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

Finite element analysis

Coarse graining

Molecular dynamics
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
  – Pressure transferability
• 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

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?*

**Polyethylene**

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
- 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

( Electron density Function )
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**

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

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<th>Pressure (MPa)</th>
<th>Density (g/cc)</th>
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<td>1.16120</td>
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<tr>
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Calibrated state points
Calibration of Embedding Energy

Virial pressure equation

\[ p = \frac{1}{3V} \sum_i (m_i \mathbf{v}_i \cdot \mathbf{v}_i + \mathbf{r}_i \cdot \mathbf{f}_i) \]

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

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

Taylor polynomial derivatives

$$
P = \begin{bmatrix} A_k \bar{\rho}^{(k-1)} \end{bmatrix}_{n \times m}
$$

Taylor polynomial coefficients

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

Embedding energy coefficients are solved by least-squares minimization

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

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

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

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

Hugoniot us-up Calculations for PE

Sound Speed  \( c_0 = \left( \frac{\kappa_0}{\rho_0} \right)^{1/2} \)

Jump Conditions

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

\[ u_p = \left[ 1 + \frac{V}{V_0} \right] \]

“pseudo” us-up plane

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

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

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

Mie-Gruneisen EOS

\[
\frac{\gamma}{V} = \left( \frac{dP}{dE} \right)_V = \left( \frac{dP}{dT} \right)_V \left( \frac{dT}{dE} \right)_V
\]

\( \gamma \) 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

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

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

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

\[ \frac{\partial P}{\partial T} \text{ and } \frac{\partial E}{\partial T} \text{ for PE} \]

- \( \frac{\partial P}{\partial T} \) and \( \frac{\partial E}{\partial T} \) are significantly different between MD and CG
- The ratio of these two are not very high
- For most metals, \( \gamma/v \) 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