Least Squares Fit
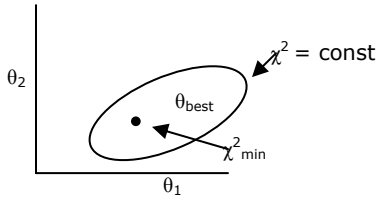
$\underline{Y}_{model} = \Sigma\theta_i f_i(\underline{x})$

Use probability $(\chi^2 > \chi^2_{measured}) > $ tol to set contour boundary for consistent or not consistent.

Nonlinear Least Squares

Away from "θ_{best}", no idea about contours. Close to minima, looks like ellipses. Nonlinear case can have numerous local minima and arbitrary shape. It is possible for the problem to be poorly constrained, to have multiple minima, and to have bad directions. The result is big error bars and a complete mess.

$\underline{Y}_{model}(\underline{\theta}, \underline{x}) \approx \underline{Y}_{model}(\theta_{best}) + {}^{\partial Y_{model}}/_{\partial\theta}(\theta-\theta_{best}) + O((\Delta\theta)^2)$

close to θ_{best} will be linear   neglect
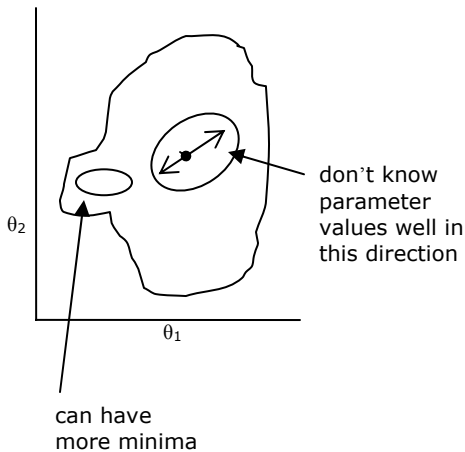
Standard confidence intervals – covariance matrix, assume ellipses for confidence intervals. To tell the actual shape of the region, use Bayesian view: report probability distribution of the region. Can cut across the region to get more information.

Experimental Error Sources (Causes for Irreproducibility)

- human error, typographic errors
- variables out of control, often unknown to researcher
    - building vibrations
- calibration discrepancies: instrument drift (error bars, can control)
- actual matter intrinsically varies (molecules are always in motion); have some control in terms of knowledge of the phenomena
    - impractical to measure/record
    - impossible (Heisenberg Uncertainty Principle)
    - turbulent – perfectly random

With least squares fitting (nonlinear), might find local minima but might miss global minima.

Monte Carlo Integration

$$P(\underline{x}_1,\underline{x}_2,...,\underline{x}_{10^{23}}) \sim \frac{e^{-E(\underline{x}_1,...,\underline{x}_{10^{23}})/k_bT}}{N}$$

q

$U = <E>$ over some ensemble

$$\frac{\iint \cdots \iint p(q)E(q)dq}{\iint \cdots \int\int p(q)dq} = <E>$$

Ideal Gas – Integral is easy to work out

Liquids and polymers - difficult

Monte Carlo

f(x)

a   b
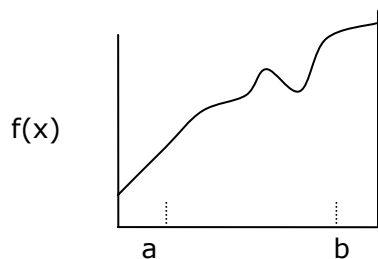
$$\int_a^b f(x)dx = (b-a)<f> \qquad \text{Choose enough points}$$

$$I = \int p(q)f(q)dq \qquad \text{p(q) is the distribution function}$$

10.34, Numerical Methods Applied to Chemical Engineering
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Lecture 27
Page 2 of 2