Pressure Transferable Coarse-Grained Potentials for Polymers under Isothermal and Shock Compressions

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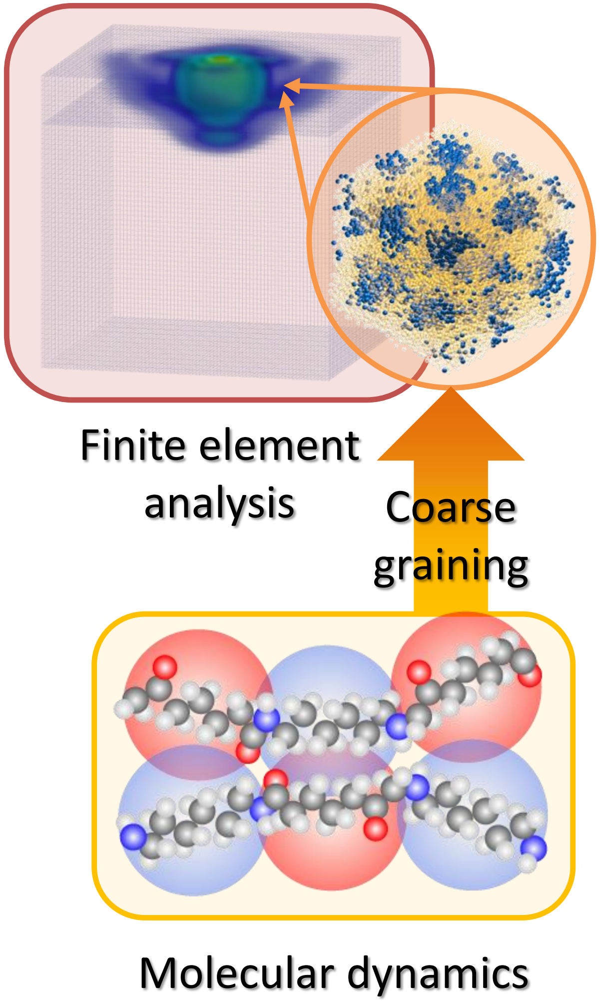
Overall goals

- Advance fundamental understanding of polymer stress response from materials-by-design perspective under extreme loading conditions

- Improve thermodynamically-consistent, coarse-grained molecular dynamics for polymer materials

  Representability: predict more than just structural properties

  Transferability: predict properties across a range of thermodynamic states



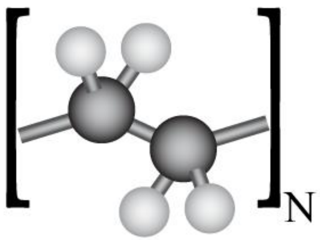
Outline

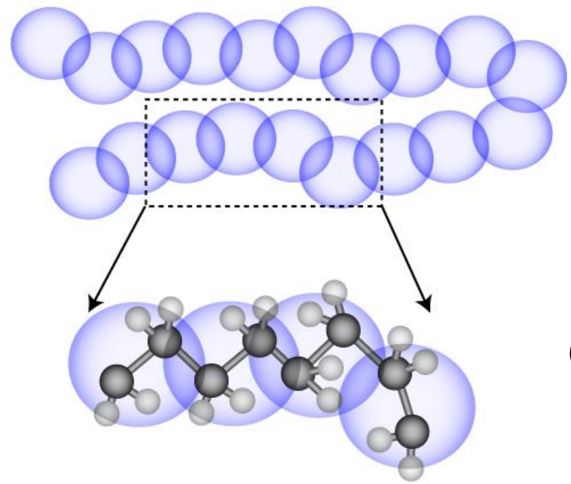
- Transferability problem for CG potentials of soft materials: *the CG potential is only accurate at the thermodynamic state where it was calibrated.*
  - Temperature transferability
  - <u>Pressure transferability</u>
- IBI-EAM and many body CG potential
  - Pressure optimization algorithm
- Model verification and validation
  - Bulk modulus
  - Shock hugoniot response

Coarse-Grained mapping

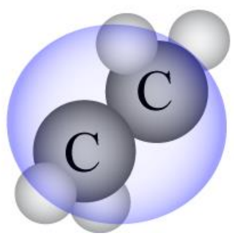
Groups of atoms represented by super atoms

All-atom
molecule





Coarse-Grained
mapping

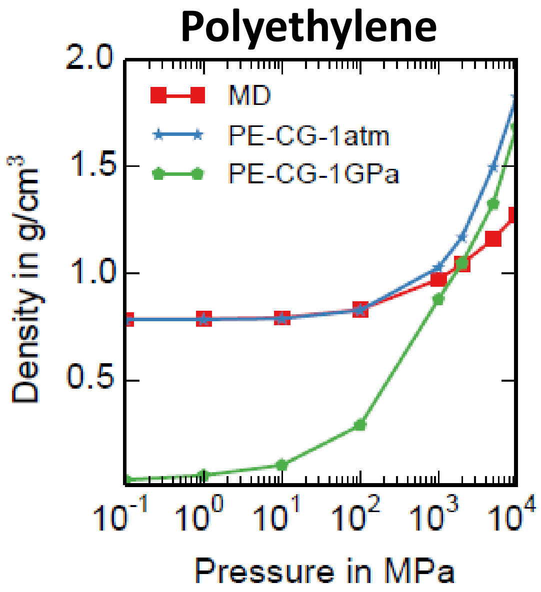


Coarse-Grained
molecule

What coarse-grained potential will reproduce
the same thermodynamics of the MD system?

Transferability and representability

- Representability: *does the CG model accurately reproduce thermodynamic properties?*
- Transferability: *is the CG potential accurate at a different thermodynamic state than where it was calibrated?*



For CG models, naïve application of IBI-derived potentials are overly soft in volumetric compression.

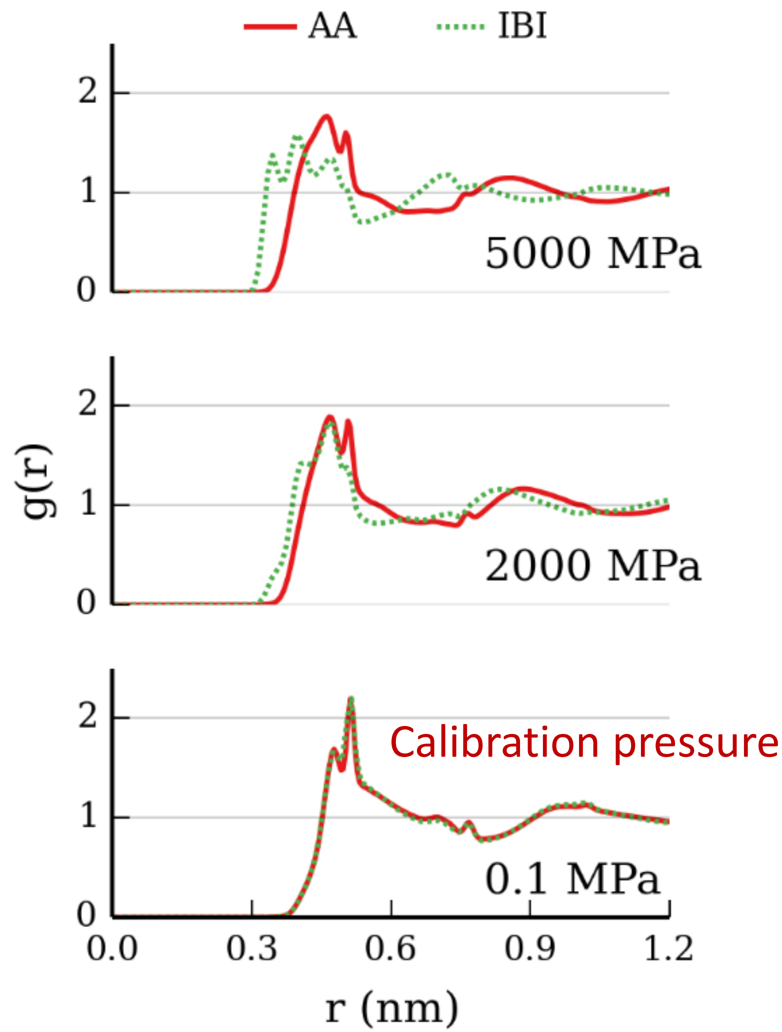
Equation of state of polyethylene at T=300K computed from CG models derived by iterative Boltzmann inversion.

Transferability of IBI polyethylene potential

- Probability of finding a particle at distance r from a reference point

$$g(r) = A\exp\left[-\frac{u(r)}{k_B T}\right]$$

U(r) – potential mean force



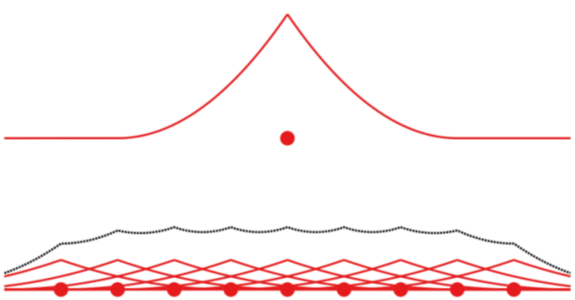
Many body Coarse-Grained potential

$$E_i = F_i\left(\sum_{j\neq i}\rho_j(r_{ij})\right) + \frac{1}{2}\sum_{j\neq i}\phi_{ij}(r_{ij})$$

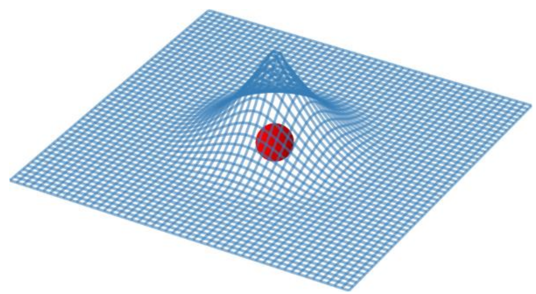
Energy of atom i | **Embedding energy function** | **local density function (Electron density Function)** | **Pair Potential**

$$\rho(r_{ij}) = \left(1 - \frac{r}{r_c}\right)^2$$

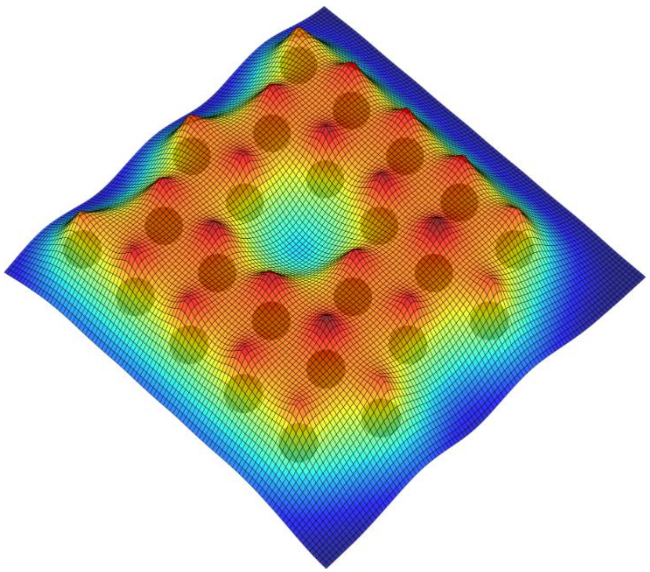
Arbitrary density function



1D density profiles



2D density profile (1 atom)



Multi-atom density profile

Calibration of the IBI-EAM Potential

Pair Potentials

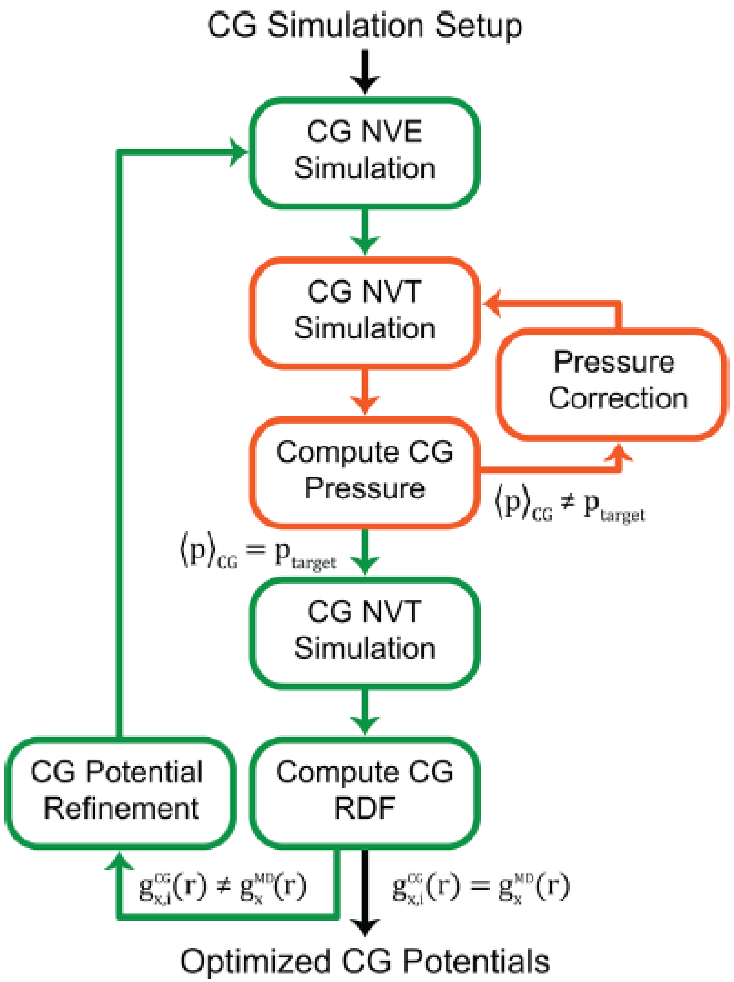
$$V(r) = -k_B T \ln(g(r))$$

Angle Potentials

$$V(\theta) = -k_B T \ln\left(\frac{P(\theta)}{\sin(\theta)}\right)$$

Bond Potentials

$$V(l) = -k_B T \ln\left(\frac{P(l)}{l^2}\right)$$



Pressure (MPa)	Density (g/cc)
-50.7	0.74857
-10.1	0.78123
0.1	0.78417
1.0	0.78585
10.0	0.79213
100	0.82962
1000	0.97115
2000	1.04353
5000	1.16120
10000	1.27479

Calibrated state points

Calibration of Embedding Energy

Virial pressure equation
$$p = \frac{1}{3V}\sum_i \left(m_i \mathbf{v}_i \cdot \mathbf{v}_i + \mathbf{r}_i \cdot \mathbf{f}_i\right)$$

Decomposition of pressure
$$p = p_{ke} + p_{\phi} + p_F$$

Kinetic pressure
$$p_{ke} = \frac{1}{3V}\sum_i m_i \mathbf{v}_i \cdot \mathbf{v}_i$$

Pairwise pressure
$$p_{\phi} = \frac{1}{3V}\sum_i \mathbf{r}_i \cdot \hat{\mathbf{r}}_{ij} \sum_{j>i} \phi_{ij}^{'}(r_{ij})$$

Embedded pressure
$$p_F = \frac{1}{3V}\sum_i \mathbf{r}_i \cdot F_i^{'}\left(\sum_j \rho(r_{ij})\right)\sum_{j \neq i} \rho^{'}(r_{ij})\hat{\mathbf{r}}_{ij}$$

Pressure optimization algorithm

The mean density at a particle can be computed from the radial density function *g(r)*

$$\langle \bar{\rho}_i \rangle = \sum_j \rho(r_{ij}) = \frac{N}{V} \int_0^{r_c} g(r) \rho_i(r) 4\pi r^2 dr$$

Taylor series expansion of the embedding energy

$$F(\bar{\rho}) = \sum_{k=1}^{n} a_k \langle \bar{\rho} \rangle^k$$

Derivative of embedding energy and corresponding **vector form**

$$F'(\bar{\rho}) = \sum_{k=1}^{n} k a_k \langle \bar{\rho} \rangle^{(k-1)} = \mathbf{C} \cdot \mathbf{P}^T$$

Taylor polynomial derivatives

$$\mathbf{P} = \left[A k \bar{\rho}^{(k-1)} \right]_{\mathrm{n \times m}}$$

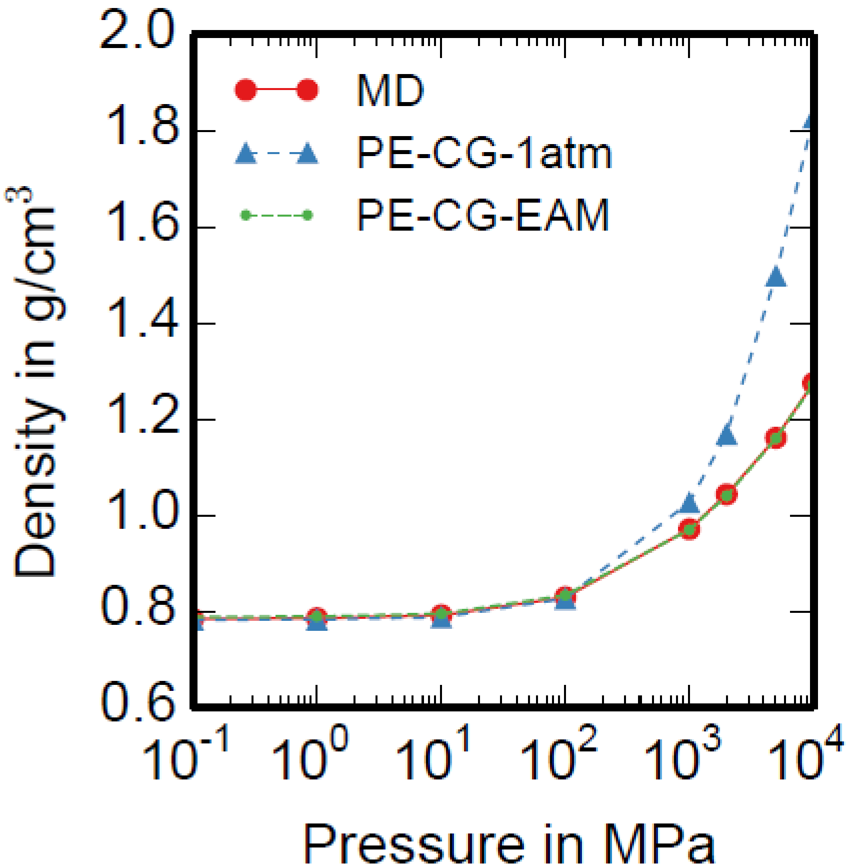
Taylor polynomial coefficients

$$\mathbf{C} = [a_k]_{\mathrm{1 \times m}}$$

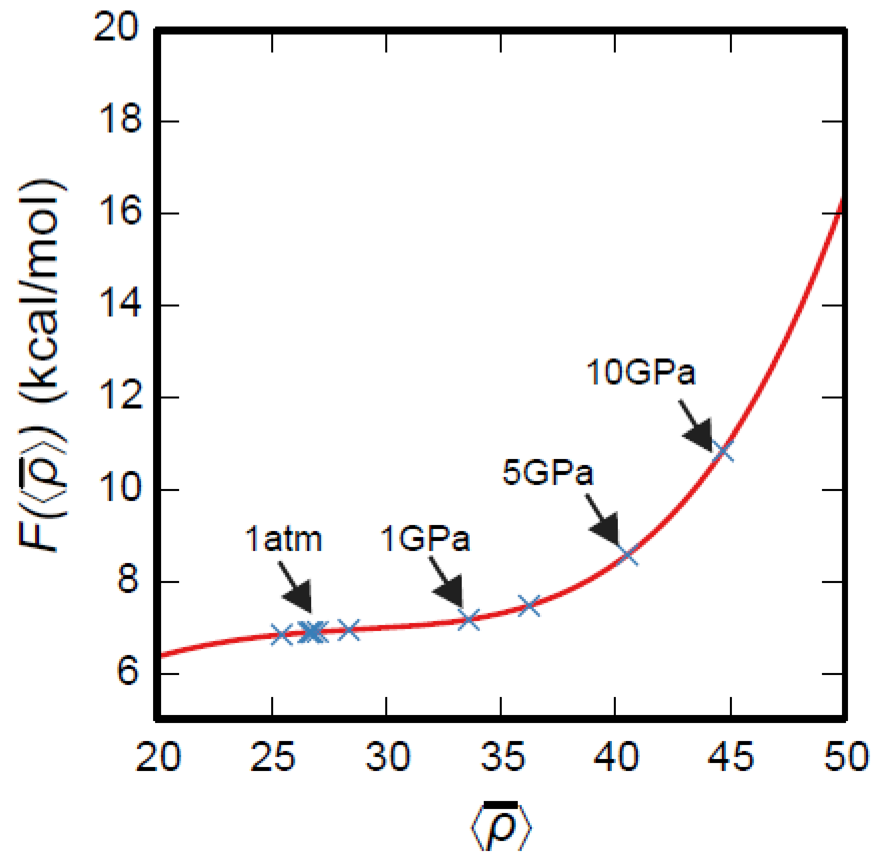
Embedding energy coefficients are solved by least-squares minimization

$$\Delta \mathbf{C} = \left(\mathbf{P}^T \mathbf{P} \right)^{-1} \mathbf{P}^T \Delta \mathbf{p}$$

Calibrated IBI-EAM model for polyethylene

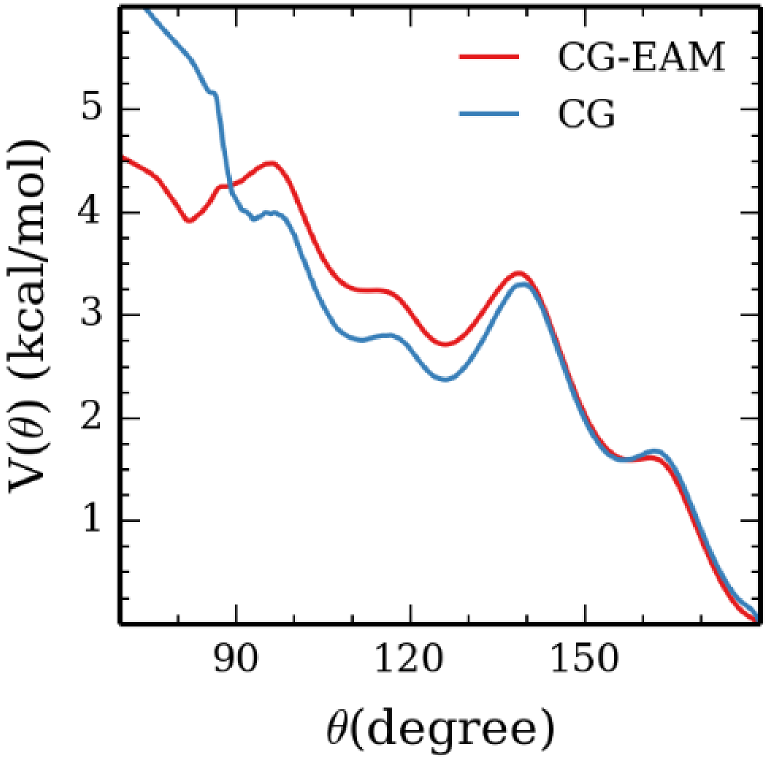


Pressure vs Density

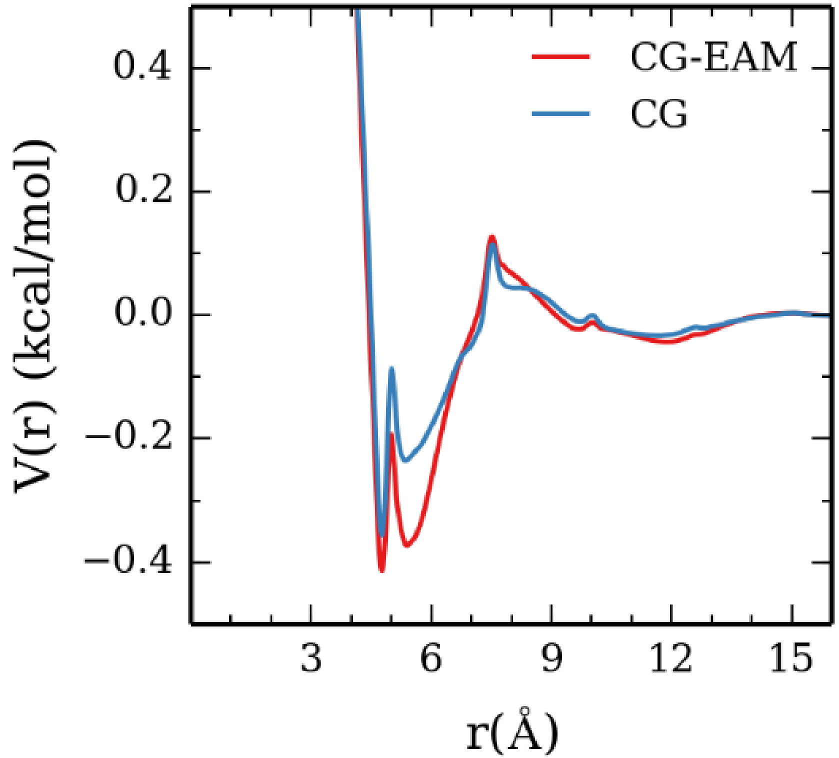


Optimized Embedded Function

Calibrated IBI-EAM model for polyethylene

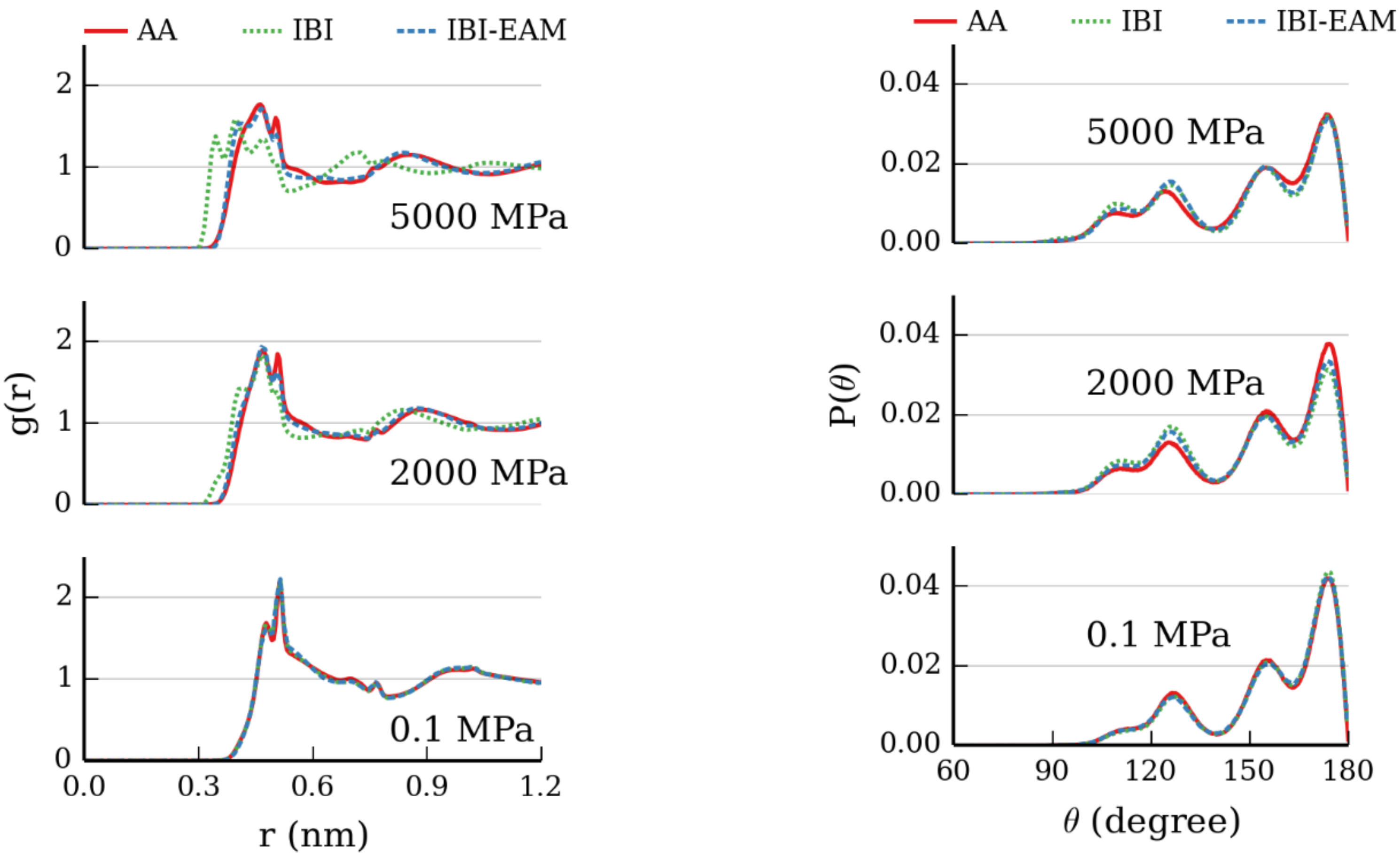


Optimized Angle Potentials



Optimized Pair Potentials

Transferability of IBI-EAM model for PE



Pair and angle distributions are well-reproduced over a wide pressure range!

MODEL VALIDATION AND VERIFICATION

Isothermal Bulk modulus comparison for PE

Tait EOS

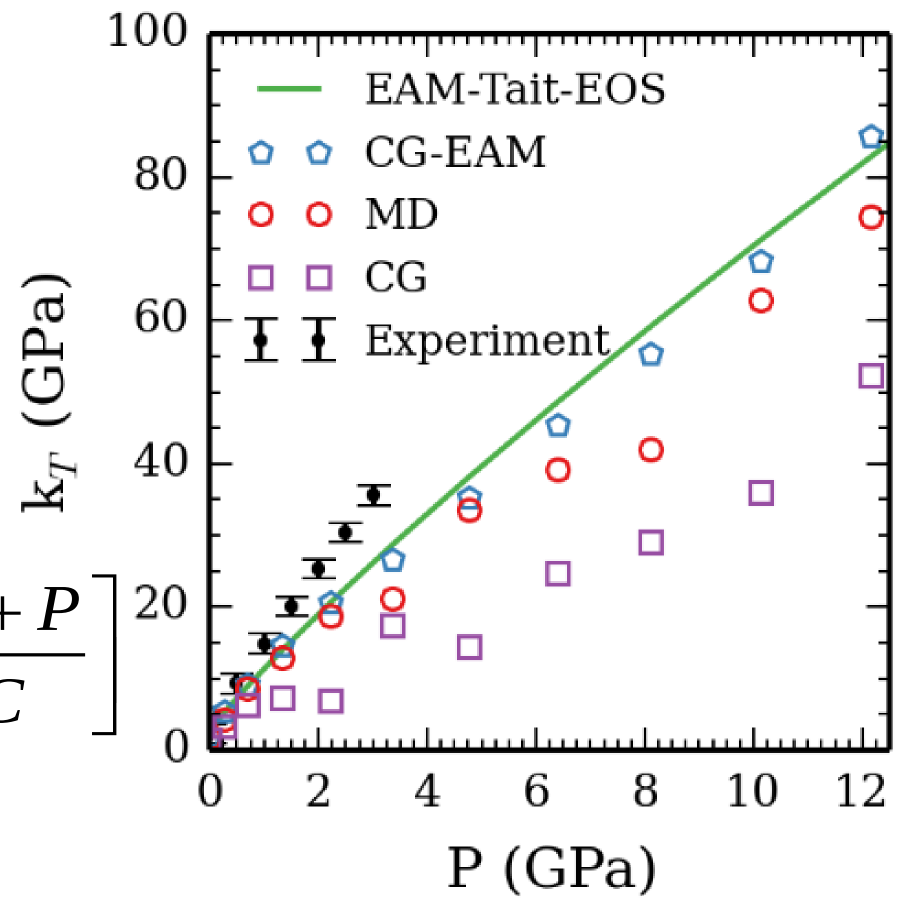
$$\frac{V(P)}{V_0} = 1 - C\ln\left(1 + \frac{P}{B}\right)$$

Isothermal Bulk Modulus

$$k_T(P) = -V\left(\frac{\partial P}{\partial V}\right)_T$$

$$k_T(P) = \left[1 - C\ln\left(1 + \frac{P}{B}\right)\right]\left[\frac{B+P}{C}\right]$$

$$k_T(P) = \frac{k_B T\langle V\rangle}{\langle \delta V^2\rangle}$$



Heydemann, P. L. M., and J. C. Houck. "Bulk modulus and density of polyethylene to 30 kbar." *Journal of Polymer Science Part A-2: Polymer Physics* 10.9 (1972)

Hugoniot us-up Calculations for PE

Sound Speed $c_0 = (\kappa_0 / \rho_0)^{1/2}$

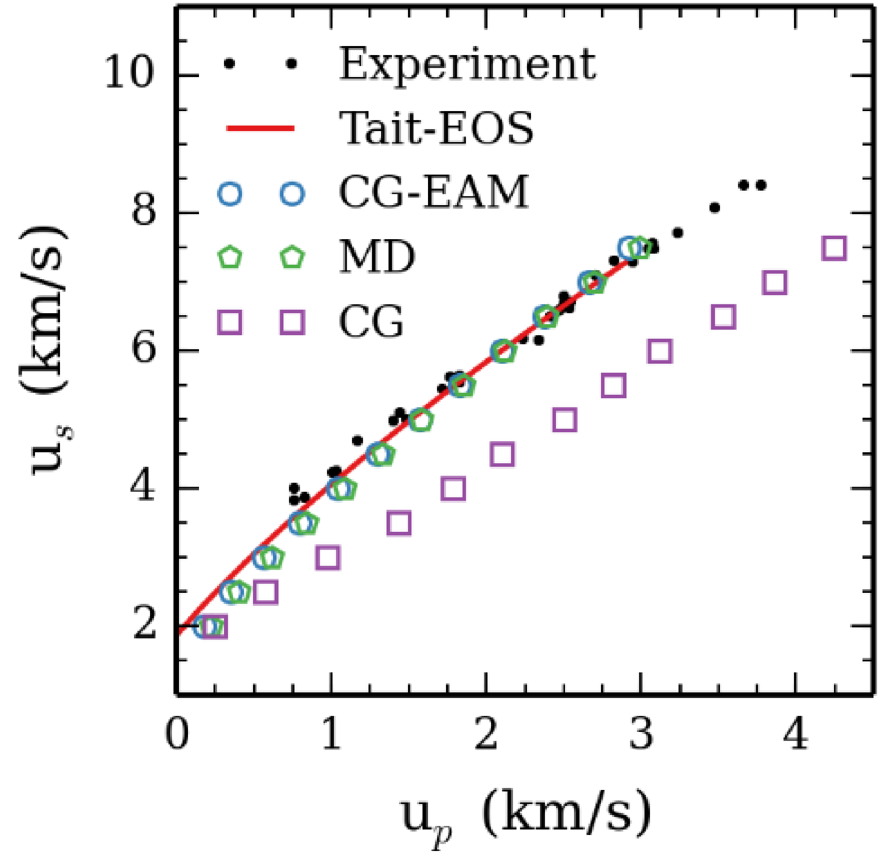
Jump Conditions

$$u_s = \left\{ \frac{P - P_0}{\rho_0} \frac{1}{1 - V/V_0} \right\}^{1/2} \quad u_p = [1 + V/V_0]$$

“pseudo” us-up plane

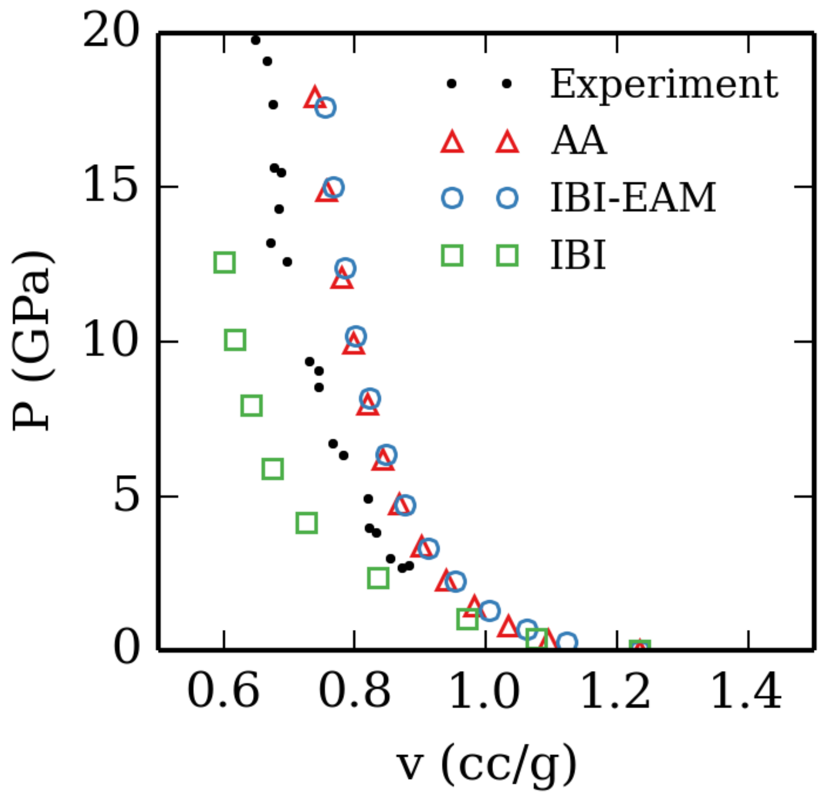
$$\frac{u_s}{c_0} = \left\{ \frac{P}{k_0} \frac{1}{C \ln\left[1 + \frac{P}{k_0 C}\right]} \right\}^{1/2}$$

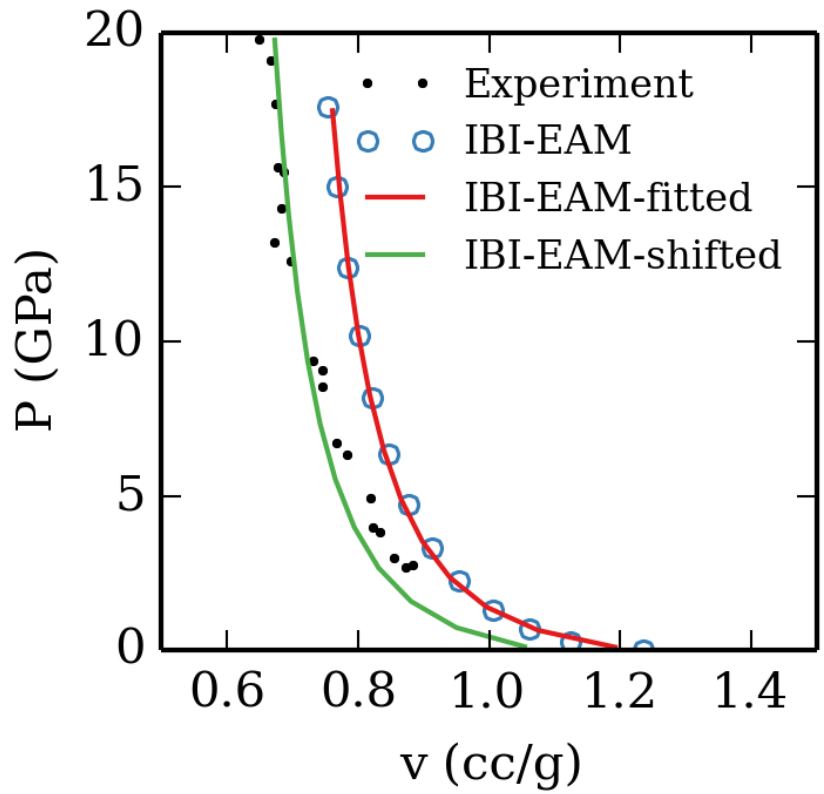
$$\frac{u_p}{c_0} = \left\{ \frac{P}{k_0} \frac{1}{C \ln\left[1 + \frac{P}{k_0 C}\right]} \right\}^{1/2} C \ln\left[1 + \frac{P}{k_0 C}\right]$$



Marsh, Stanley P. *LASL shock Hugoniot data*. Vol. 5. Univ of California Press, 1980

Shock Hugoniot Curve for PE





Experimental PE density – 0.916 g/cc
MD PE density = 0.81 g/cc

Marsh, Stanley P. *LASL shock Hugoniot data*. Vol. 5. Univ of California Press, 1980.

Mie-Gruneisen EOS

Gruneisen EOS $\frac{\gamma}{V} = \left(\frac{dP}{dE}\right)_V = \frac{(dP/dT)_V}{(dE/dT)_V}$ **γ is Gruneisen parameter**

$$dE = TdS - PdV \Rightarrow C_v = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right) dV$$

Temperature Rise Along the Hugoniot

$$\left(\frac{dE}{dv}\right)_H = C_v\left(\frac{dT}{dv}\right)_H + T\frac{\gamma}{v}C_v - P_H$$

From Hugoniot conditions

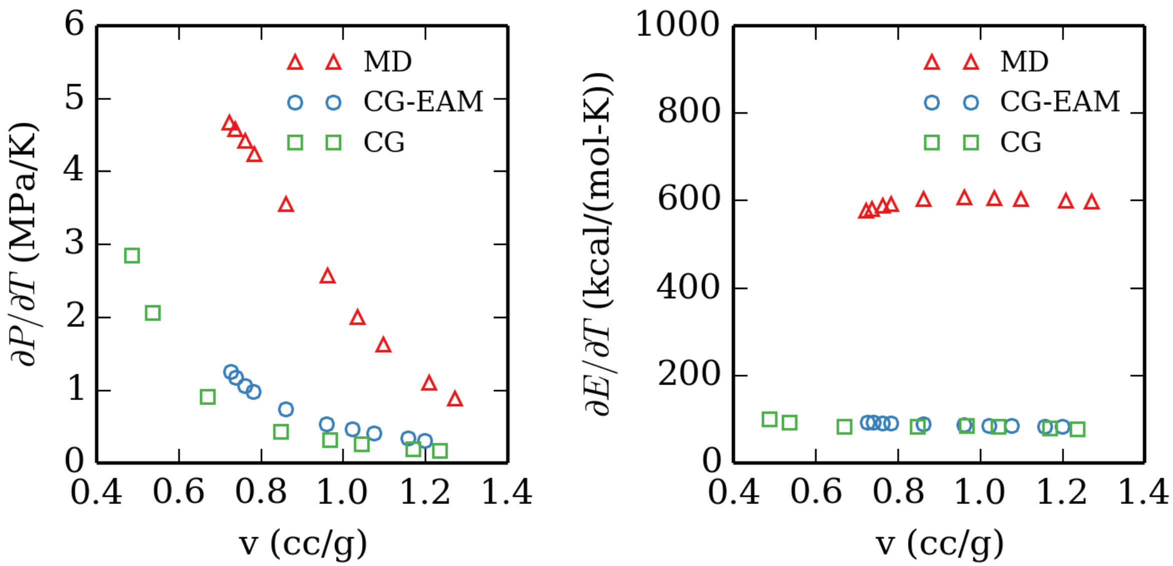
$$\left(\frac{dE}{dv}\right)_H = \frac{1}{2}\left(\frac{dP}{dv}\right)_H (v_0 - v) = f(v)$$

$$\frac{dT}{dv} + \frac{\gamma}{v}T = \frac{f(v)}{C_v} + P_H$$

$$T_H(v) = T_0 e^{-\eta} + e^{-\eta}\int \frac{f(v)}{C_v} e^{\eta} dv \qquad \eta = \int \frac{\gamma}{v} dv$$

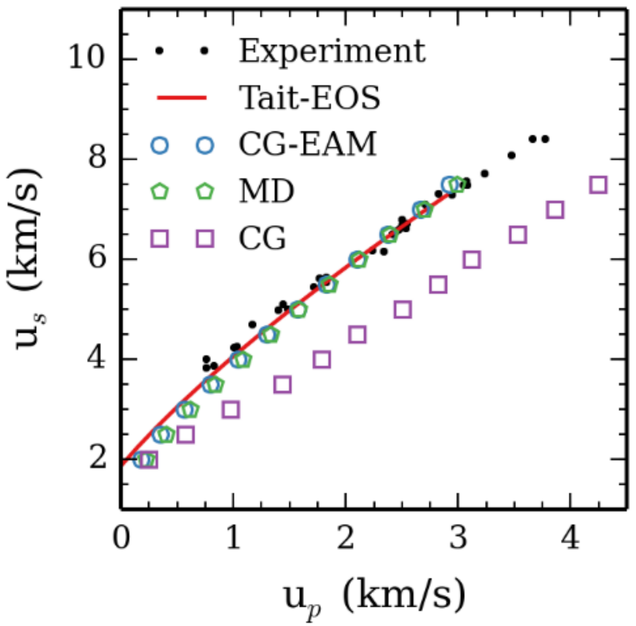
Forbes, Jerry W. *Shock wave compression of condensed matter: a primer*. Springer, 2013

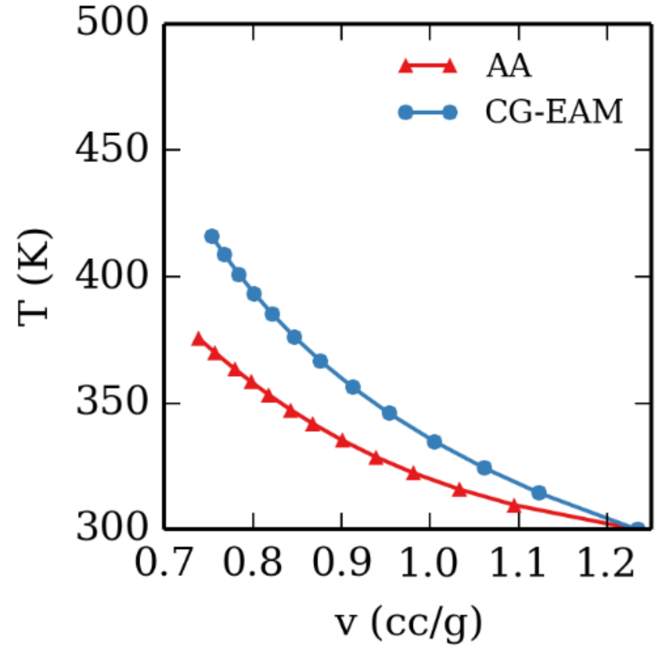
∂P/∂T and ∂E/∂T for PE



- ∂P/∂T and ∂E/∂T are significantly different between MD and CG
- The ratio of these two are not very high
- For most metals, ϒ/v assume to be constant while calibrated ratio from MD simulations increases with volumetric compression

Summary of IBI-EAM shock study





IBI-EAM PE potential

✓ Matches mechanical properties reasonably well

❑ Temperature rise along the Hugoniot shows deviations