# Characterizing Errors and Uncertainties in NEMD Simulations of Phonon Transport

Manav Vohra[†], Sankaran Mahadevan[†]

Collaborators: Seungha Shin[§], Ali Y. Nobakht[§]

[†]Vanderbilt University

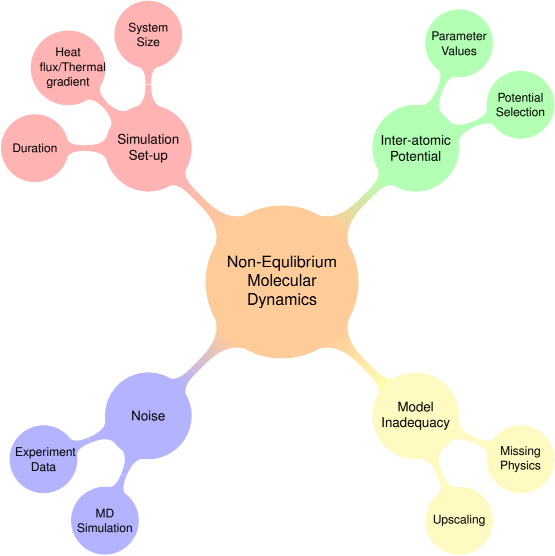
[§]University of Tennessee, Knoxville

April 11, 2018

# NON-EQUILIBRIUM MD

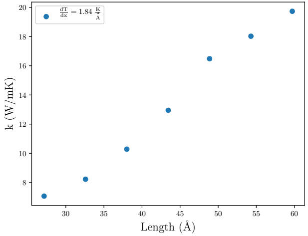
- Widely used to study thermal (phonon) transport in non-metallic systems (C,Si,Ge).
- System subjected to a temperature gradient using thermostats.
- Steady-state thermal energy exchange between the thermostats is used in Fourier's law to estimate bulk thermal conductivity ($\kappa$).
- Estimates are uncertain and severely under-predicted.
  - Simulation length-scales $\ll$ phonon mean free path.
  - Thermostats reduce correlation b/w vibration modes.

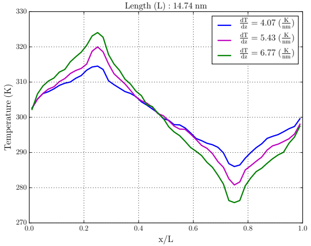
# Sources of Uncertainty



# SOURCES OF UNCERTAINTY

- Bulk thermal conductivity is size-dependent.
- Variability in applied thermal gradient (Kapitza effect).
- Choice of the inter-atomic potential.
- Nominal estimates of the potential parameters.



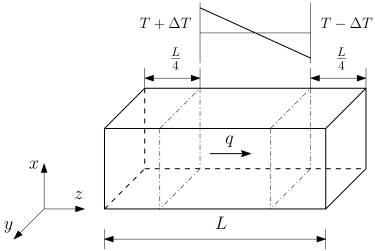



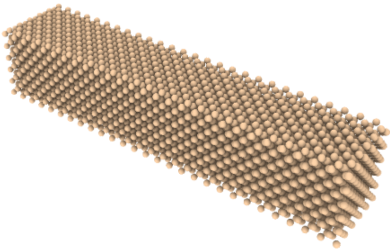
# Specific Research Goals

- Quantify discrepancy in $\kappa$ between predictions and data.
  - Construct a response surface for $\kappa(s, \frac{d\theta}{dx})$.
- Perform sensitivity analysis of the potential parameters.
  - Estimate derivative-based sensitivity measures (DGSM).
- Construct a reduced order surrogate for $\kappa$ using sparse NEMD predictions.
  - Use the surrogate for forward propagation of uncertainty, and global sensitivity analysis.
- Calibrate the *important* parameters in a Bayesian setting.

# PROBLEM SET-UP

| | |
|---|---|
| Lattice Constant, $a$ (Å) | 5.43 |
| Width, Height (Å) | $22a$ |
| $\Delta t$ (ps) | 0.0005 |
| Boundary Condition | Periodic |
| Lattice Structure | Diamond |
| Inter-atomic Potential | Stillinger-Weber |



# Problem Set-up

- Stages:

NVT → NVE → NVE

[Eqilibrate system to 300 K] [Equilibrate thermostats] [Generate Data]

N: Number of Atoms V: Volume T: Temperature E: Energy

- Observable: Avg. energy exchange b/w thermostats ($q$)
- QoI: Bulk thermal conductivity ($\kappa$)

$$\kappa = \frac{q}{\left|\frac{dT}{dz}\right|}$$

- Appropriate selection of width, height, and simulation-time was ensured.

# Response Surface: Discrepancy

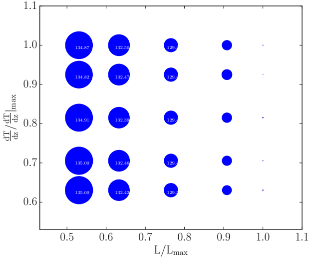
- PC representation of the discrepancy, $\epsilon_{\text{d}}$:

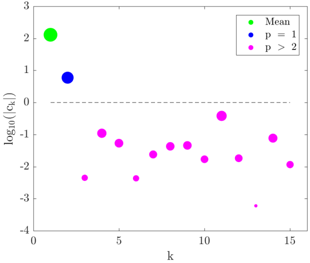
$$\epsilon_{\text{d}} \approx \epsilon_{\text{d}}^{\text{PCE}} = \sum_{k\in\mathcal{I}} c_k(T)\Psi_k(\boldsymbol{\xi}(\boldsymbol{\theta}))$$

- Uncertain parameters, $\boldsymbol{\theta}$: $\{L, \frac{dT}{dz}\}$

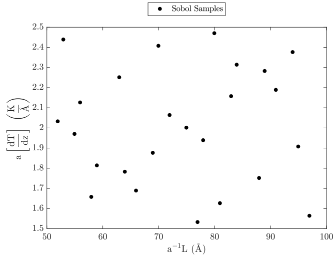
$$L \sim \mathcal{U}[50a, 100a](\text{Å})$$

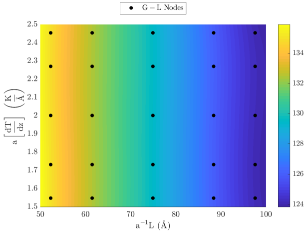
$$\frac{dT}{dz} \sim \mathcal{U}[\frac{1.5}{a}, \frac{2.5}{a}](\frac{K}{\text{Å}})$$



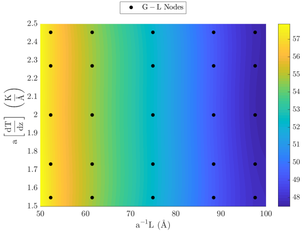



# VERIFICATION



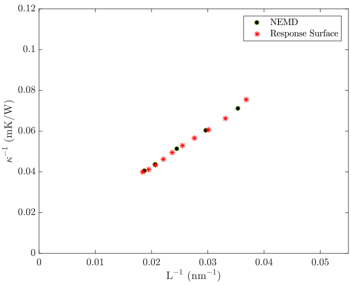

300 K



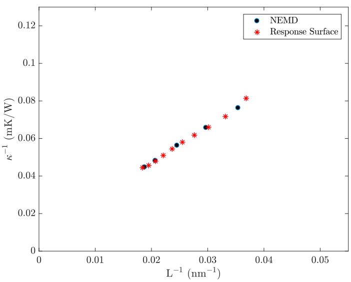

500 K

$$\varepsilon_{\text{L-2}} = \frac{\left[\sum_j (\epsilon_{\mathrm{d},j}^{\mathrm{MD}} - \epsilon_{\mathrm{d},j}^{\mathrm{PCE}})^2\right]^{\frac{1}{2}}}{\left[\sum_j (\epsilon_{\mathrm{d},j}^{\mathrm{MD}})^2\right]^{\frac{1}{2}}} \sim \mathcal{O}(10^{-3})$$

# Direct Method




300 K




500 K

- y-intercept of the straight line fit to the above plot provides an estimate of the bulk thermal conductivity.

# The Stillinger-Weber Potential

## Functional Form

$$\Phi(1,\ldots,N) = \sum_{i,j(i<j)} v_{ij}^{(2)}(A,B,p,q,\alpha) + \sum_{i,j,k(i<j<k)} v_{ij}^{(3)}(\lambda,\gamma)$$

## Shortcomings

- Inadequate functional representation.
- Estimates based on a limited search.
- Do not account for measurement error and MD noise.
- Parametric uncertainties were not considered.

# The Stillinger-Weber Potential

## Functional Form

$$\Phi(1,\ldots,N) = \sum_{i,j(i<j)} v_{ij}^{(2)}(A,B,p,q,\alpha) + \sum_{i,j,k(i<j<k)} v_{ij}^{(3)}(\lambda,\gamma)$$

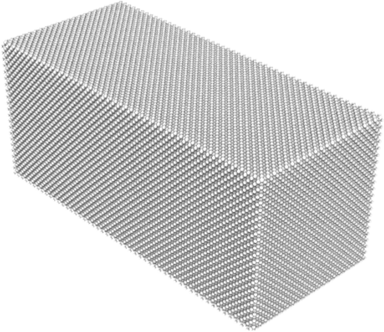
## Mitigation Strategies

- Sensitivity Analysis of the parameters.
- Forward propagation of the uncertainty.
- Bayesian calibration of the key parameters.

# Sensitivity Analysis

## Challenges

- Global sensitivity analysis is computationally intractable.
- Perturbing potential parameters $\rightarrow$ loss of structural integrity.



# Sensitivity Analysis

- Derivative-based sensitivity measures (DGSM) are estimated to identify *unimportant* parameters.

$$\mu_i = \mathbb{E}\left[\left(\frac{\partial G(\boldsymbol{\theta})}{\partial \theta_i}\right)^2\right] \rightarrow \hat{\mathcal{C}_i\mu_i} = \frac{\mathcal{C}_i\mu_i}{\sum_i \mathcal{C}_i\mu_i} \rightarrow \mathcal{T}_i \leq \frac{\mathcal{C}_i\mu_i}{V} \; (\propto \hat{\mathcal{C}_i\mu_i})$$

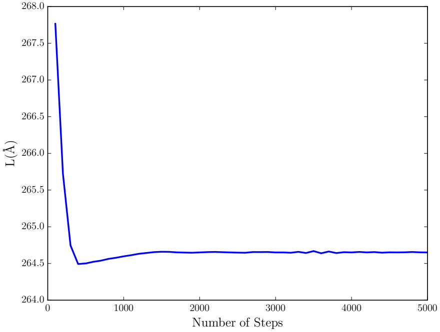
- DGSM estimates are used to compute upper bound on Sobol total effect index ($\mathcal{T}_i$).

# Sensitivity Analysis

- Add an NPT ensemble prior to NVT and run it for a sufficiently long time.

| NPT | → | NVT | → | NVE | → | NVE |
|---|---|---|---|---|---|---|
| [Relax system length] | | [Eqilibrate system to 300 K] | | [Equilibrate thermostats] | | [Generate Data] |

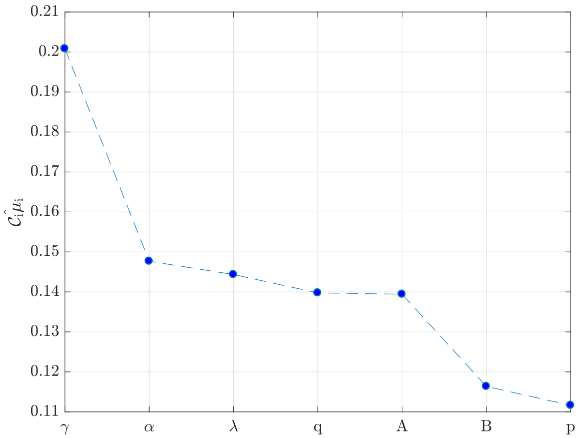
N: Number of Atoms  P: Pressure  V: Volume  T: Temperature  E: Energy



# Parameter Screening

Generate $n_1$ points in $\mathbb{R}^d$.;
% $d$: Number of parameters;
Perturb each point along the $d$ directions to obtain a set of $n_1(d+1)$ points.;
Compute $\mu_i$ using model evaluations at the $n_1(d+1)$;
Determine initial ranks, $\mathcal{R}^{old}$ based on $\hat{\mathcal{C}_i\mu_i}$ values for $\theta_i$;
Set $k$ = 1;
**repeat**
  Generate $n_k$ new points in $\mathbb{R}^d$.;
  Perturb each point along the $d$ directions to obtain a set of $n_k(d+1)$ points.;
  Compute and store model evaluations at the $n_k(d+1)$ points.;
  Compute $\mu_i$ using prior model evaluations at $(d+1)(n_1 + \sum_j^k n_j)$ points.;
  Determine new ranks, $\mathcal{R}^{new}$ based on updated $\hat{\mathcal{C}_i\mu_i}$ values.;
  Compute $max\_pdev$ = $\max\left(\frac{|\mu_{i,k}-\mu_{i,k-1}|}{\mu_{i,k-1}}\right)$.;
  % $max\_pdev$: Maximum percentage deviation in $\mu_i$ between successive iterations.;
  Set $k$ = $k$ + 1;
**until** $(\mathcal{R}^{new} \neq \mathcal{R}^{old}$ **or** $max\_pdev > \tau)$;

# Parameter Screening

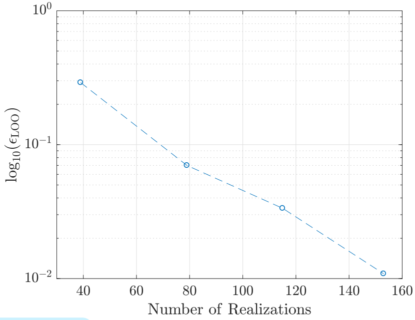


# Reduced Order Surrogate

- PCE for $\kappa$:

$$\kappa = \sum_{s \in \mathcal{A}} c_s(T)\Psi_s(\boldsymbol{\xi})$$

$\boldsymbol{\xi}$ : $\{\xi_1(A), \xi_2(q), \xi_3(\alpha), \xi_4(\lambda), \xi_5(\gamma)\}$




- Regularized least-squares minimization problem:

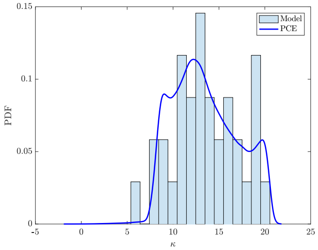
$$\hat{\boldsymbol{c}} = \underset{\boldsymbol{c} \in \mathbb{R}^{|\mathcal{A}|}}{\arg\min}\, \mathbb{E}\left[\left(\boldsymbol{c}^{\mathsf{T}}\Psi(\boldsymbol{\xi}(\boldsymbol{\theta})) - \kappa_{\boldsymbol{\theta}}^{\mathsf{MD}}\right)^2\right] + \lambda\|\boldsymbol{c}\|_1$$

# VERIFICATION

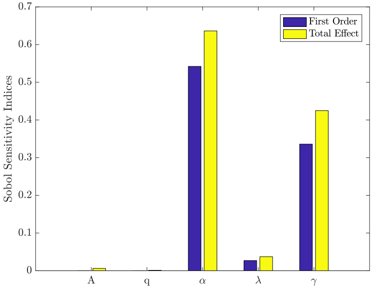
## L-2 NORM

$$\epsilon_{\text{L-2}} = \frac{\left[\sum_{i=1}^{N=25}\left(\mathcal{M}(\boldsymbol{\theta}_{\text{7D}}^{(i)}) - \mathcal{M}^{PCE}(\boldsymbol{\theta}_{\text{5D}}^{(i)})\right)^2\right]^{\frac{1}{2}}}{\left[\sum_{i=1}^{N}\left(\mathcal{M}(\boldsymbol{\theta}_{\text{7D}}^{(i)})\right)^2\right]^{\frac{1}{2}}} \rightarrow \mathcal{O}(10^{-2})$$

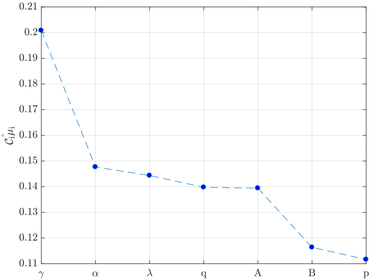
## PROBABILISTIC



# GLOBAL SENSITIVITY ANALYSIS




$10^6$ samples



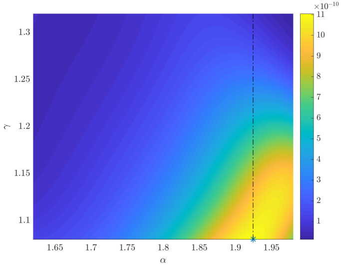

25 samples

# Bayesian Calibration

- Bayes' rule:

$$\mathcal{P}(\boldsymbol{X}|\boldsymbol{Y}) \propto \mathcal{P}(\boldsymbol{Y}|\boldsymbol{X})\mathcal{P}(\boldsymbol{X})$$

$$\boldsymbol{X} : \{\alpha, \gamma\}$$




- Likelihood, $\mathcal{P}(\boldsymbol{Y}|\boldsymbol{X})$:

$$\mathcal{P}(\boldsymbol{Y}|\boldsymbol{X}) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\kappa_{\mathrm{E}} - \kappa_{\mathrm{MD}})^2}{2\sigma^2}\right]$$

# CONCLUDING REMARKS