Atomistic Calculations of Dynamic Compression of Materials

July 2, 2013

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OUTLINE

- What’s a shock wave and how is it used?
- Tractable atomistic shock simulations (Multi-scale Shock Technique)
- When classical MD isn’t good enough
- Semiclassical quantum nuclear effects in classical molecular dynamics: An initial approach
How does a shock wave in a material look?

Typical laser-driven shocks exhibit pressures up to a few Mbar (few million atm) and temperatures up to several eV (few 10,000 K).

SHOCK COMPRESSION ENABLES STUDY OF HIGHER P, T STATES THAN STATIC METHODS

Proposed SiO$_2$ phase diagram

FIG. 1 (color). Proposed phase diagram for liquid silica illustrating the bonded liquid regime, where chemical bonds dominate, and the highly conducting atomic fluid regime, where they do not. Several known and proposed [25] solid phases are also illustrated. Shock temperatures determined in this study (densely packed diamond symbols) are given along with predictions from two EOS models: Kerley [14] (dashed lines) and qEOS [15] (dotted lines), where blue identifies quartz and red identifies fused silica. Also shown are shock data from Lyzenga and Ahrens [13] (purple dots for fused silica, light blue for quartz).

D. G. Hicks, T. R. Boehly, J. H. Eggert, J. E. Miller, P.M. Celliers, and G. W. Collins
PRL 97, 025502 (2006)
Shock waves are routinely generated in a controlled lab setting using projectiles from guns, lasers (including table-top scale), explosives, and other means.

Pressures >> 10 Mbar achievable, much greater than ~1-3 Mbar static pressures in diamond anvil cells. (Earth core is ~3.8 Mbar).

SHOCK COMPRESSION ENABLES STUDY OF HIGHER P, T STATES THAN STATIC METHODS
1. The shock propagation speed \( (v_s) \) exceeds the sound speed in the pre-shock material \( (c_0) \)
2. The shock propagation speed is less than the sound propagation speed behind the shock \( (c_1+u_1) \)

Mechanical shock wave stability criteria

\[
\begin{align*}
\text{Pressure} & \quad \text{Position} \\
& \quad \downarrow \quad \downarrow \\
u_1+c_1>v_s & \quad c_0<v_s
\end{align*}
\]
A DESCRIPTION OF THE THERMODYNAMIC STATES BEHIND THE SHOCK FRONT

- Conservation of mass, momentum, and energy for a material give the 1D Euler equations:
  \[
  \frac{d\rho}{dt} + \rho \frac{\partial u}{\partial x} = 0 \\
  \frac{du}{dt} + \tilde{v} \frac{\partial p}{\partial x} = 0 \\
  \frac{d\tilde{e}}{dt} + p \frac{d\tilde{v}}{dt} = 0
  \]

- Find steady state solutions by considering the variables to be functions of \( x - v_s t \):
  \[
  u - u_0 = (v_s - u_0) \left(1 - \frac{\rho_0}{\rho}\right) \\
  p - p_0 = (u_0 - v_s)^2 \rho_0 \left(1 - \frac{\rho_0}{\rho}\right) \quad \text{(Rayleigh line)} \\
  \tilde{e} - \tilde{e}_0 = p_0 \left(\frac{1}{\rho_0} - \frac{1}{\rho}\right) + \frac{(u_0 - v_s)^2}{2} \left(1 - \frac{\rho_0}{\rho}\right)^2
  \]

- Integration and some manipulation yields local equations for thermodynamic variables in a shock wave.
Rayleigh line slope is greater than Hugoniot slope at $P = 0, v_o$

uniaxial stress $\quad p - p_0 = \left(u_0 - v_s\right)^2 \rho_0 \left(1 - \frac{\rho_0}{\rho}\right)$  \hspace{1cm} (Rayleigh line)

Entropy change during (small) shock compression:

\[ S - S_0 \approx \frac{1}{3!} \frac{d^3S}{dv^3} \bigg|_{P=0,v_o} (v - v_o)^3 \]

Isentropic compression can occur in the limit of an infinite number of small amplitude shocks.

The high strain rates, temperatures and stress in shocked materials introduce extreme atomic scale distortions and electronic excitation: Must use an atomic description

The effects of shock compression can be studied using molecular dynamics

Atomic equation of motion

\[ \ddot{r}_j(t) = \frac{\ddot{r}_j(t)}{m_j} = \frac{1}{m_j} \frac{\partial E(\vec{r}_1, \ldots, \vec{r}_N)}{\partial \vec{r}_j} \]

- The energy function \( E(\vec{r}_1, \ldots, \vec{r}_N) \) determines the nature of the atomic interactions.
- \( E(\vec{r}_1, \ldots, \vec{r}_N) \) can be parameterized using analytical functions and fitted to experimental observations, but such approaches are not accurate far from the fitting conditions.
- For conditions with little experimental data, quantum approaches like density-functional theory are required for \( E(\vec{r}_1, \ldots, \vec{r}_N) \).
A variety of atom-based energy models exist

Quantum chemical methods (CI, MP2, MCSCF, etc.)
Density functional theory
Tight-binding
Analytical models

Quantum energy models like DFT are (hopefully) generally more accurate than empirical models, but at the price of increased computational expense

Slower
More accurate, more transferrable
Fewer assumptions

Faster
Less accurate, less transferrable
More assumptions

$10^1$ $10^2$ $10^3$ $10^4$ $10^6$ $10^9$
For analytical potentials:
  • Typical simulations:
    • Thousands to millions of atoms and 10-100 ps timescales
  • Big simulations (need parallel computer):
    • Billions of atoms, 10 nanosecond timescales

For DFT:
  • Typical simulations:
    • Fewer than 100 atoms and 1-10 ps
  • Big simulations (need parallel computer):
    • 100-1000 atoms and 100 ps
A MULTI-SCALE METHOD FOR SIMULATION OF MICROSCOPIC DYNAMICS IN SHOCK WAVES

Direct shock MD method:
Exact hydrodynamics, but requires cheap (poor) atomic potentials.
Computational work $\sim t^2$ at best

Multi-scale method:
Approximate hydrodynamics, few atoms,
more expensive (accurate) potentials
including quantum methods.
Computational work $\sim t$

Thermodynamic constraints of a steady shock in a continuum are applied to a MD simulation as if the shock were passing over it.

Conservation of mass, momentum, and energy for a continuum material give the 1D Navier-Stokes equations.

Steady solutions are:

\[
\frac{d\rho}{dt} + \rho \frac{\partial u}{\partial x} = 0
\]
\[
\frac{du}{dt} + \tilde{v} \frac{\partial}{\partial x} \left( p - \mu \frac{\partial u}{\partial x} \right) = 0
\]
\[
\frac{d\tilde{e}}{dt} + \left( p - \mu \frac{\partial u}{\partial x} \right) \frac{d\tilde{v}}{dt} = 0
\]

uniaxial stress \( p - \mu \frac{\dot{\tilde{v}}}{\tilde{v}} - p_0 = \left( u_0 - v_s \right)^2 \rho_0 \left( 1 - \frac{\rho_0}{\rho} \right) \) (Rayleigh line)

energy per unit mass \( \tilde{e} - \tilde{e}_0 = p_0 \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right) + \left( \frac{u_0 - v_s}{2} \right)^2 \left( 1 - \frac{\rho_0}{\rho} \right)^2 \)

These relations hold everywhere in the wave (i.e., they are more than jump conditions).

Equations of motion for the atoms and volume of a computational cell are chosen to satisfy the steady solution conditions.

There are 1 or 2 empirical parameters (computational cell mass and NS viscosity).

Molecular dynamics MSST equations of motion

Computational cell volume:

\[ Q \ddot{\mathbf{v}} = \sum_i m_i A \dot{s}_i \cdot \frac{dA}{dv} \dot{s}_i - \frac{d\phi}{dv} - \frac{v_s^2}{\bar{v}^2_0} (\bar{v}_0 - \bar{v}) - p_0 - \mu \frac{\dot{\bar{v}}}{\bar{v}} \]

Atom positions (scaled):

\[ \ddot{s}_i = -\frac{1}{m_i} A^{-1} \frac{\partial \phi}{\partial r_i} - G^{-1} G \dot{s}_i + M \frac{\mu \dot{v}^2}{m_i \bar{v}} \sum_j |A \dot{s}_j|^2 \]

- thermal stress
- cold stress
- Hugoniot external potential
- damping (empirical viscosity)
- shock speed is specified
- interatomic forces
- fictitious force due to computational cell motion
- energy from volume damping
Conservation of mass, momentum, and energy for a continuum material give the 1D Navier-Stokes equations.

\[ \frac{d\rho}{dt} + \rho \frac{\partial u}{\partial x} = 0 \]
\[ \frac{du}{dt} + \tilde{v} \frac{\partial}{\partial x} (p - \mu \frac{\partial u}{\partial x}) = 0 \]
\[ \frac{d\tilde{e}}{dt} + \left( p - \mu \frac{\partial u}{\partial x} \right) \frac{d\tilde{v}}{dt} = 0 \]

Steady solutions are:

uniaxial stress \( p - \mu \frac{\dot{\tilde{v}}}{\tilde{v}} - p_0 = (u_0 - v_s)^2 \rho_0 \left(1 - \frac{\rho_0}{\rho}\right) \) (Rayleigh line)

energy per unit mass \( \tilde{e} - \tilde{e}_0 = p_0 \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right) + \frac{(u_0 - v_s)^2}{2} \left(1 - \frac{\rho_0}{\rho}\right)^2 \)

These relations hold everywhere in the wave (i.e., they are more than jump conditions).

Equations of motion for the atoms and volume of a computational cell are chosen to satisfy the steady solution conditions.

There are 1 or 2 empirical parameters (computational cell mass and NS viscosity).

Excellent agreement is demonstrated between MSST and direct approach for shocks in Lennard-Jones, amorphous C (Tersoff potential) and other materials.
Snapshots of shocked nitromethane:

- **5 ps:** Hot unreacted liquid.


- **96 ps:** A dynamic composition exists including water and numerous transient metastable species.

We’ve been treating them as point particles, e.g. $E=E(r_j)$. Is this assumption valid?

The de Broglie wavelength is a rough measure of the length scale over which a quantum particle can be localized.

When the distance between particles is less than the de Broglie wavelength, quantum effects are important.
Typical distances between atoms range from 1 to 3 Angstroms (H$_2$ bond length is $\sim$0.74 Angstroms)

When the quantum wavelength exceeds the atomic separation, quantum effects play a role.

Electrons can be treated as classical point particles at sufficiently high temperatures and low densities

<table>
<thead>
<tr>
<th>atom</th>
<th>mass</th>
<th>temperature</th>
<th>de Broglie wavelength (Angstroms)</th>
<th>Quantum!</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>300</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>4</td>
<td>300</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>7</td>
<td>300</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>28</td>
<td>300</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>238</td>
<td>300</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

Liquid states:

<table>
<thead>
<tr>
<th>atom</th>
<th>mass</th>
<th>temperature</th>
<th>de Broglie wavelength (Angstroms)</th>
<th>Quantum!</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>20</td>
<td>5.59</td>
<td></td>
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<tr>
<td>He</td>
<td>4</td>
<td>4</td>
<td>6.25</td>
<td></td>
</tr>
<tr>
<td>Electron</td>
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<td>300</td>
<td>62.37</td>
<td>Quantum!</td>
</tr>
<tr>
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<td>19.72</td>
<td>Quantum!</td>
</tr>
<tr>
<td>Electron</td>
<td>0.000535294</td>
<td>100000</td>
<td>3.42</td>
<td>Quantum!</td>
</tr>
</tbody>
</table>
CLASSICAL VERSUS QUANTUM PARTICLES: SOME CONSEQUENCES

• Classical particles obey Boltzmann statistics while quantum particles obey Fermi or Bose statistics
  • Quantum particles have zero-point energy: fluctuations even at $T=0$

• Classical particles evolve according to Newton’s equation while quantum particles obey a wave equation
  • Quantum particles can tunnel
Post classical MD corrections of shock temperatures for quantum nuclear effects show temperature shifts of hundreds of K for organic molecular liquids.

<table>
<thead>
<tr>
<th>Shock velocity (km/s)</th>
<th>Pressure (GPa)</th>
<th>$T_{CI}$ (K)</th>
<th>$T_{QM}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.3 ± 0.1</td>
<td>434 ± 14</td>
<td>609</td>
</tr>
<tr>
<td>6.5</td>
<td>18.2 ± 0.2</td>
<td>791 ± 7</td>
<td>1064</td>
</tr>
<tr>
<td>7.5</td>
<td>26.5 ± 0.4</td>
<td>1167 ± 4</td>
<td>1531</td>
</tr>
<tr>
<td>9</td>
<td>42.0 ± 0.3</td>
<td>1995 ± 8</td>
<td>2478</td>
</tr>
<tr>
<td>10</td>
<td>53.8 ± 0.3</td>
<td>2744 ± 10</td>
<td>3284</td>
</tr>
<tr>
<td>11</td>
<td>67.8 ± 0.2</td>
<td>3654 ± 6</td>
<td>4234</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Shock velocity (km/s)</th>
<th>Pressure (GPa)</th>
<th>Density (g/cm³)</th>
<th>$T_{CI}$ (K)</th>
<th>$T_{QM}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>32.4 ± 0.4</td>
<td>1.12 ± 0.01</td>
<td>2448 ± 10</td>
<td>3243</td>
</tr>
<tr>
<td>12.2</td>
<td>42.2 ± 0.3</td>
<td>1.2 ± 0.01</td>
<td>3229 ± 8</td>
<td>4063</td>
</tr>
</tbody>
</table>

Heat capacity of liquid methane

- Heat capacity may differ from classical values by over 50%
- This alters Hugoniot temperatures from classical values
Bose-Einstein vibration energy spectrum can shift molecular formation energies by order tens of percent.

- Zero point energy for HN$_3$ formation is 10 kcal/mol.
- Reactions with many bonds breaking or forming can have large quantum nuclear energy components.
We would like to incorporate quantum nuclear effects into shock simulations to describe:

- Quantum heat capacity (to describe shock temperatures)
- Bose-Einstein spectrum (to describe chemistry and the chemical equilibrium)
- Wave-particle effects (e.g. tunneling for transport and kinetics)

Wish list:

- Calculations will be self-consistent and on the fly
  - Not a post-classical MD temperature correction method
- Same computational cost (or nearly so) as classical MD
  - Path integral approaches are expensive for lower temperatures
- Easy to use (like classical MD) and publically available

A new method that accomplishes most of these goals:

QBMSST: Quantum Bath Multi-Scale Shock Technique
LANGEVIN THERMOSTAT APPROACH TO 
SEMICLASSICAL QUANTUM THERMAL BATH

Langevin-type thermostats have been proposed to couple atoms to a Bose-Einstein thermal bath:


In equation of motion, introduce both a random force $R(t)$ and a dissipative force

$$m\ddot{r}(t) = f(r(t)) + R(t) - m\gamma \dot{r}(t),$$

The random force spectrum is:

$$< R(t)R(t+\tau) > = 2m\gamma \int_{-\infty}^{+\infty} \tilde{\Theta}(\omega,T) \exp[-i\omega\tau] \frac{d\omega}{2\pi}. $$

$$\tilde{\Theta}(\omega,T) = k_B T$$

For classical (canonical) ensemble averages

$$\tilde{\Theta}(\omega,T) = \frac{1}{2} \hbar \omega + \hbar \omega[\exp(\hbar \omega / k_B T) - 1]^{-1}.$$ 

For quantum, Bose-Einstein ensemble averages

Liquid methane vibrational velocity autocorrelation spectrum computed using classical MD (red) and the quantum bath of Dammak et al. (red).
Heat capacity is corrected within the quantum thermal bath.


METHANE EXPERIMENTAL HEAT CAPACITY IS REPRODUCED BY QUANTUM BATH

Liquid methane heat capacity

EAM Aluminum exhibits pressure-dependent zero-point energy

Langevin quantum bath describes the temperature and pressure dependence of quantum heat capacity.

\[(QB)\text{MSST EQUATIONS OF MOTION}\]

**Volume EOM**

\[
\ddot{Q} = \sum_i m_i A \frac{dA}{dv} \dot{s}_i - \frac{d\phi}{dv} - \frac{v_s^2}{\tilde{v}_0^2} (\tilde{v}_0 - \tilde{v}) - p_0 - \mu \frac{\dot{v}}{\tilde{v}}
\]

**Atom EOM**

\[
\ddot{s}_i = -\frac{1}{m_i} A^{-1} \frac{\partial \phi}{\partial \bar{r}_i} - G^{-1} \ddot{G} s_i + M \frac{\mu \tilde{v}^2}{m_i \tilde{v}} \sum_j |A s_j|^2 + \frac{1}{m_i} \left( -A^{-1} \ddot{R}_i - \gamma s_i \right)
\]

**Constraint quantity**

\[
\bar{\epsilon} = \sum_i \frac{1}{2M} m_i |A \dot{s}_i|^2 + \frac{1}{M} \phi(\bar{\epsilon}) - p_0 (\tilde{v}_0 - \tilde{v}) - \frac{v_s^2}{2} \left( 1 - \frac{\tilde{v}}{\tilde{v}_0} \right)^2 + \frac{1}{2} Q \tilde{v}^2
\]

**Quantum temperature EOM**

\[
\dot{T}^{QM}(t) = \gamma \eta \frac{M(\bar{\epsilon}(t) - \bar{\epsilon}_0)}{3Nk_B}
\]

\(\gamma\) and \(\eta\) are new parameters to be chosen.

We combine quantum thermal bath with MSST (QB-MSST) for the efficient generation of colored noise.

\[ \theta(t) = \frac{R_{ik}(t)}{\sqrt{2m_i\gamma}} \]

\[ \tilde{\theta}(\omega) = \tilde{H}(\omega)\tilde{r}(\omega) \]

\[ \theta(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{H}(\omega)\tilde{r}(\omega)e^{-i\omega t} \]

\[ \theta(t) = \int_{-\infty}^{\infty} H(\tau)r(t-\tau)d\tau \]

\[ R_{ik}(n\delta h) = \sqrt{2m_i\gamma} \sum_{m=-N_f}^{N_f-1} H_m r_{n-m} \]

QB-MSST incorporates quantum nuclear effects with performance within factor of 2 of classical MSST.


\( N_f \) is the number of discrete points used to represent the Bose-Einstein spectrum.

N. spectral filter

N. random force

N. white noise

N. spectral filter
We combine quantum thermal bath with MSST (QB-MSST) for Methane.

ReaxFF potential of Mattson et al, 216-molecules, 6 km/s shock speed, initial temperature: 111K, initial density: 0.432 g/cc.

Deviation from the constraint energy ($\Delta T$) fluctuates around zero for QBMSST.
QBMSST LIQUID METHANE HUGONIOT COMPARISON

QBMSST and MSST simulation durations of 300 ps

QBMSST Hugoniot differs from MSST by up to 5 GPa and 1000K at a given density


The onset of methane dissociation occurs 15 GPa (~35%) lower pressure and 800 K lower T for QBMSST.

SUMMARY

- Quantum nuclear effects in liquid methane:
  - Shift Hugoniot temperature by over 30% (over 1000 K)
  - Shift onset of chemistry to ~35% lower pressure

- We have developed a semi-classical approach to self-consistent quantum nuclear effects in classical MD shock calculations
  - Runs only ~20% slower than classical MD

Acknowledgements

• Tingting Qi (now at LLNL)

Conclusions

ACKNOWLEDGEMENTS

Computational resources for this work:
• National Energy Research Science Computing Center (NERSC)
• National Nanotechnology Infrastructure Network (NNIN)