Uncertainty quantification of Molecular Dynamics Simulations for Crosslinked Polymers

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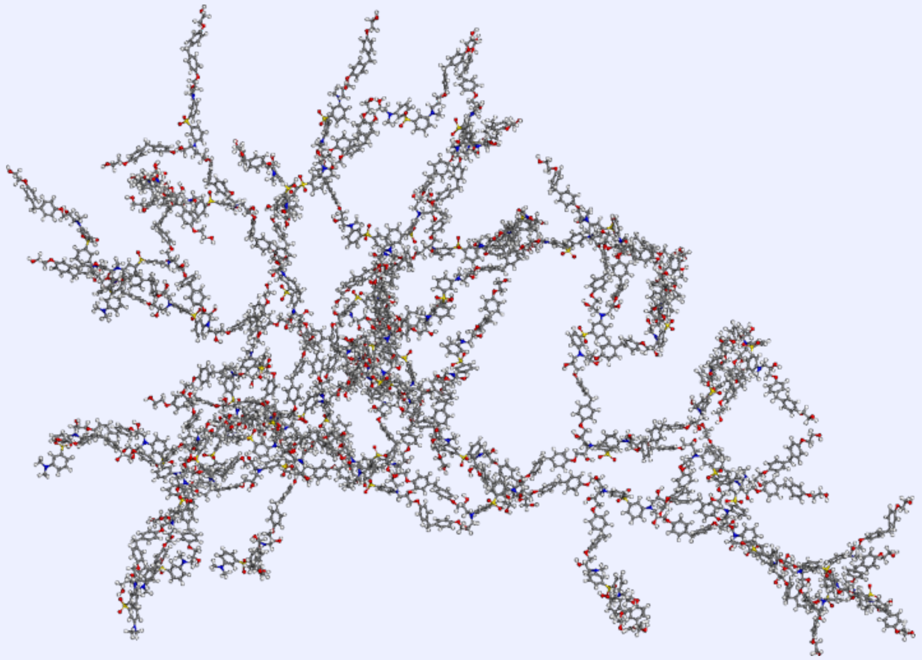


Backstory:
Macro-economics of materials science

Advent of composites dramatically altered design space in aerospace engineering.

Example: Boeing 787

1st aircraft with majority carbon-composite structural components

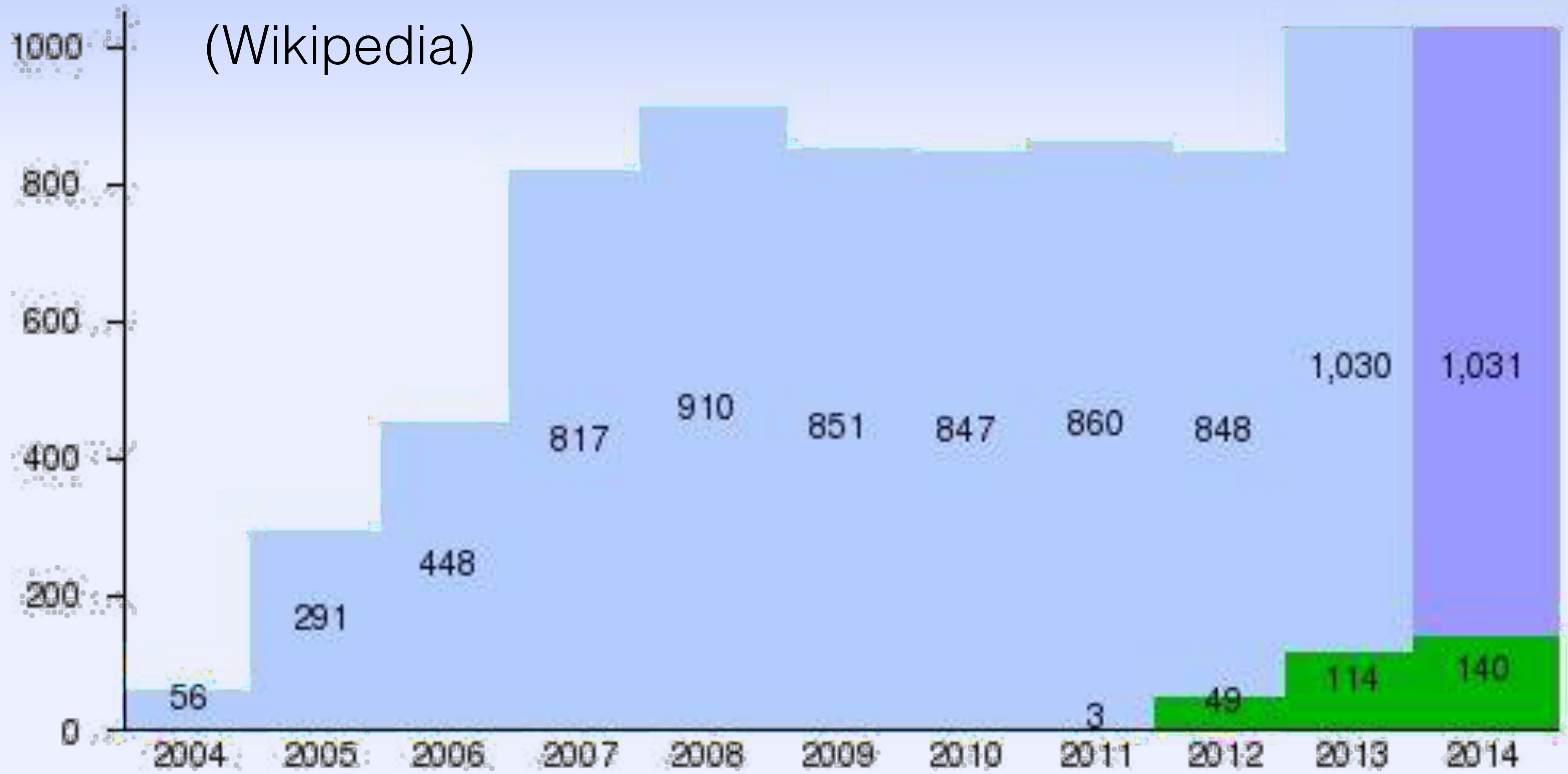
Lighter aircraft —> fuel savings (20%)

Scale of economics

(~ 1000 orders) x (~ $250 Million / order) = $250 Billion

Impact of advanced materials

Cumulative orders of 787 (blue) and deliveries (green)



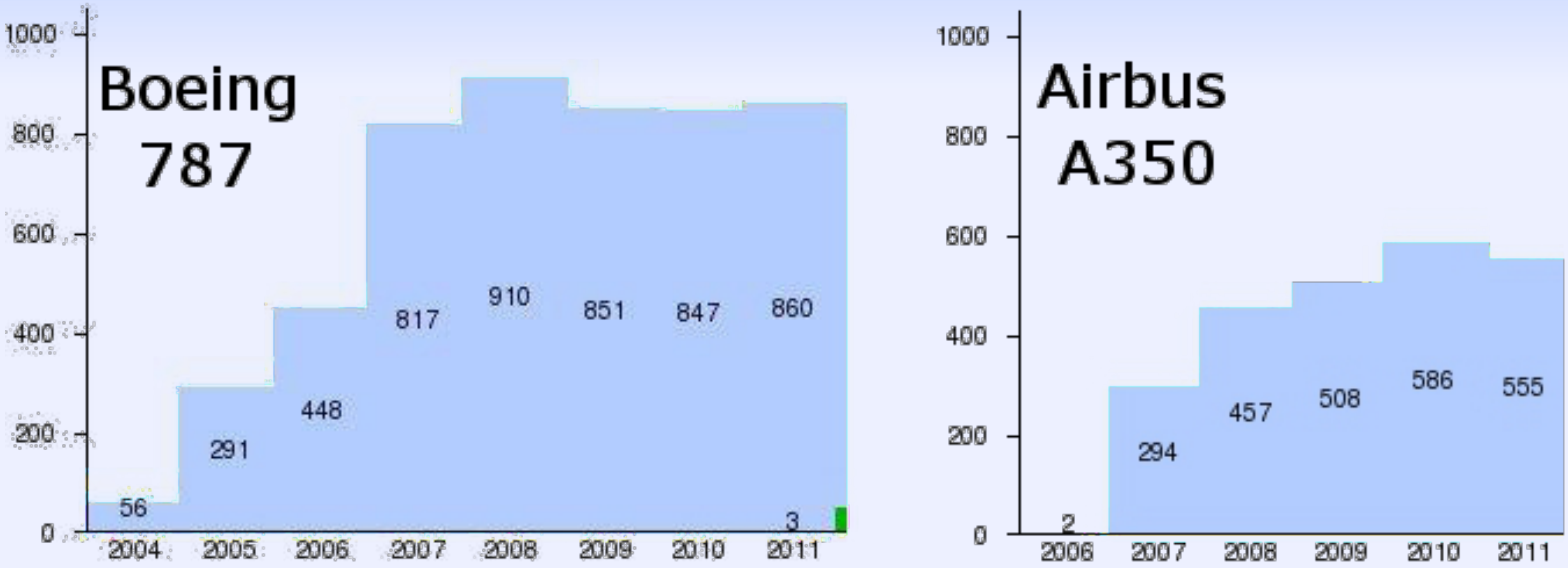
2006 Seattle Times headline

Airplane kingpin tells Airbus: Overhaul A350

"That's probably an $8 billion to $10 billion decision."

Impact of advanced materials

Cumulative orders of 787 and A350



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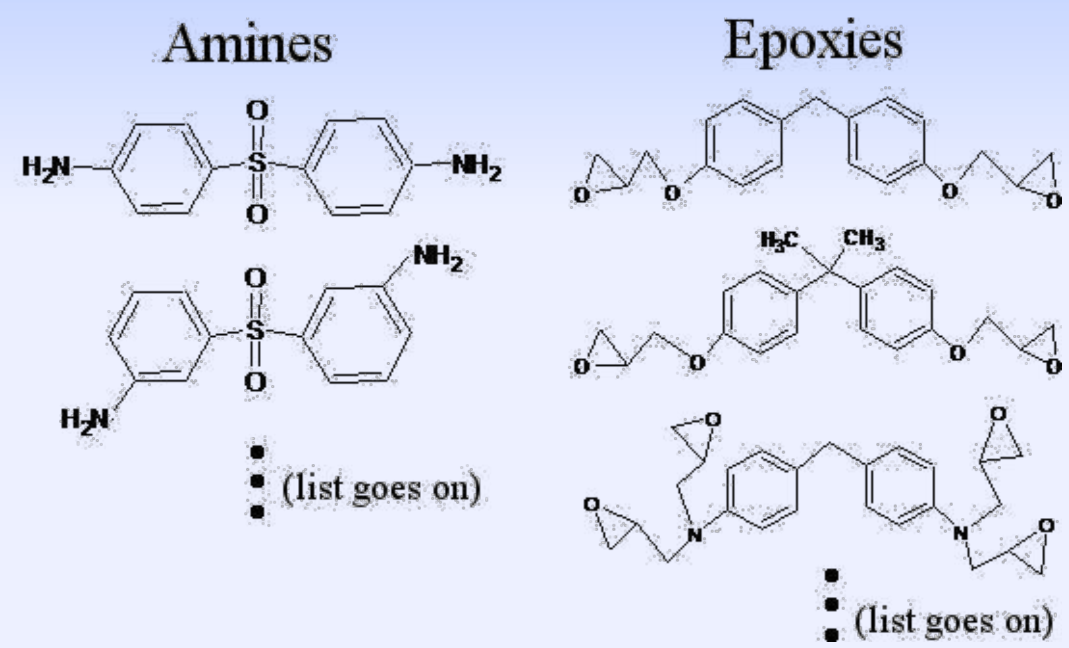
Accelerating market insertion: materials by design

Assume

"Design space" of ingredients

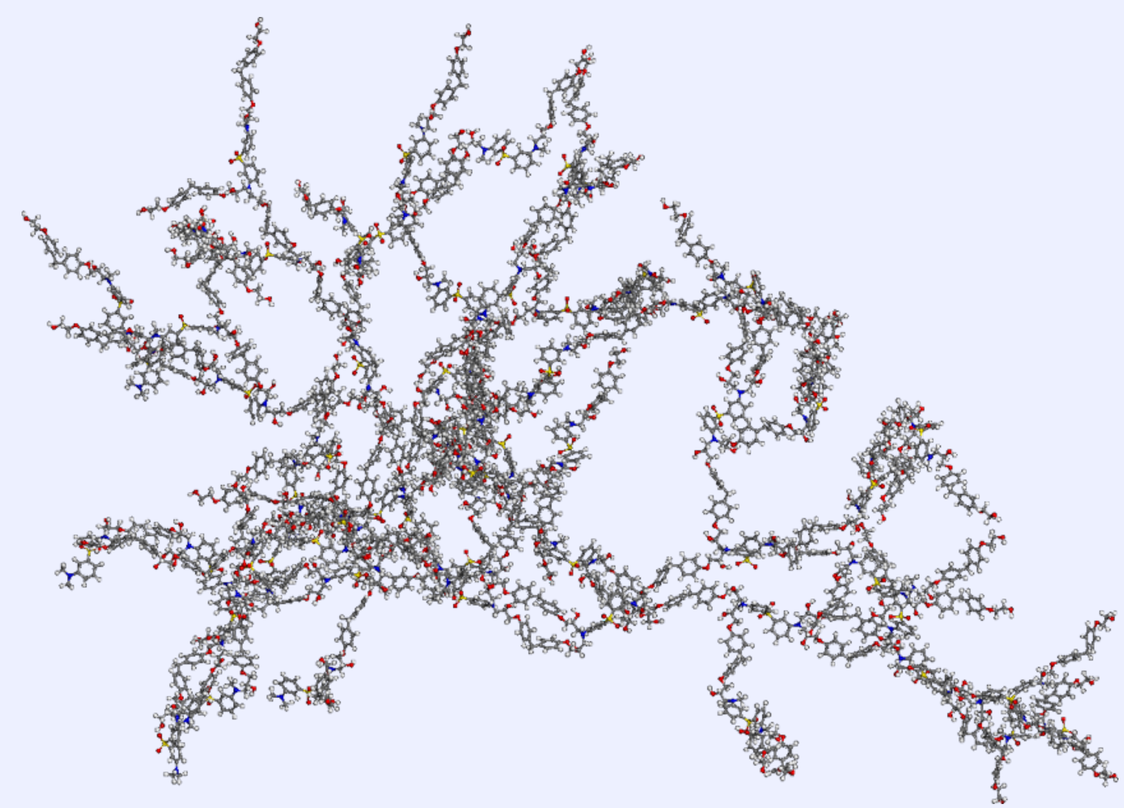
Finite simulation resources

(Very) Few experiments



Goal

Find chemistry with,
e.g. highest T_g



Roles of UQ in modeling workflows

Verification

Check math,
remove bugs

Does data look
like I expect?

Data of sufficient quality
to make predictions?

Compute uncertainties
arising **from within model**.

Validation

Calibrate model

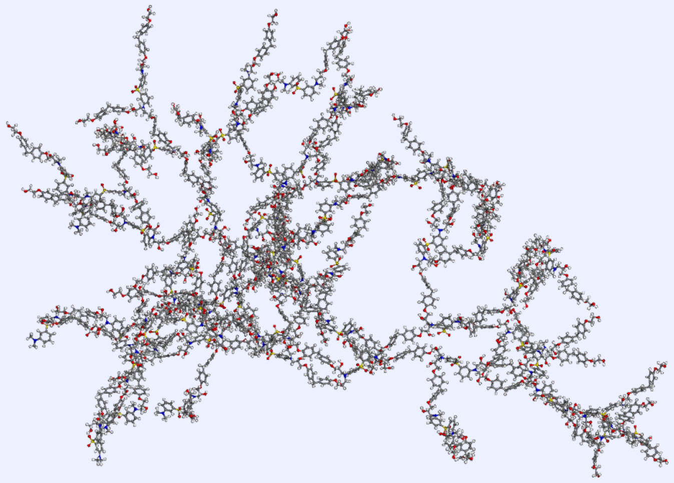
Estimate uncertainties
arising from ….

calibration parameters

missing physics

model form error

Otherwise assume model is valid at this stage



Test "real-world" predictive power

Roles of UQ in modeling workflows

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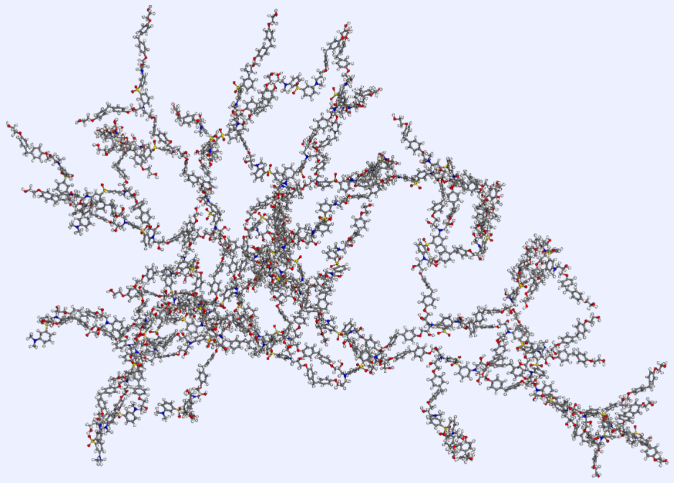


Today's focus on verification

Helps modelers to be precise about what they mean

Improves reproducibility

Streamlines validation

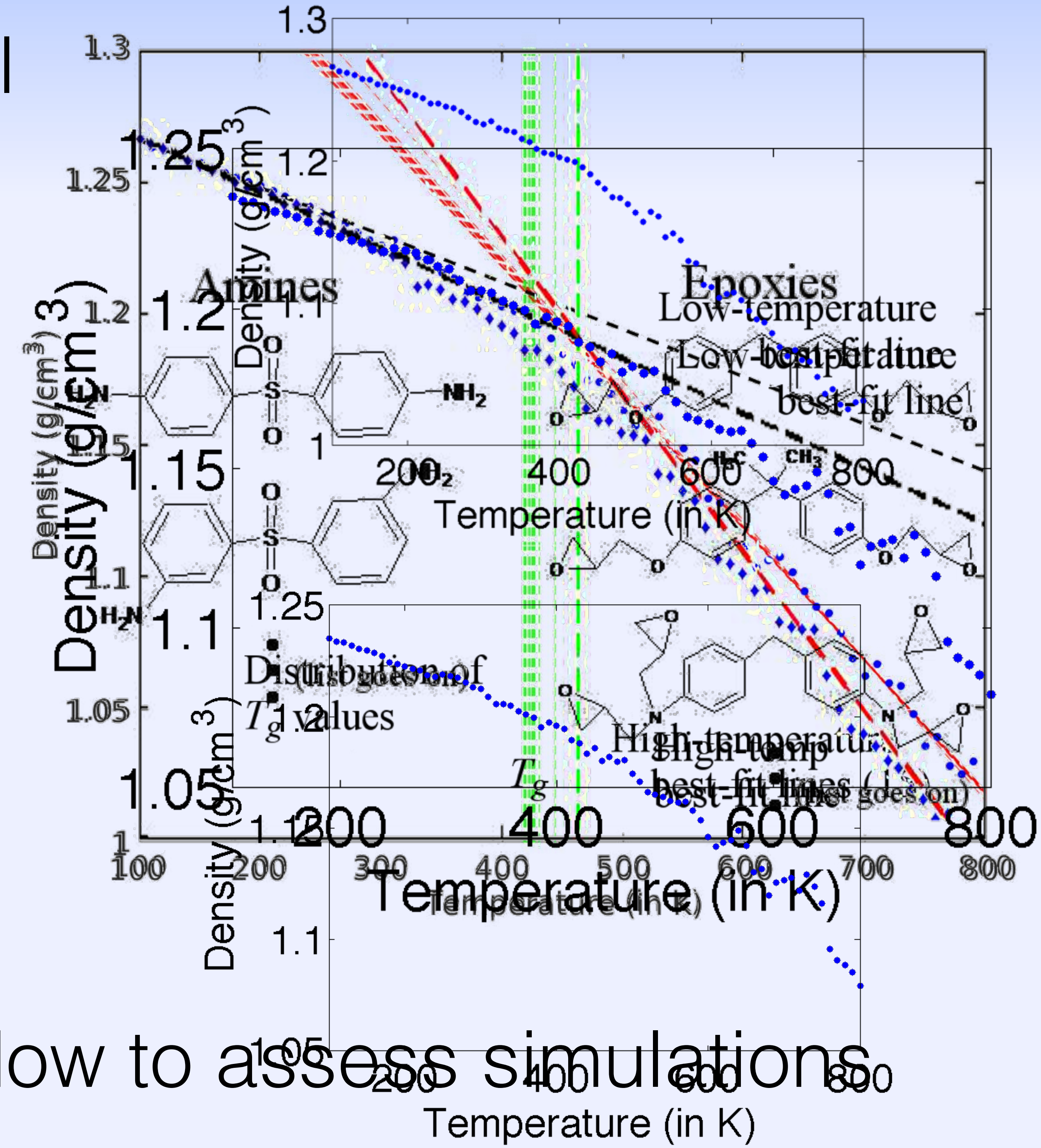
Some complicating issues for Tg

Incomplete list

1. Can we extract meaningful T_g from simulated data

2. How to combine data?

3. How to work within non-analytic design space?



Hardened & verified workflow to assess simulations

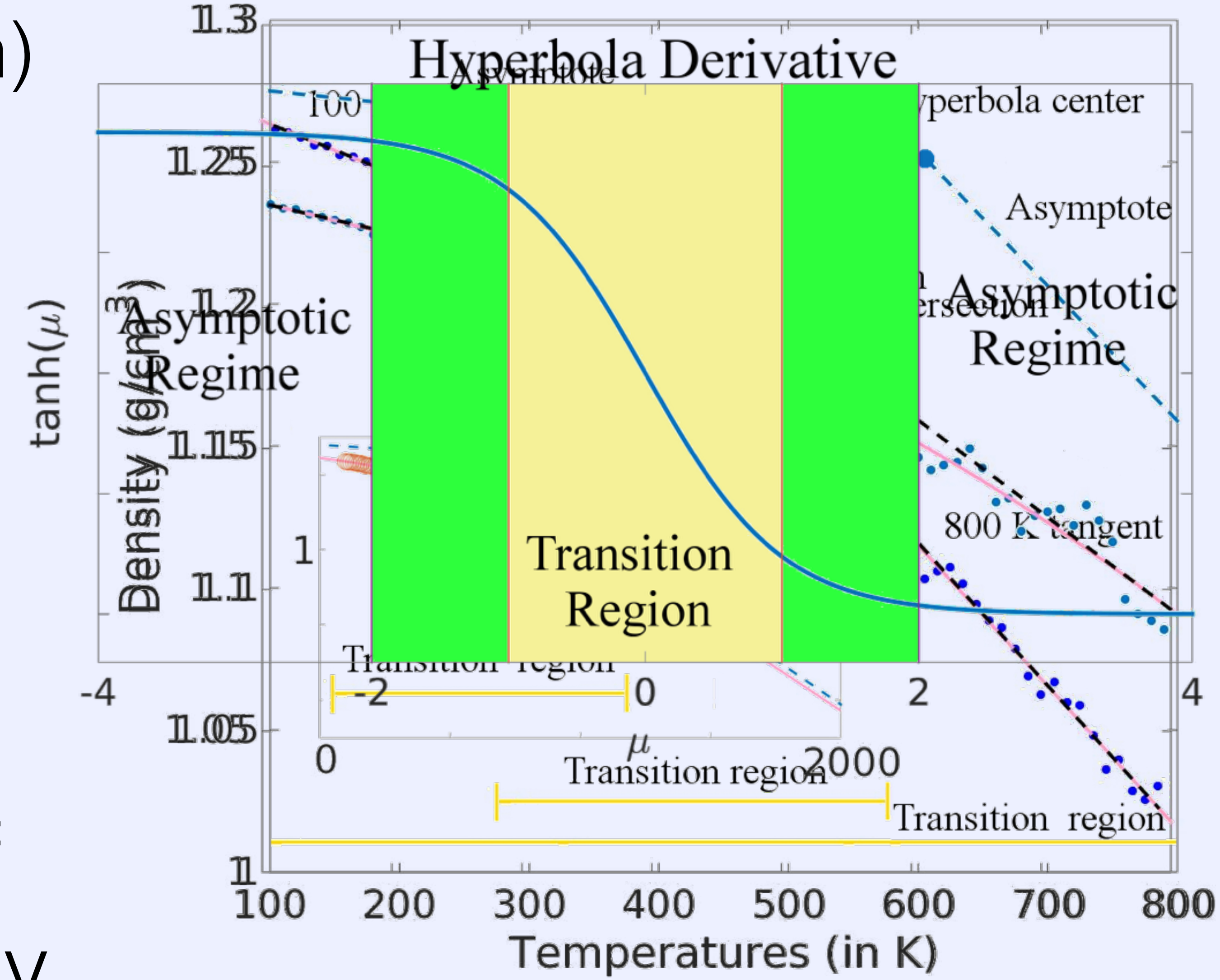
Assessing ability to extract T_g

Consistency with underlying definitions

T_g defined as hyperbola center
(same as asymptote intersection)

Automatically finds
“asymptotic regimes”

Data inconsistent with T_g if
asymptotic regimes far away



Assessing ability to extract T_g

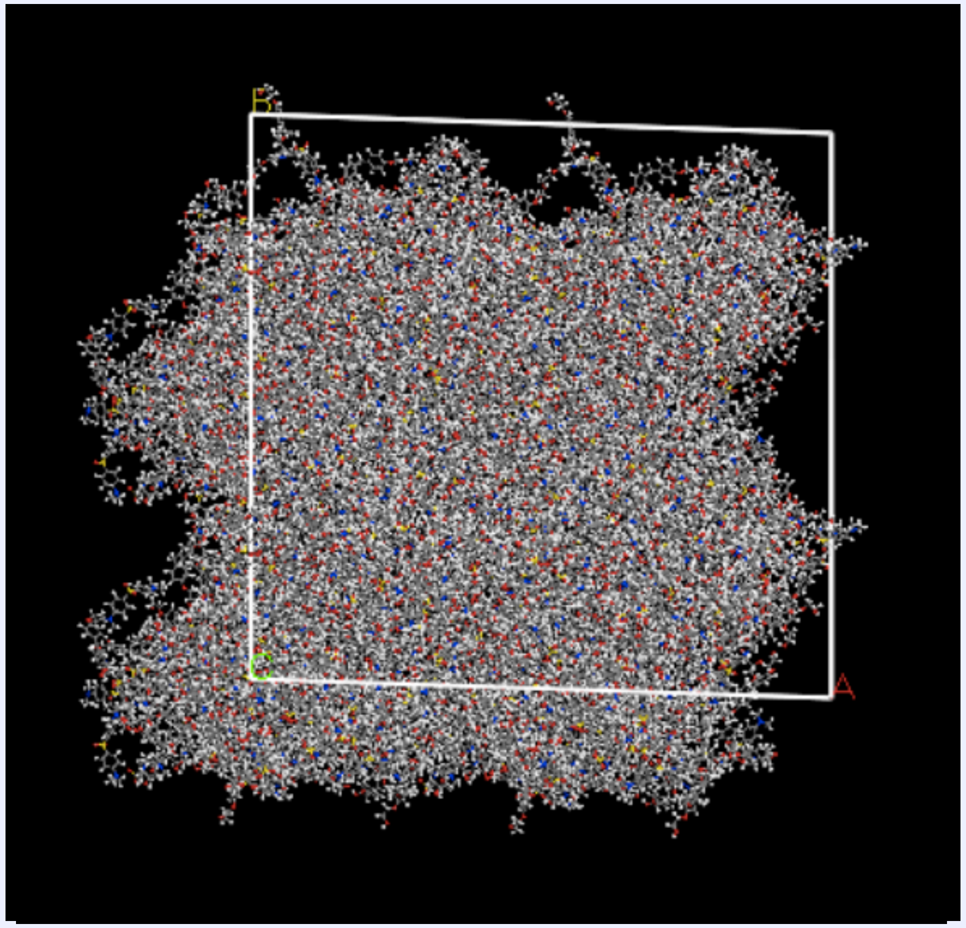
Convergence to bulk limit

An industry oxymoron:

high-throughput, bulk-scale, atomistic-detail MD

This is not bulk…?

How do we know?



Observations from statistical mechanics

As # of particles $N \to \infty$

1) measurable quantities are independent of N
2) variances of measurable scale as $1/N$

Hyperbola fit **(non-linear)**

Analytically: $T_g = H(T, \rho)$

density data

temperatures

$$As\ N \to \infty,\ T_g \approx H(T, \bar{\rho}) + \delta\rho(N) \cdot \nabla_\rho H \Big|_{(T, \bar{\rho})} + O\left(\|\delta\rho\|^2\right)$$

bulk mean

Hyperbola fit approximately linear

$1/N$ fluctuations

Observations from statistical mechanics

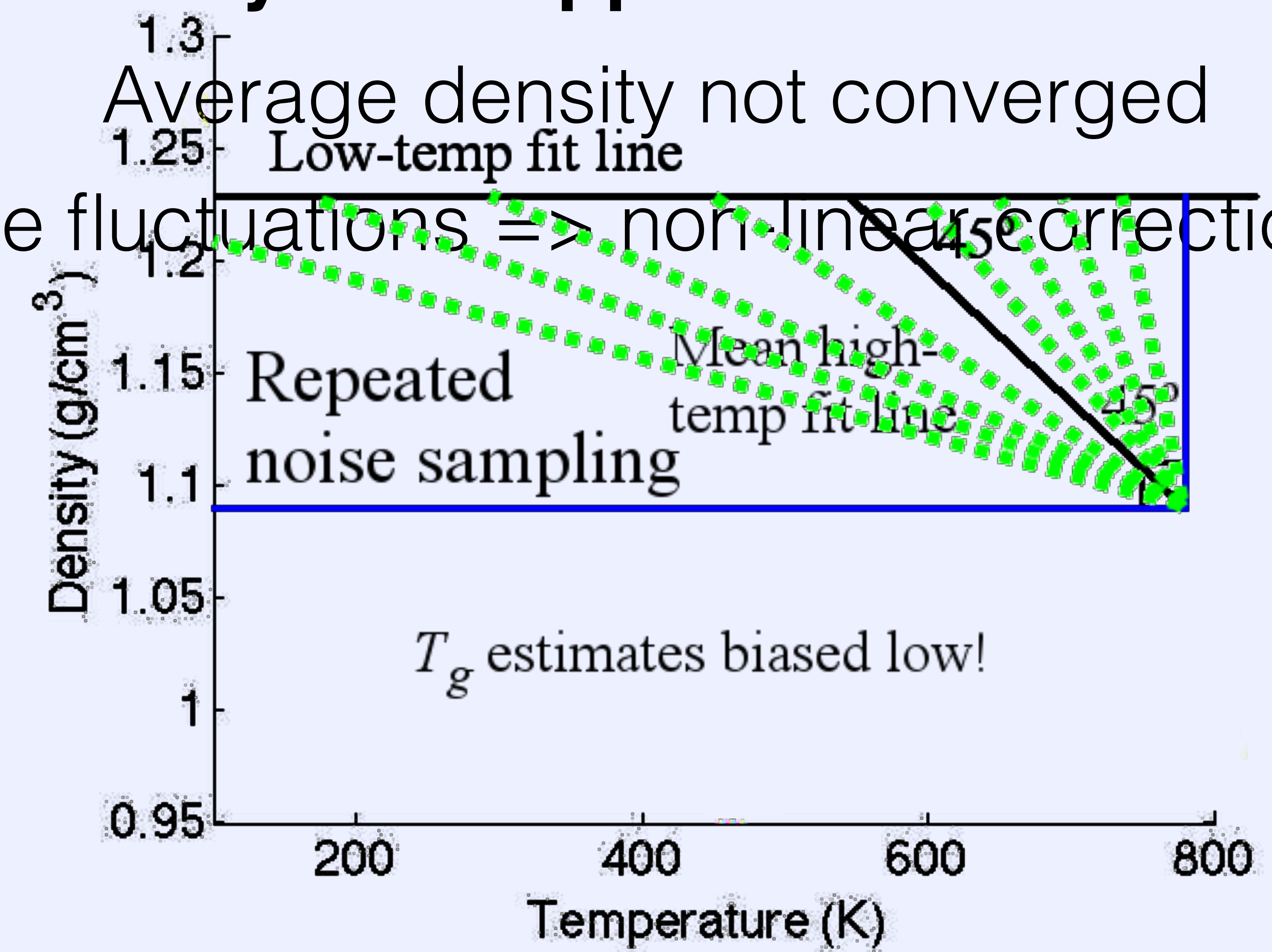
$$As\ N \to \infty,\ T_g \approx H\left(T, \bar{\rho}\right) + \delta\rho\left(N\right) \cdot \nabla_\rho H \Big|_{(T,\bar{\rho})} + O\left(\|\delta\rho\|^2\right)$$

Large fluctuations => non-linear correction bias

Two ways this approximation can fail

Average density not converged

Large fluctuations => non-linear correction bias

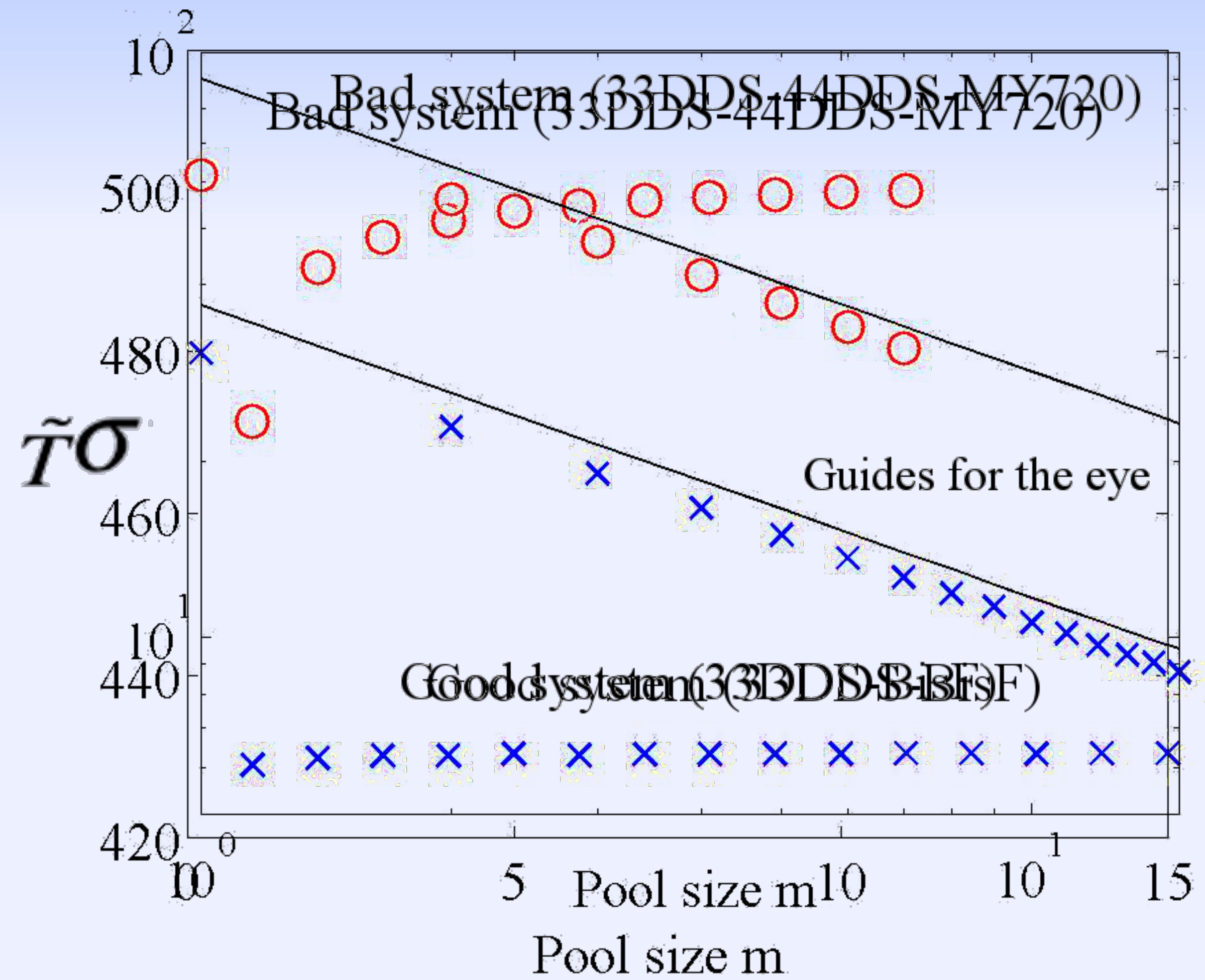


Assessing ability to extract T_g

Is hyperbola fit biasing results?

Test for bias (pooling)

Construct $\binom{M}{m}$ average $T_{g,i}$ from every combination of m data sets chosen from a total of M



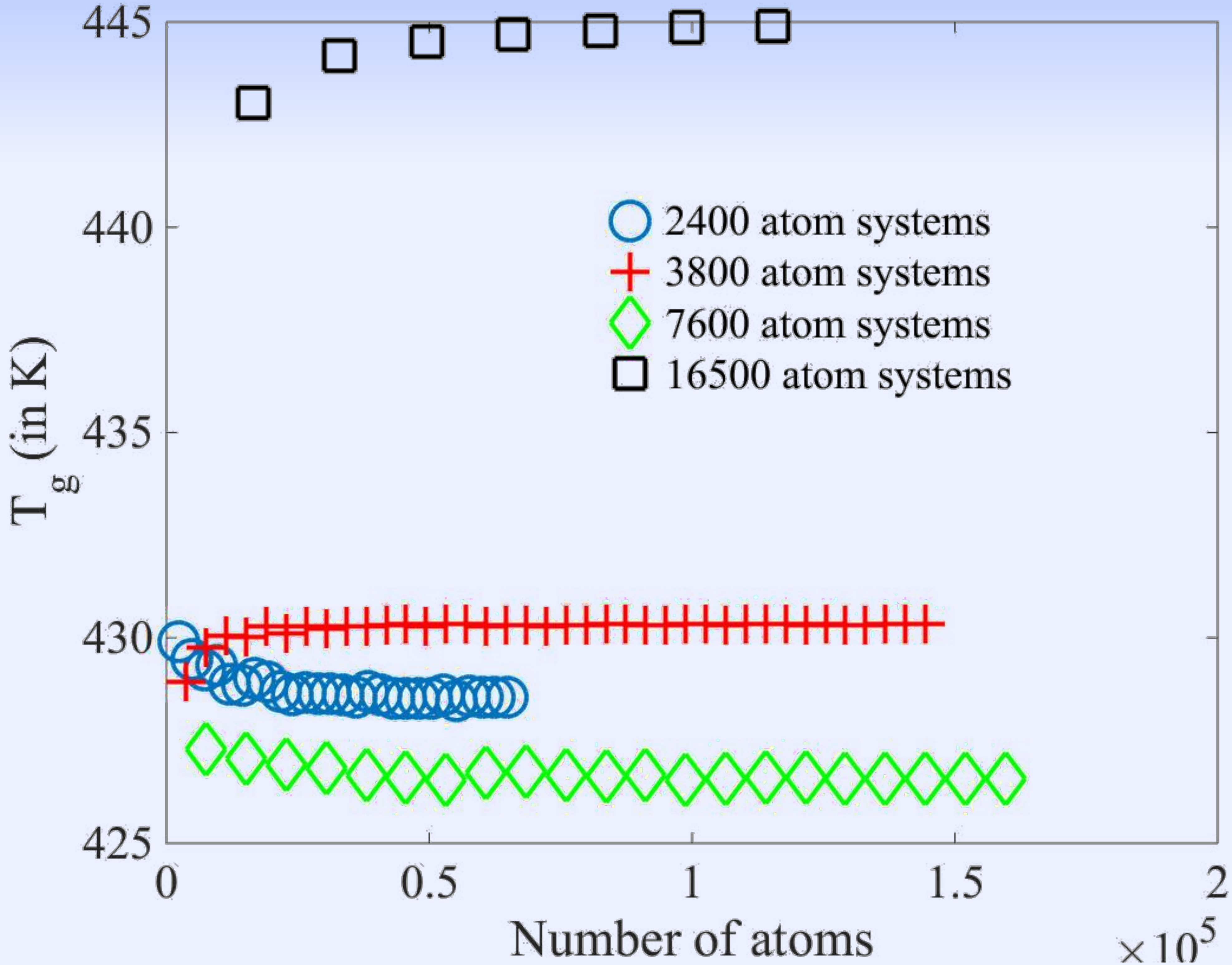
$$\tilde{T} = \binom{M}{m}^{-1} \sum_i T_{g,i} = \text{constant}$$

$$\sigma^2 = \frac{1}{M-m} \sum_i \left(T_{g,i} - \tilde{T}\right)^2 \propto \frac{1}{m}$$

IF linearity holds

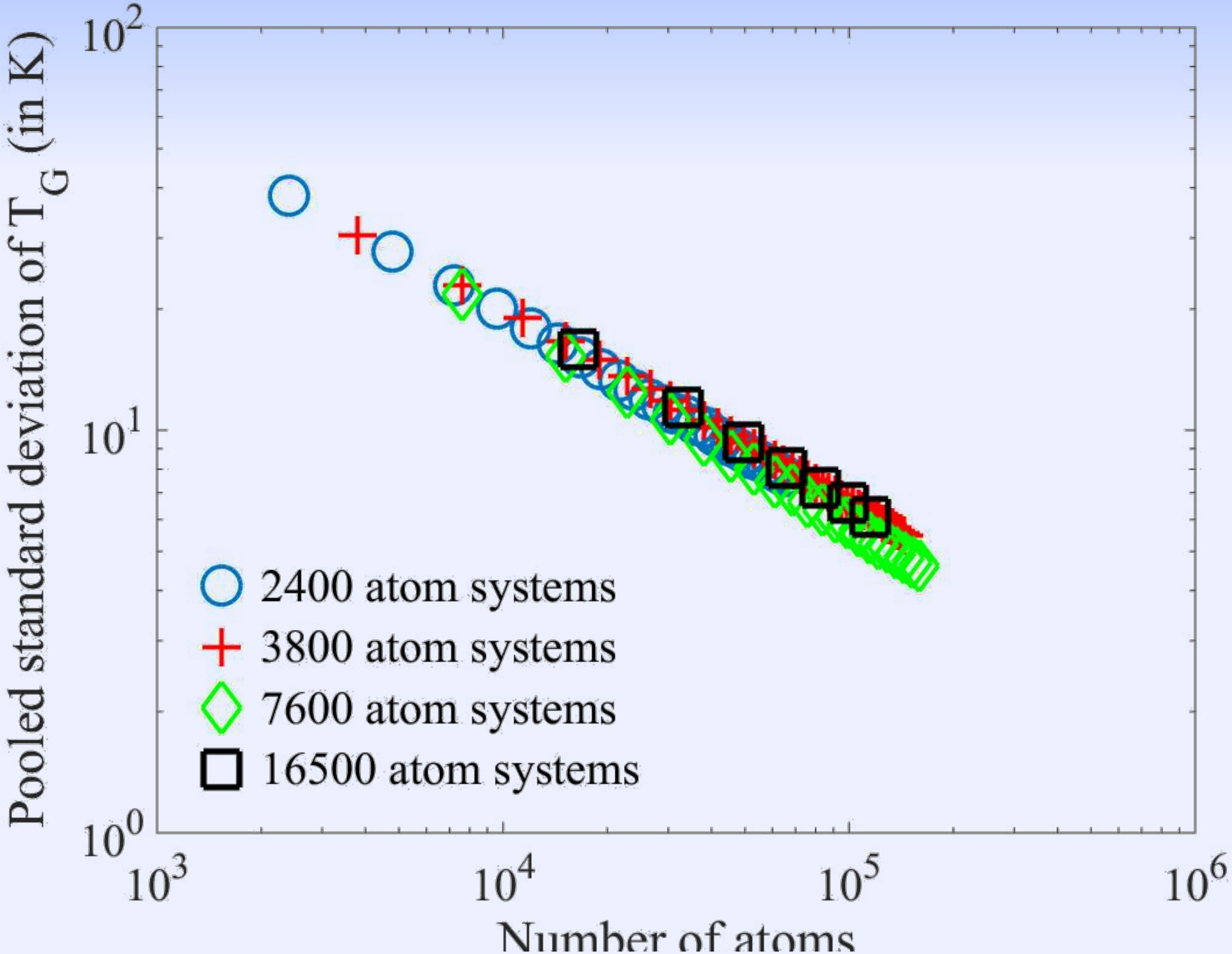
Assessing ability to extract T_g

Is average density converged?



Assessing ability to extract T_g

Is average density converged?



Assessing ability to extract T_g

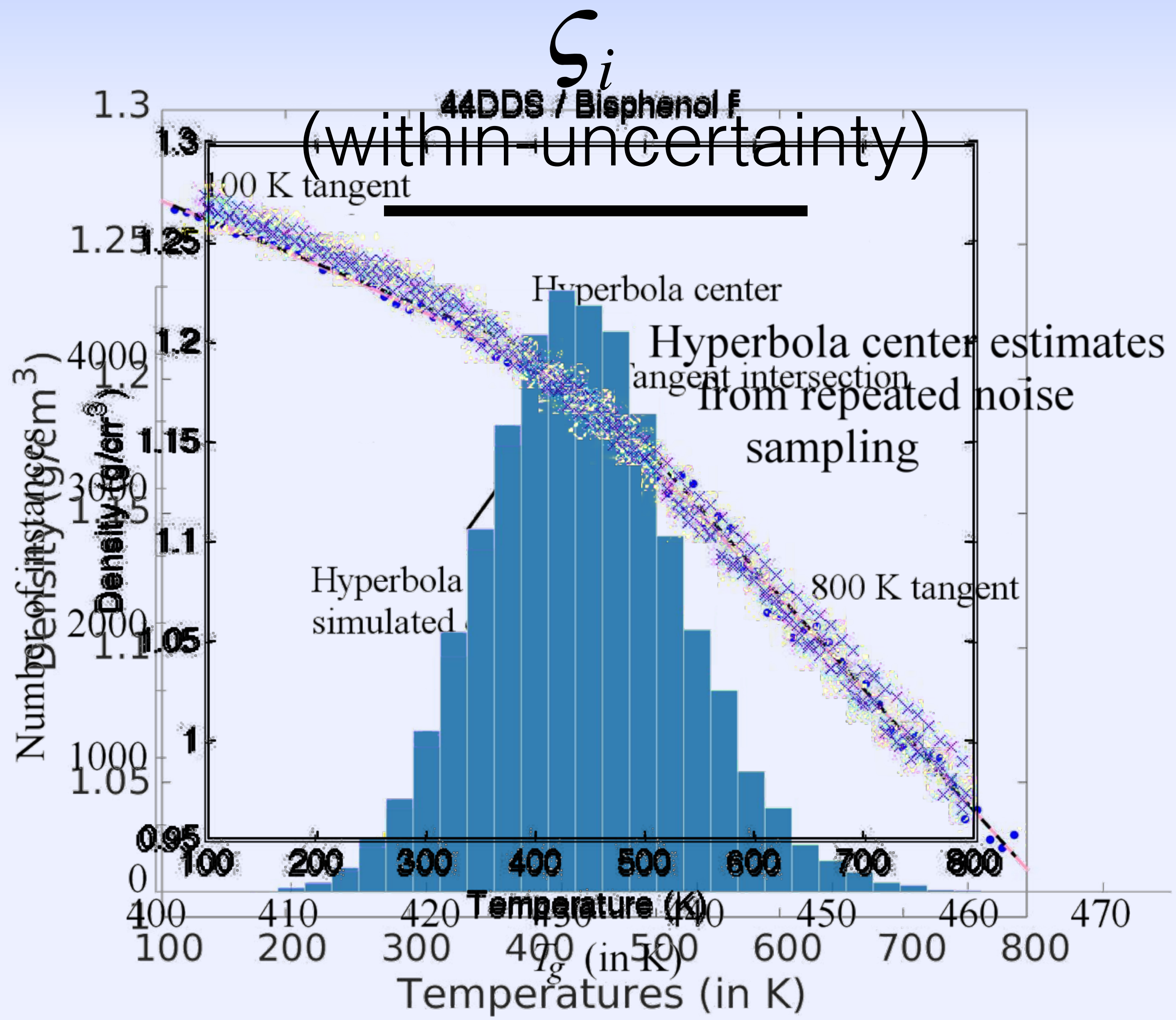
Did we extract a “precise” T_g value from the fit?

Noise affects fit, & hence our T_g estimate

Noise model for residuals

$$\rho(T) = \bar{\rho}(T) + \eta$$

Sample noise η & fit hyperbola to yield new T_g



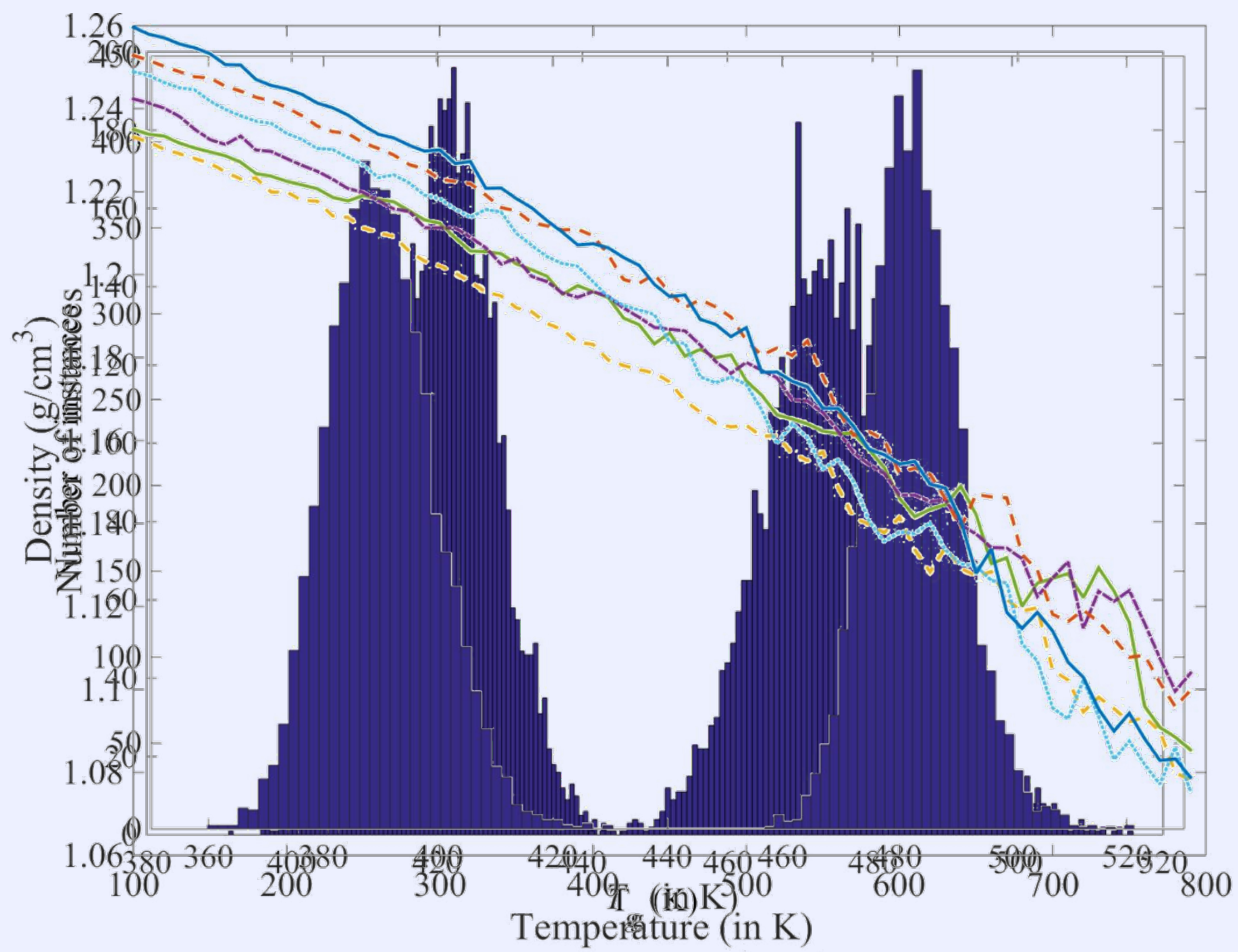
Combining data

Should all data sets be treated equally?

Two simulations may yield different within-uncertainties

Worse, predictions may not overlap

How do we account for missing physics?



Combining data

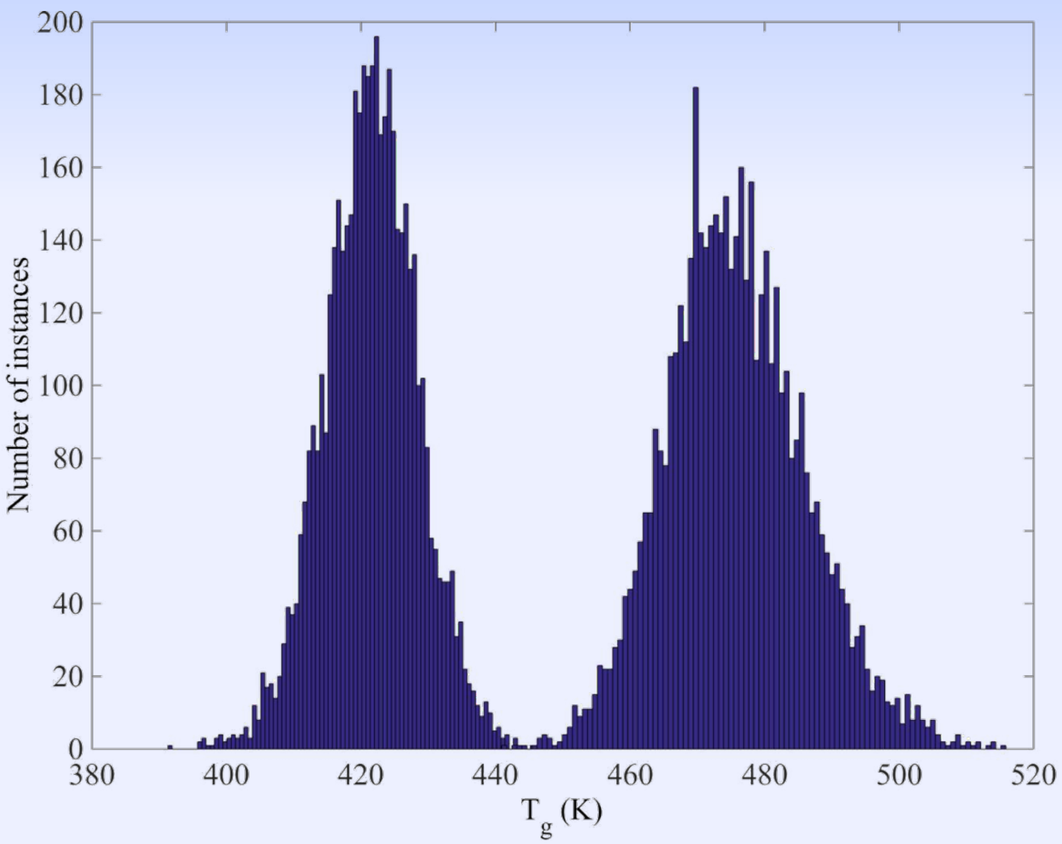
Should all data sets be treated equally?

Weighted-mean statistic model:

T_g from ith simulation

$$\tau = \left[\frac{1}{\sum_i y^2} \right]^{-1} \sum_i \frac{T_{g,i}}{y^2}$$

uncertainty from
under-modeled physics

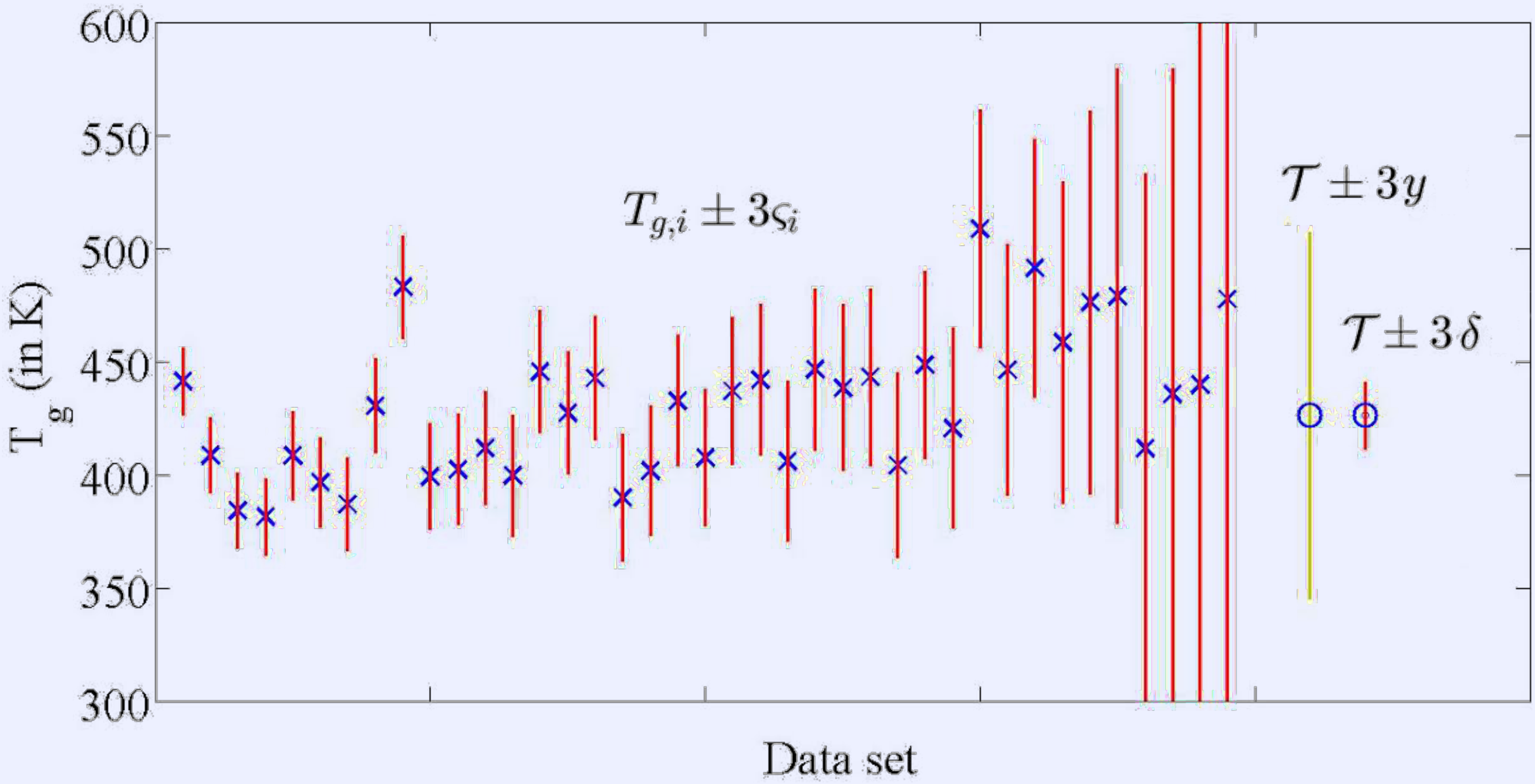


de-weights "imprecise"
& overconfident T_i

Solve for y using maximum likelihood analysis (MLE)

Combining data

Final uncertainty estimate: $\delta^2 = \left[\frac{1}{\sum_i y^2 + \varsigma_i^2} \right]^{-2} \sum_i \frac{\left(T_{g,i} - \tau\right)^2}{\left(y^2 + \varsigma_i^2\right)^2}$

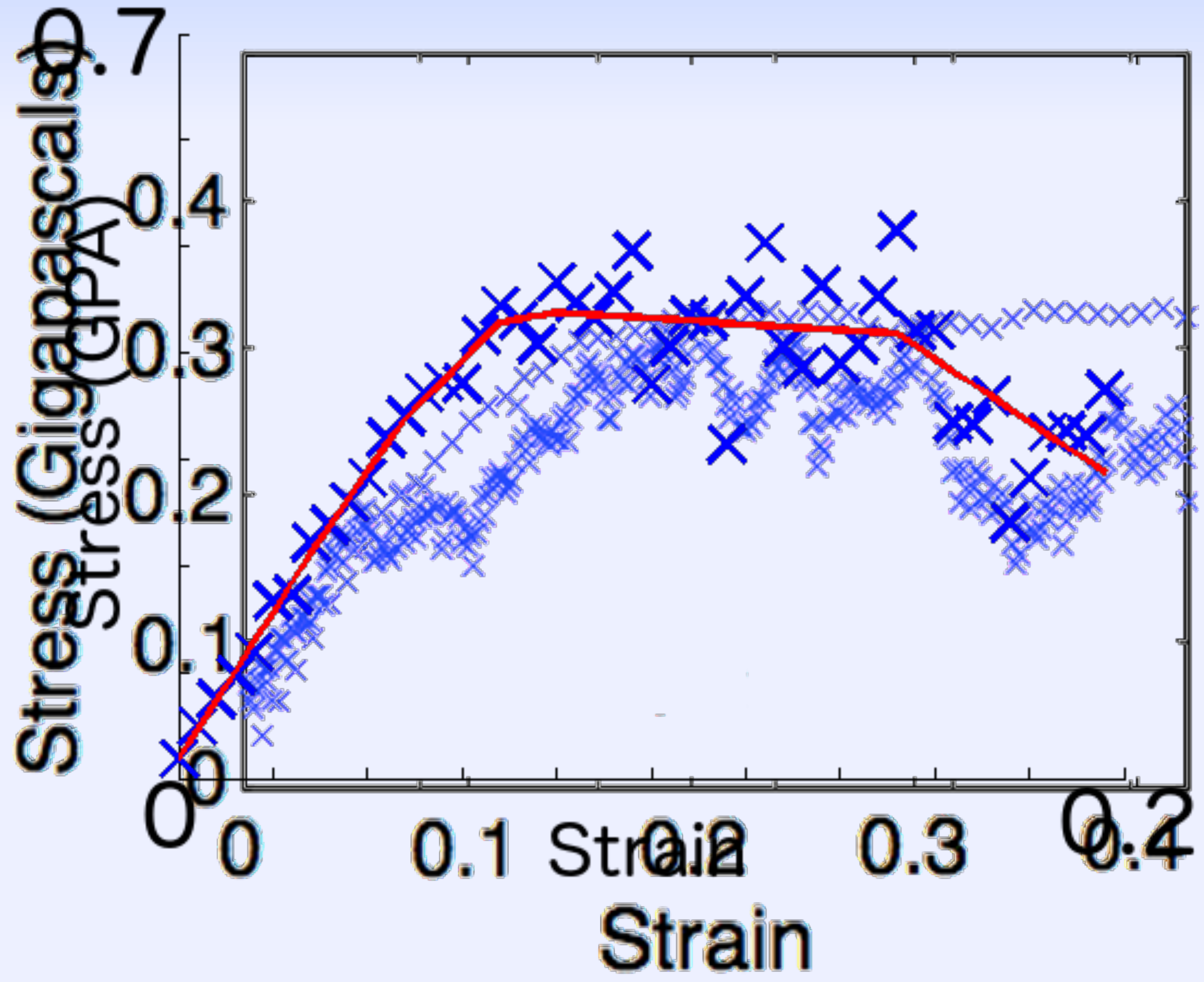


Open problems: yield strain

Strain at which material no longer resists a load

Identified as maximum of stress-strain curve

How do we deal with noisy data?



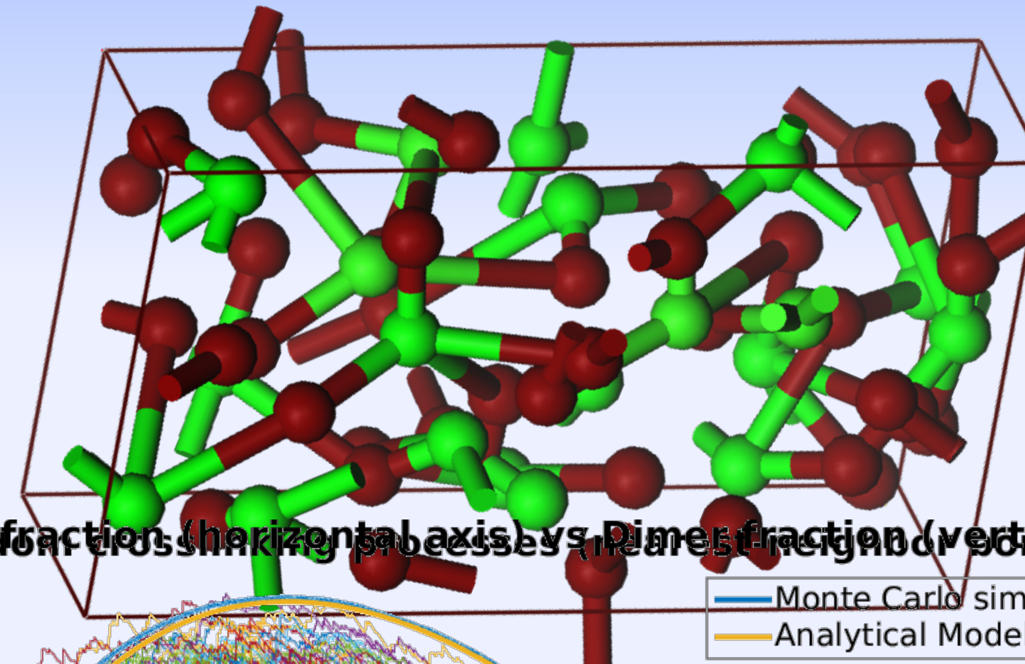
Analysis using convex functions.

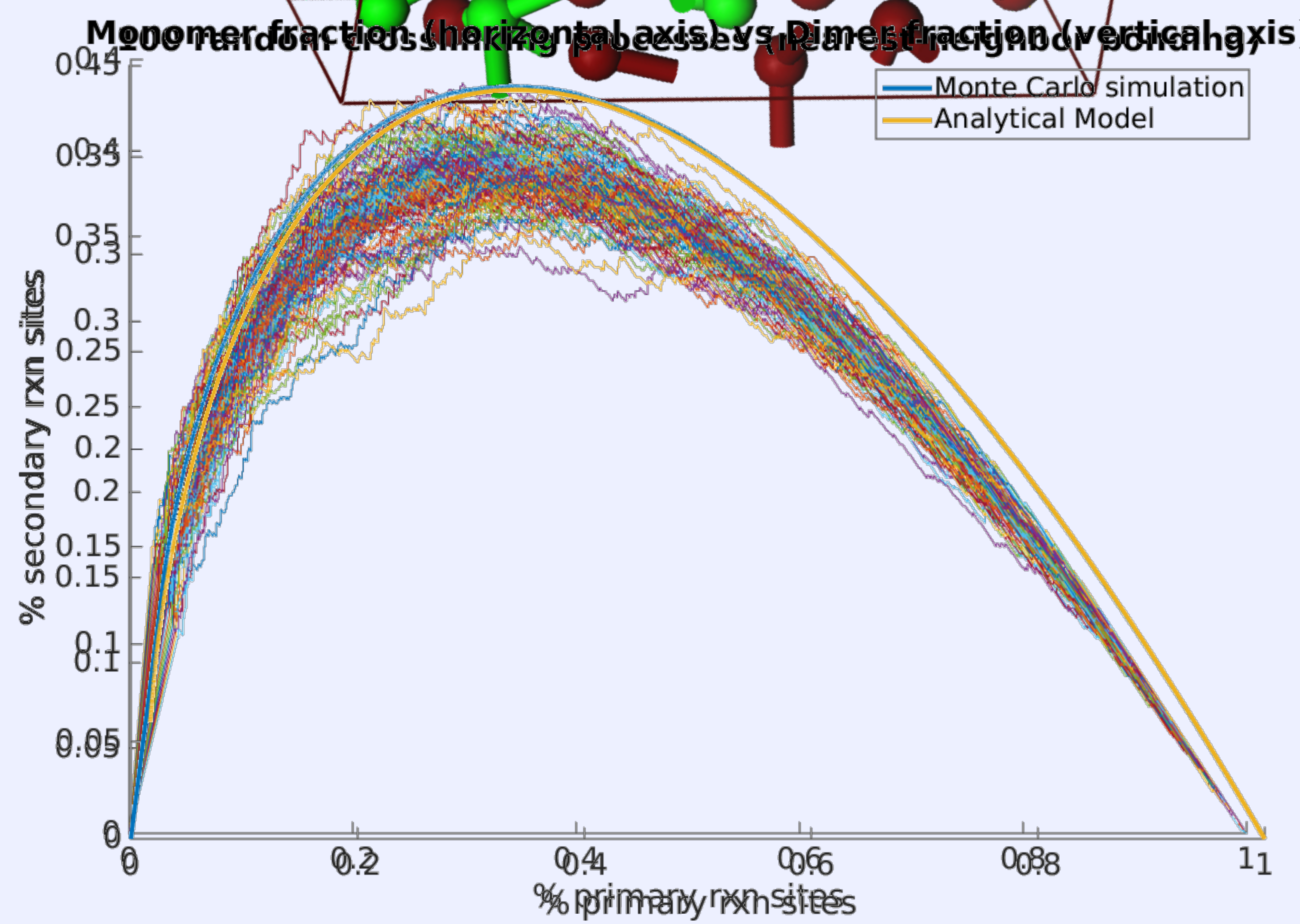
Open problems: understanding statistics of "realistic" crosslinked networks

What is mean number of edges at a given vertex?

Depends on x-link algorithm: e.g. random bonding, nearest neighbor….

Analytical (probabilistic) models to describe simulated predictions





Conclusions

MD is driving development of materials & other disruptive technologies

UQ can help industry assess usefulness of their simulations

Lots of open problems