Small-Angle Scattering Size Distributions Employing Non-Negative Histogram Constraints

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Small-angle scattering is the premier method for the size characterization of nanoscale density inhomogeneities.

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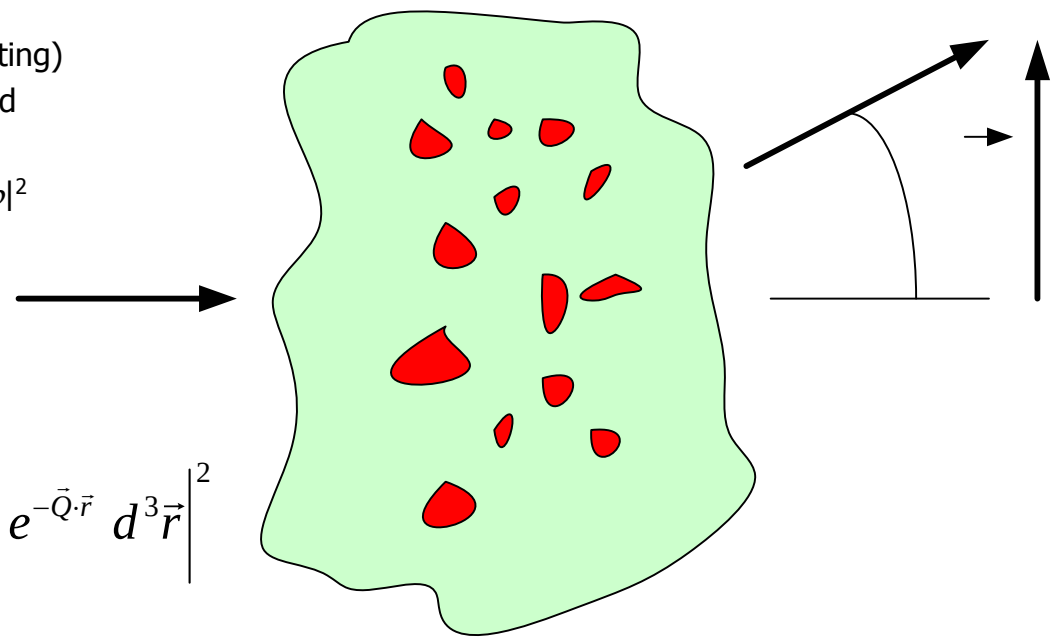
Abstract

Explanation of small-angle scattering (SAS) data by the presence of size distribution of density inhomogeneities (scatterers) is an example of an overdetermined problem in mathematics. Various methods to constrain the solution have been developed. Most simply, by assuming a functional form for the size distribution, such as Gaussian or log-normal, solution by least squares minimization of residuals is direct. In order to drop this assumption of a functional form, more powerful numerical methods need to be employed. By describing the size distribution as a population histogram against some characteristic dimension, one can employ regularization methods such as maximum entropy or maximum smoothness to provide additional constraint.

SAS is due to …

- Scattering is due to inhomogeneities in scattering length density, ρ
- Scatterers are assumed (this work):
  - –Homogeneous
  - –Dilute (non-interacting)
  - –Randomly dispersed
  - –Same morphology
  - –Same contrast, $|\Delta\rho|^2$

$$Q = \frac{4\pi}{\lambda}\sin\theta$$



$$\frac{d\Sigma}{d\Omega}(\vec{Q}) = \left| V_p^{-1} \int_{V_p^{-1}} \rho(\vec{r})\, e^{-\vec{Q}\cdot\vec{r}}\, d^3\vec{r} \right|^2$$

SAS from a size distribution

$$\frac{d\Sigma}{d\Omega}(Q) = \int_0^\infty \left|\Delta\rho\, F(Q,r)\, V(r)\right|^2 N(r)\, dr$$

restate in vector form $\vec{I} = \underline{G}\, \vec{f}$

M equations
N unknowns

$$G(Q,r) = \left|\Delta\rho\, F(Q,r)\right|^2 V(r)\, \Delta r$$

$$f(r) = V(r)\, N(r)$$

$$F(Q,r) = 3(Qr)^{-3}\left[\sin(Qr) - (Qr)\cos(Qr)\right]$$

note that:

$$V_V = \int f(r)\, dr$$

regularization solutions for f(r)

maximize $\Psi = \alpha S - \chi^2$ where $\chi^2 = \left\| \vec{I} - \underline{G}\,\vec{f} \right\|^2 = \sum \left(\frac{I - \underline{G} f}{\sigma} \right)^2$

by varying α subject to $\chi^2 = M \pm \varepsilon\sqrt{2M}$ and ***M*** is number of data & ε~0.1

maximum found at $\nabla\Psi = 0 = \alpha \nabla S - \nabla \chi^2$

least squares $S = 0$ (no need for regularization solution)

maximum entropy $S = -\sum (f/b) \log(f/b)$

J. Skilling and R.K. Bryan; ***Mon Not R Astr Soc* 211** (1984) 111-124.
J.A. Potton, G.J. Daniell, and B.D. Rainford; ***J Appl Cryst* 21** (1988) 891-897, 663-668.

smoothness $S = -\left\| \vec{f}'' \right\|$

As an additional note, could instead minimize total volume fraction : $S = -\left\| \vec{f} \right\|$

then $\underline{H} = H_{i,k} = \begin{Bmatrix} 1 & i = k \\ 0 & i \neq k \end{Bmatrix}$ (identity) matrix

regularization solutions for *f(r)* ... cont.

$\nabla \Psi = 0$ in vector form $\vec{B} = \underline{A}\,\vec{f}$

N equations
N unknowns

where $B_i = \sum_{i=1}^{M} G_{i,j} I_j \sigma_j^{-2}$ $\underline{A} = \underline{D} + \alpha\,\underline{H}$ $D_{i,k} = \sum_{i=1}^{M} G_{i,j} G_{k,j} \sigma_j^{-2}$

$$\underline{H} = \begin{bmatrix} 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & & & & & \\ -2 & 5 & -4 & 1 & 0 & 0 & 0 & 0 & & & & & 0 \\ 1 & -4 & 6 & -4 & 1 & 0 & 0 & 0 & & & \cdots & & 0 \\ 0 & 1 & -4 & 6 & -4 & 1 & 0 & 0 & & & & & 0 \\ 0 & 0 & 1 & -4 & 6 & -4 & 1 & 0 & & & & & \\ & & & & \cdots & & & & \ddots & & & & \\ 0 & & & & & & & & -4 & 6 & -4 & 1 & 0 \\ 0 & & & & \cdots & & & & 1 & -4 & 6 & -4 & 1 \\ 0 & & & & & & & & 0 & 1 & -4 & 5 & -2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 & 1 \end{bmatrix}$$

This has a direct solution for $-\infty \le f(r) \le \infty$ given α.

additional non-negative constraint

solve $\vec{B} = \underline{A}\,\vec{f}$ for ***f(r)***≥0 (above) using NNLS

C.L. Lawson & R.J. Hanson;
Solving Least Squares Problems
(1995) SIAM, Philadelphia.

test model: 2 log-normal distributions

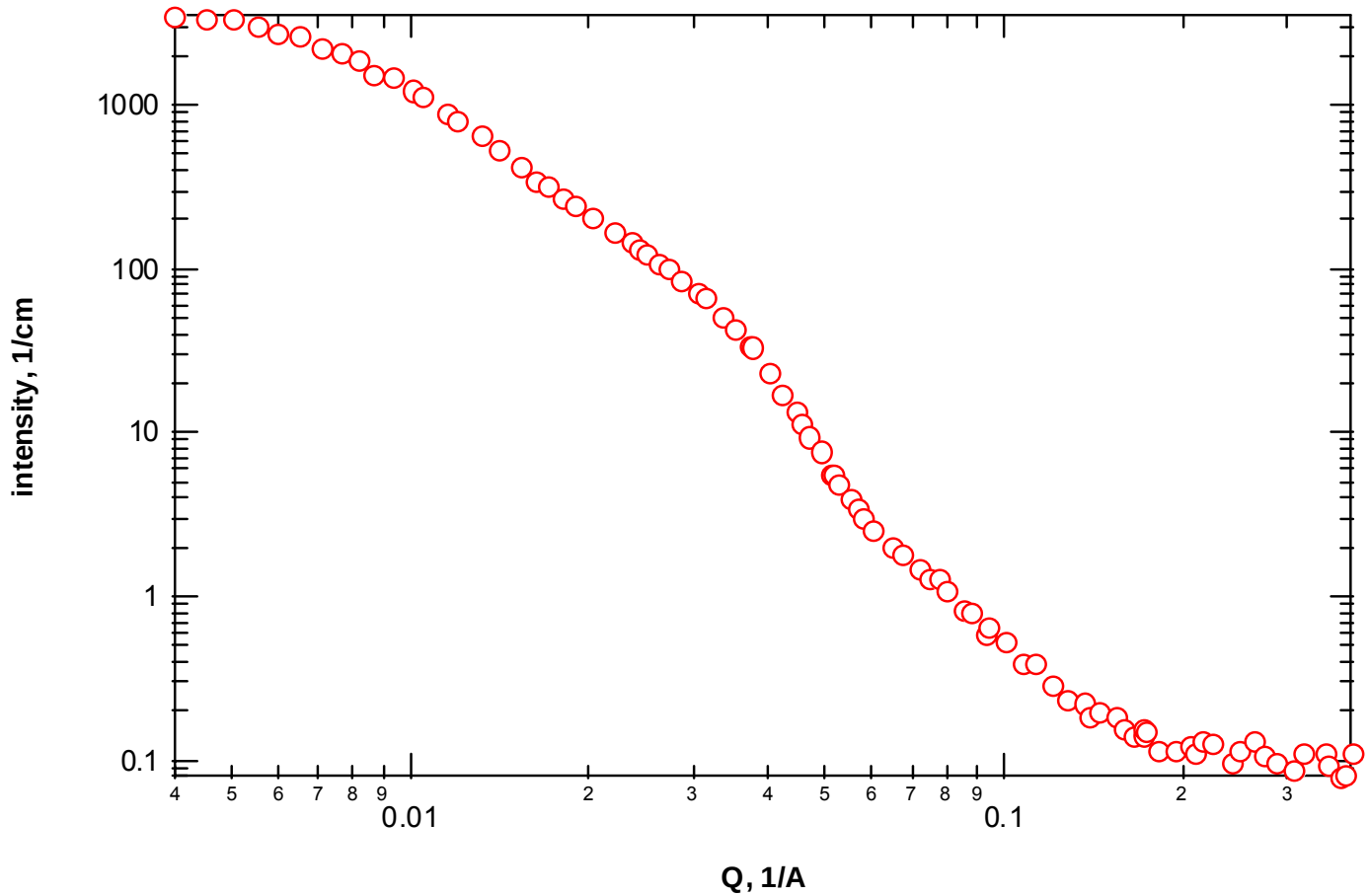
volFrac	peak D, A	sigma
1.20%	150	0.2
0.80%	360	0.333

2.5% noise level

0.1 1/cm background

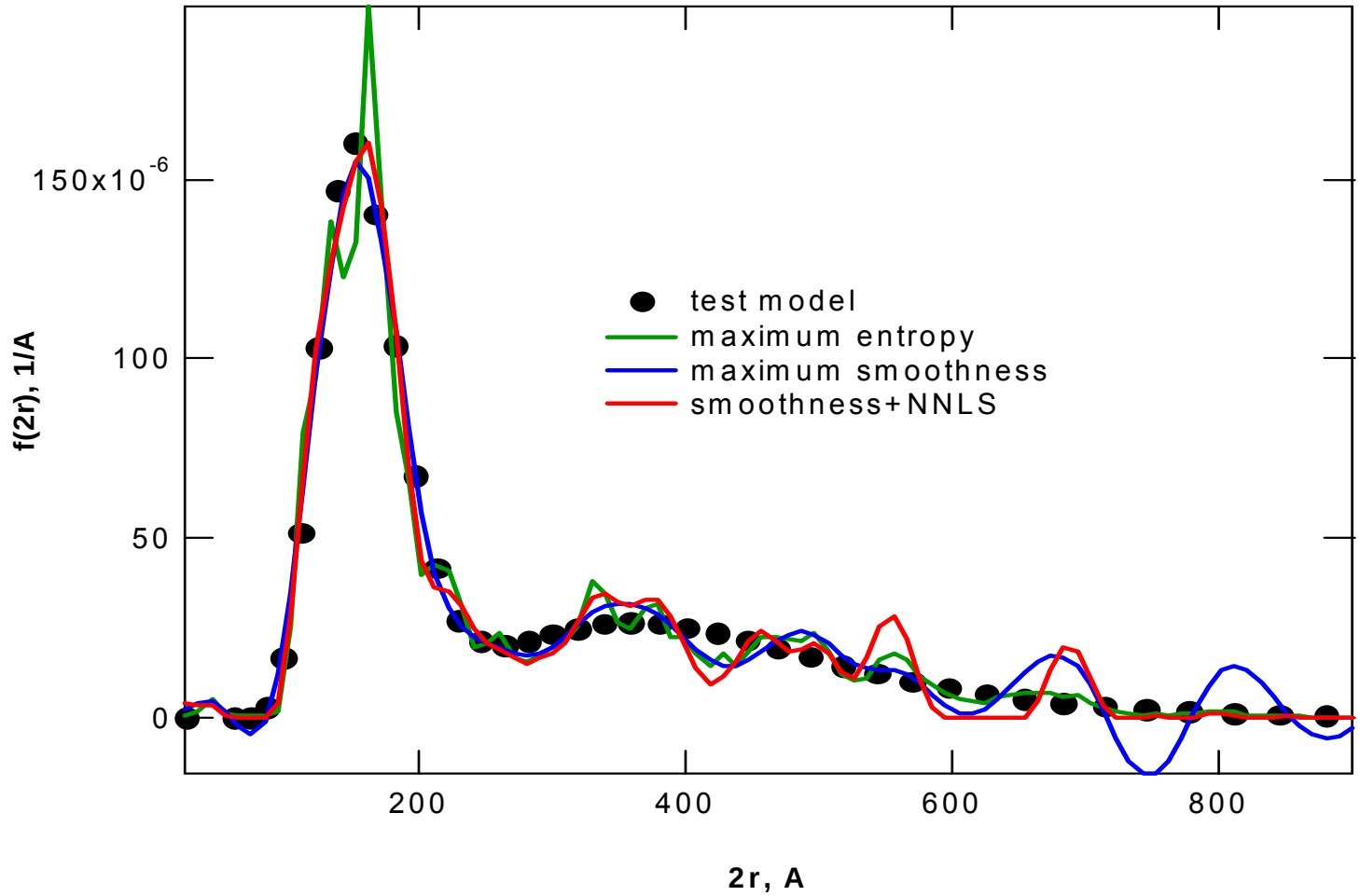
100E20 1/cm^4 contrast

test model: 2 log-normal distributions calculated scattering



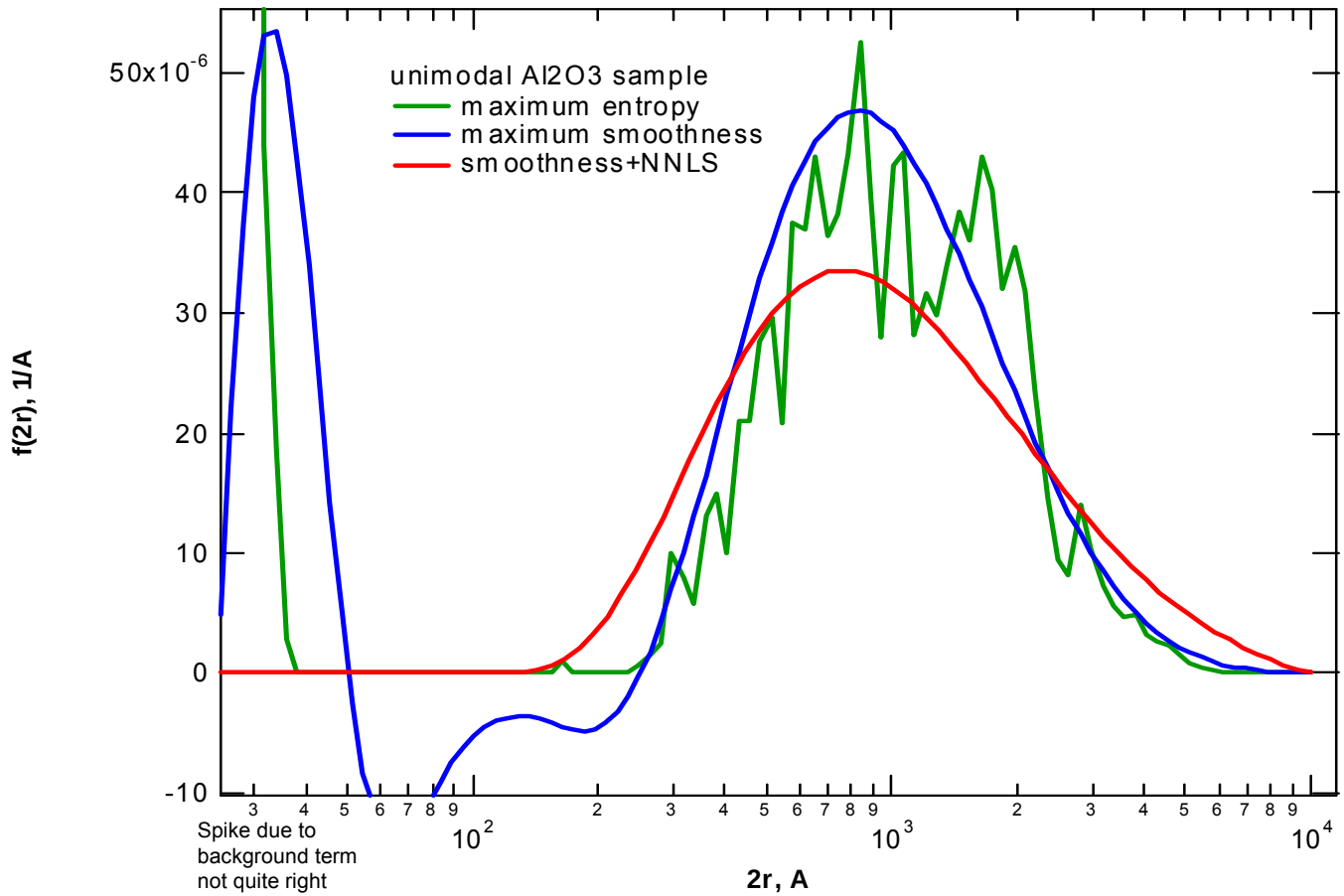
Comparisons

test data: bimodal log-normals



Comparisons

real data: unimodal Al_2O_3 powder



Conclusions

- All methods yield similar results
- MaxEnt results are more noisy
- MaxSmooth results have some $f(r)<0$
- MaxSmooth&NNLS
  - Not as stable (does not always converge)
  - Much longer computation time
  - Not ready for general use
- Need to compare with IPG/TNNLS (below)

IPG/TNNLS method

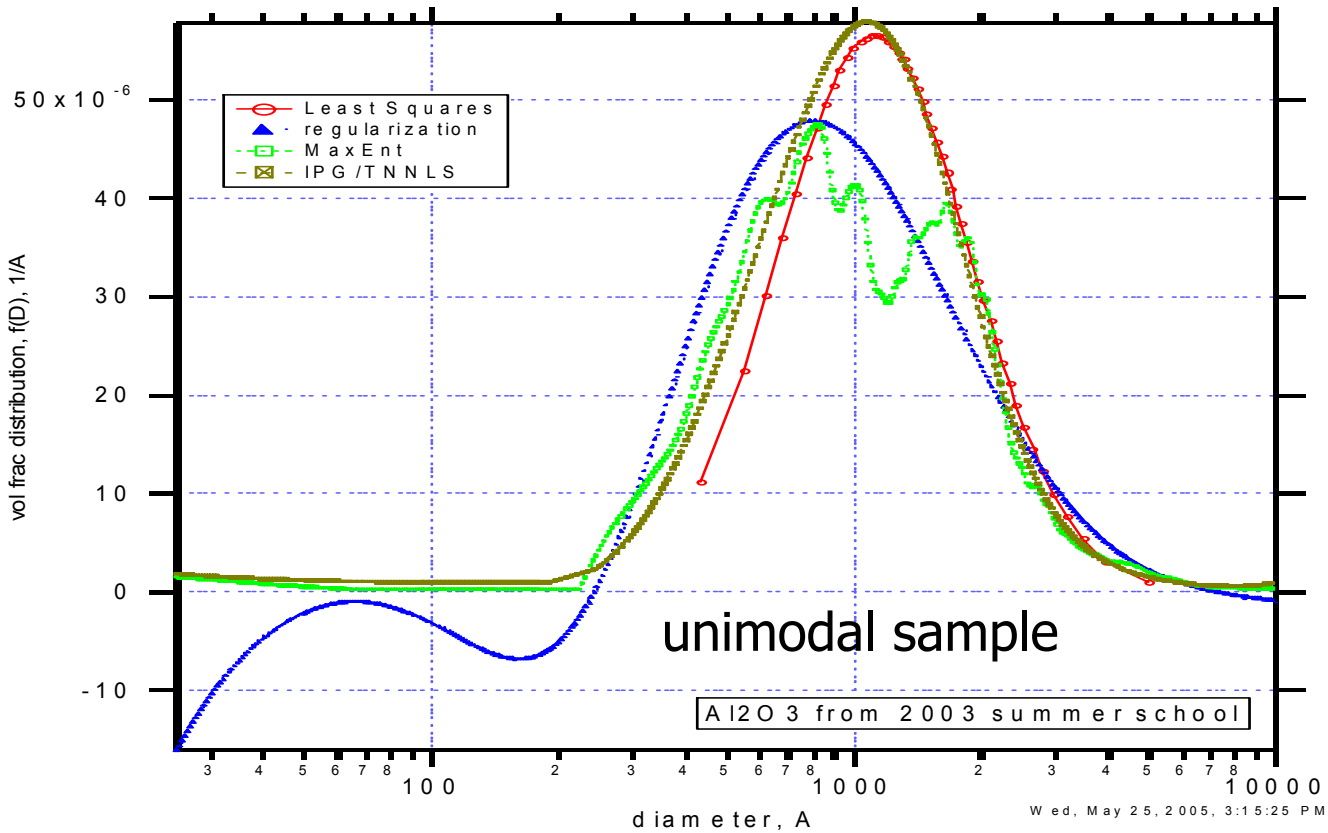
IPG/TNNLS method:

An interior-point gradient method for large-scale
totally nonnegative least squares problems
M. Merritt and Y. Zhang, (2004) Technical Report TR04-08
Department of Computational and Applied Mathematics
Rice University, Houston, Texas 77005, U.S.A.
http://www.caam.rice.edu/caam/trs/2004/TR04-08.pdf

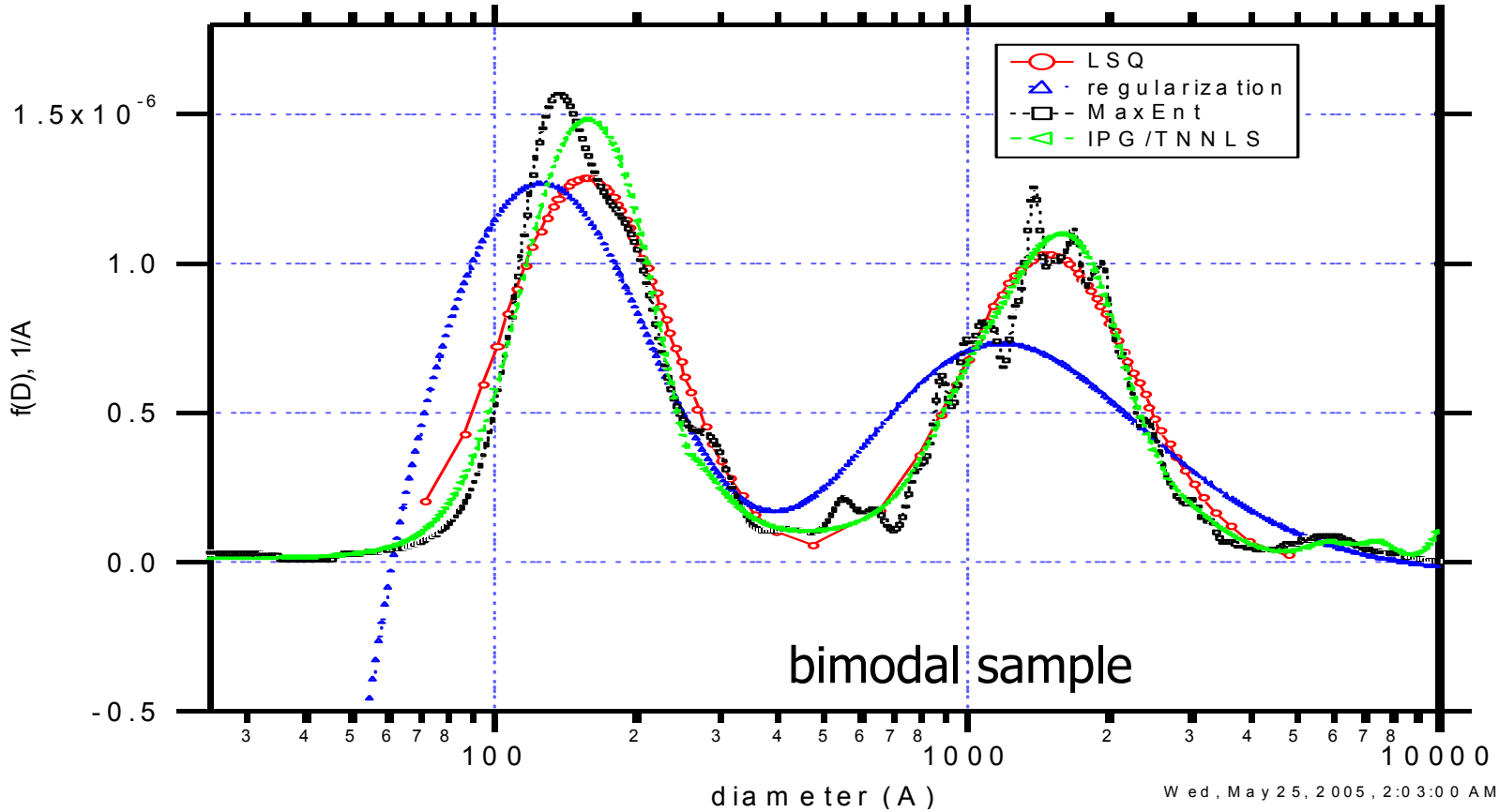
as implemented by J. Ilavsky in
http://www.uni.aps.anl.gov/~ilavsky/irena.html

Al_2O_3 polishing powder

Initial testing with IPG/TNNLS method (from Ilavsky) looks superior to regularization+NNLS method described here. Results are consistent with least squares refinement of peak shape terms.



Al_2O_3 polishing powder



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