sqw2d); sqw2d=incoherent(vdos);
  - sq=structure_factor(sqw2d)
  - sqw2d=coherent(sqw2d, sq);
- Convert
  - Sqw(sab); Sab(sqw2d);



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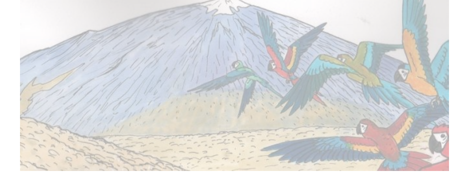

Conclusion

- There are models to get S(q,w) from not much.
- Used extensively in ENDF.
- Make up your mind about validity.
- My advices:
  - use it to estimate incoherent when you have a total scattering experiment. Cheaper than polarised beam...
  - ENDF: Extend material descriptions with coherent (structure).

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