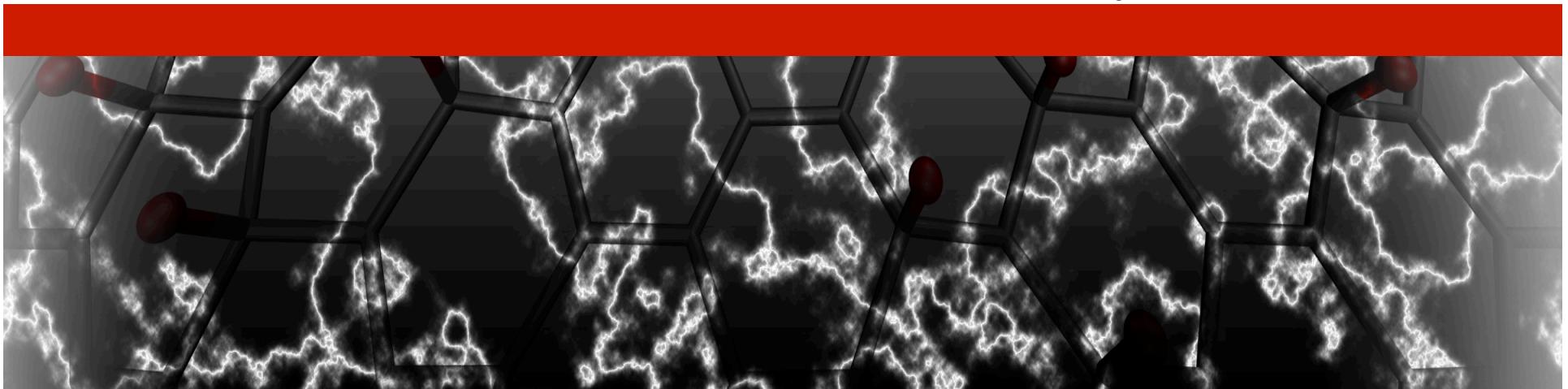


Atomistic Calculations of Dynamic Compression of Materials

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?

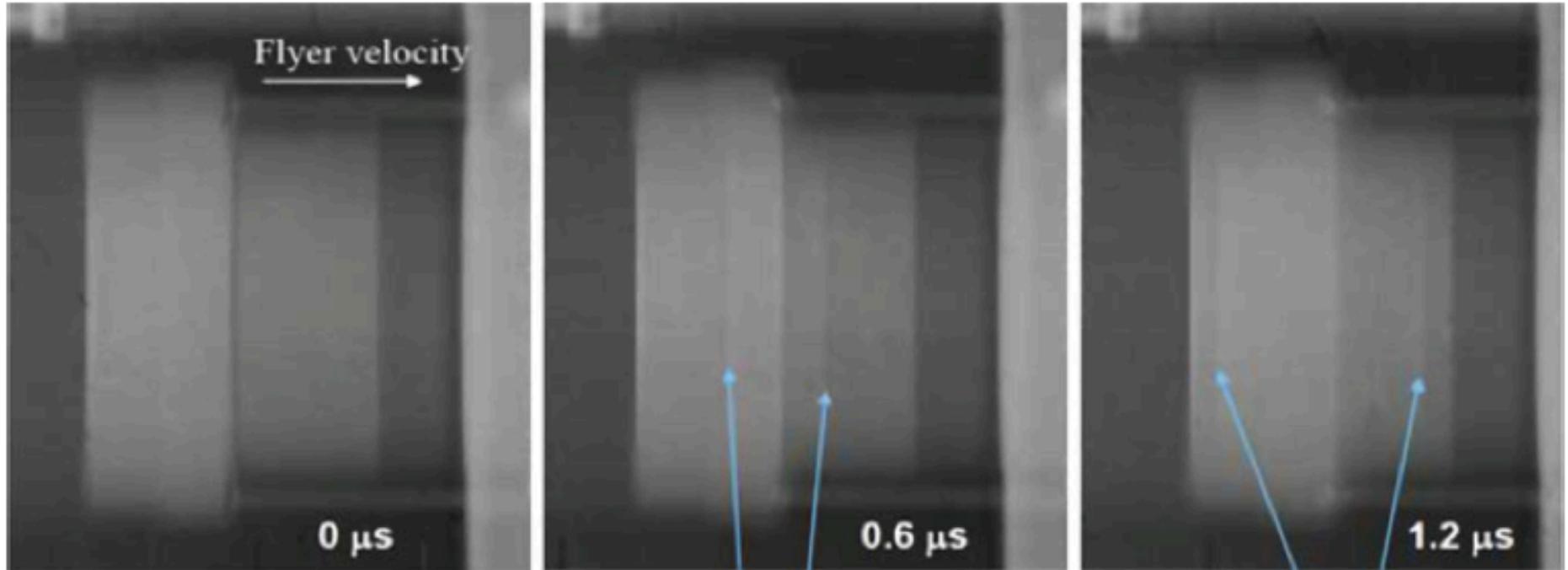
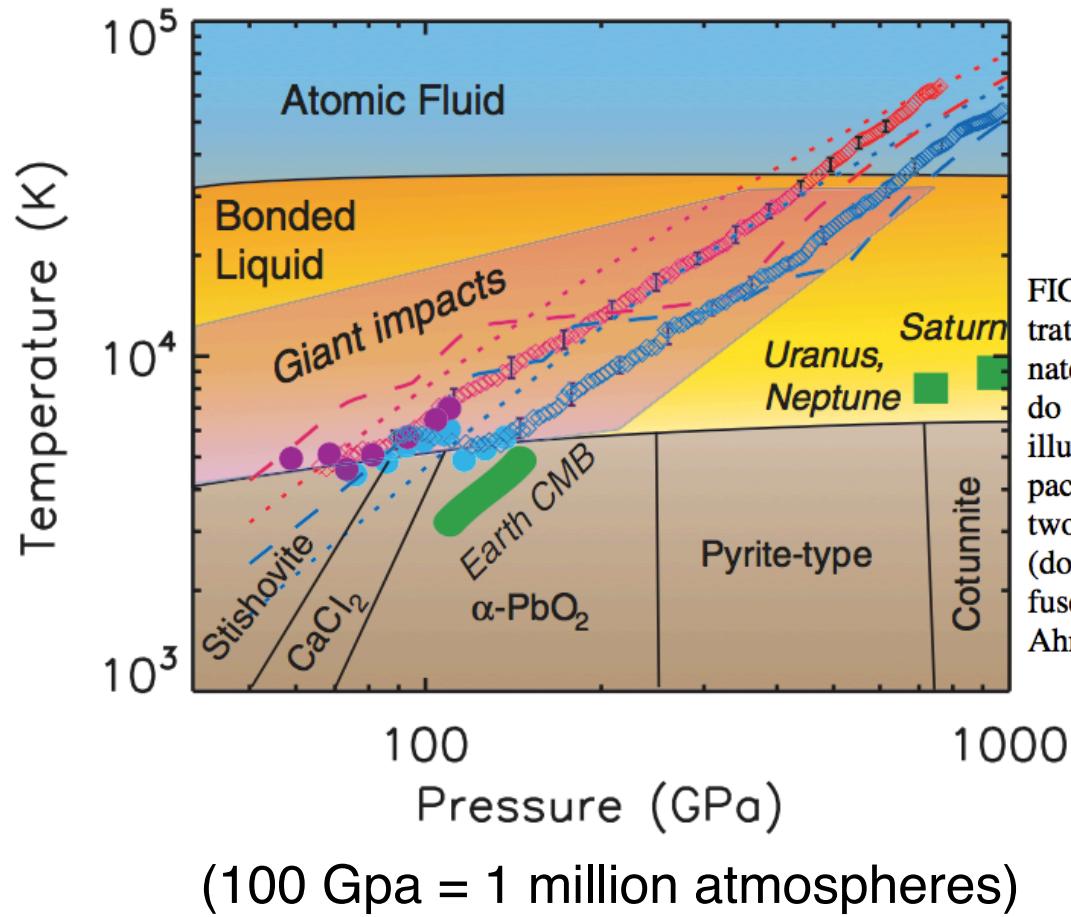


Fig. 1.1 Proton beam radiographs of shocked aluminum at three different times for an aluminum plate impacting an aluminum sample [10, 11]. The *arrows* indicate the shock fronts

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).

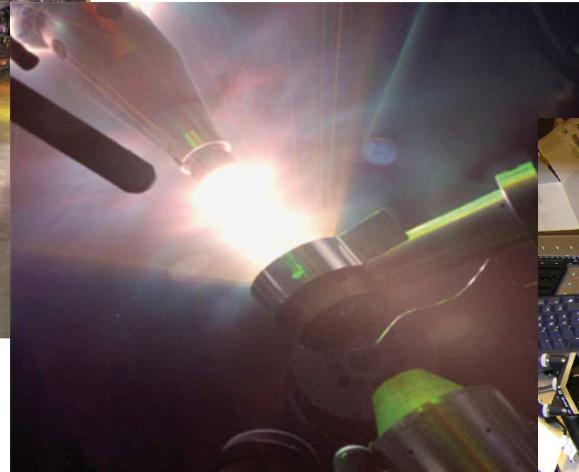
D. G. Hicks,^{1,*} T. R. Boehly,² J. H. Eggert,¹ J. E. Miller,^{2,3} P. M. Celliers,¹ and G. W. Collins¹

PRL **97**, 025502 (2006)

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



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



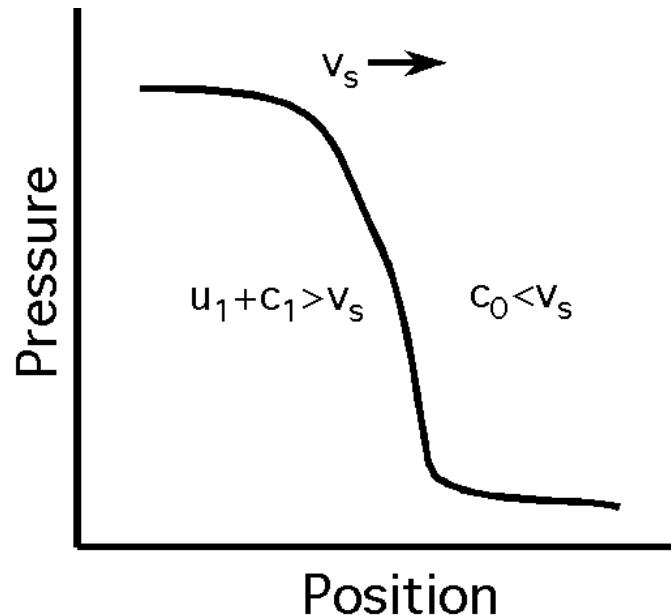
Shock waves are routinely generated in a controlled lab setting using projectiles from guns, lasers (including table-top scale), explosives, and other means.

CONDITIONS FOR SHOCK STABILITY



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



A DESCRIPTION OF THE THERMODYNAMIC STATES BEHIND THE SHOCK FRONT



- Conservation of mass, momentum, and energy for a material give the 1D Euler equations.
- Find steady state solutions by considering the variables to be functions of $x - v_s t$
- Integration and some manipulation yields local equations for thermodynamic variables in a shock wave

$$\frac{d\rho}{dt} + \rho \frac{\partial u}{\partial x} = 0$$

$$\frac{du}{dt} + \tilde{v} \frac{\partial p}{\partial x} = 0$$

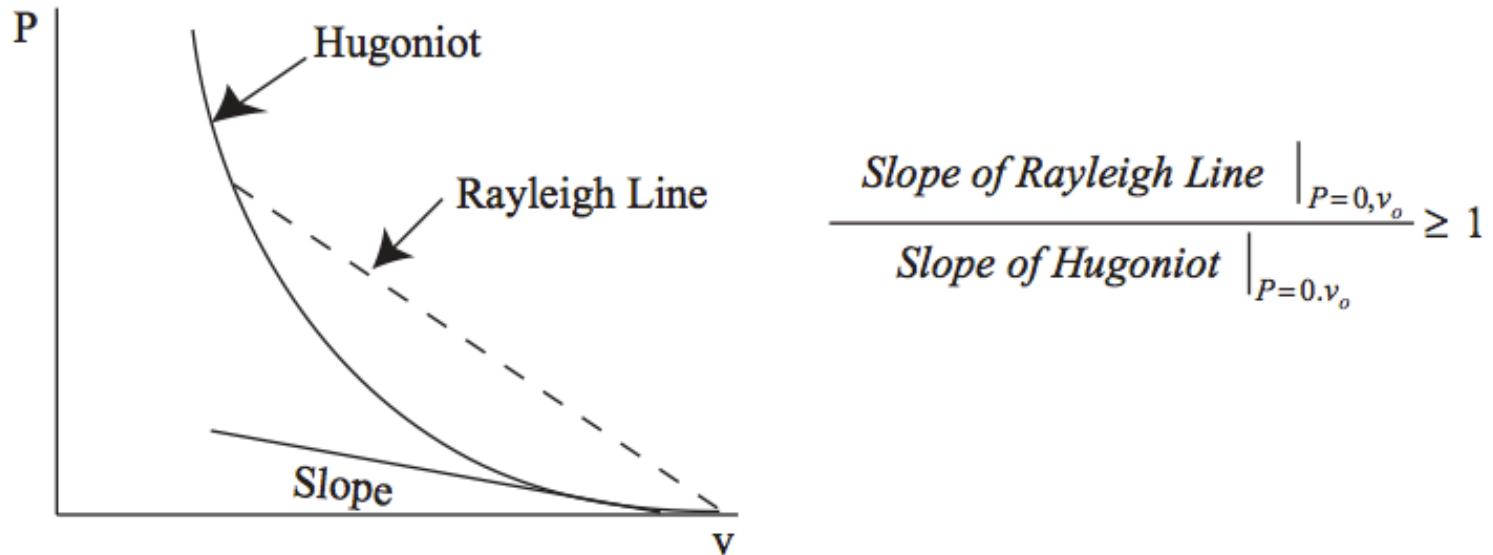
$$\frac{d\tilde{e}}{dt} + p \frac{d\tilde{v}}{dt} = 0$$

particle velocity $u - u_0 = (v_s - u_0) \left(1 - \frac{\rho_0}{\rho} \right)$

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

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

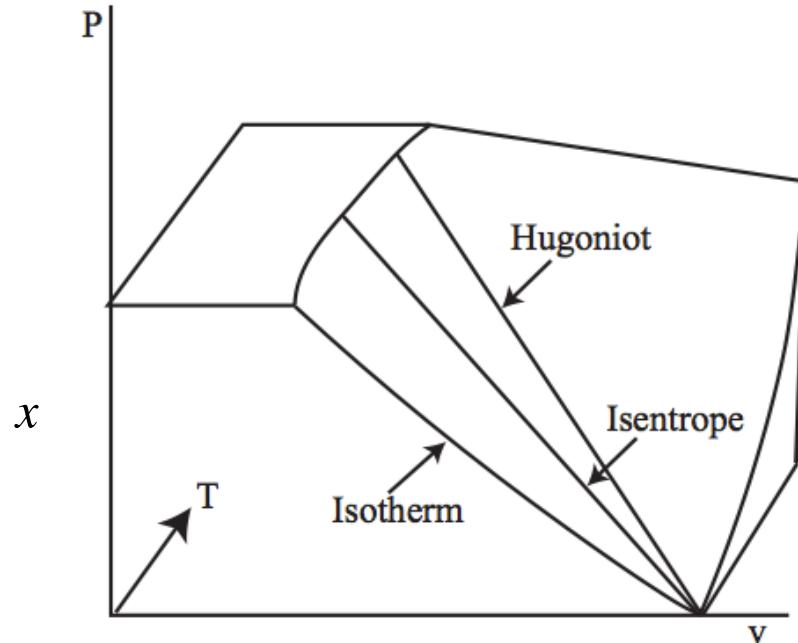
SHOCK STABILITY: THE GEOMETRICAL INTERPRETATION



.9 Rayleigh line slope is greater than Hugoniot slope at $P = 0, v_o$

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

SHOCK COMPRESSION IS NOT ISENTROPIC



Entropy change during (small) shock compression:

$$S - S_0 \approx \frac{1}{3!} \left. \frac{d^3 S}{dv^3} \right|_{P=P_0, v=v_0} (v - v_0)^3$$

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

THE EFFECTS OF SHOCK COMPRESSION CAN BE STUDIED USING MOLECULAR DYNAMICS



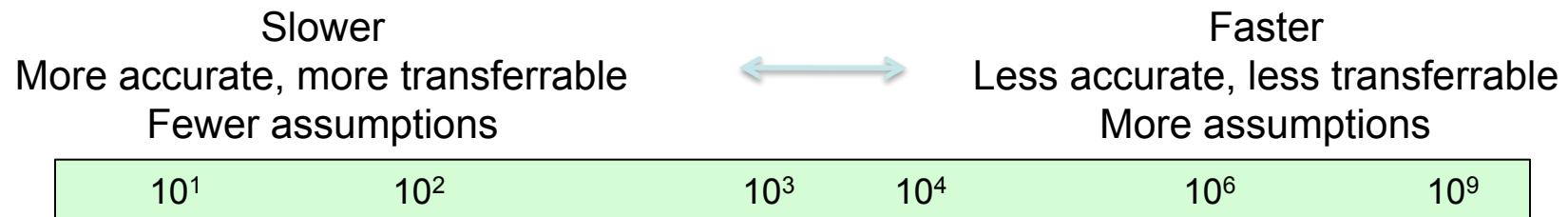
The high strain rates, temperatures and stress in shocked materials introduce extreme atomic scale distortions and electronic excitation:
Must use an atomic description

Atomic equation of motion

$$\ddot{\vec{r}}_j(t) = \frac{\vec{f}_j(t)}{m_j} = \frac{1}{m_j} \frac{\partial E(\vec{r}_1, \dots, \vec{r}_N)}{\partial \vec{r}_j}$$

- ▶ The energy function $E(\vec{r}_1, \dots, \vec{r}_N)$ determines the nature of the atomic interactions.
- ▶ $E(\vec{r}_1, \dots, \vec{r}_N)$ 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 $E(\vec{r}_1, \dots, \vec{r}_N)$.

A variety of atom-based energy models exist



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

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

CURRENT PRACTICAL LIMITATIONS OF MD



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

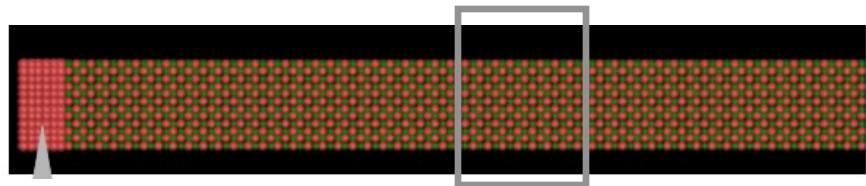
For DFT:

- 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

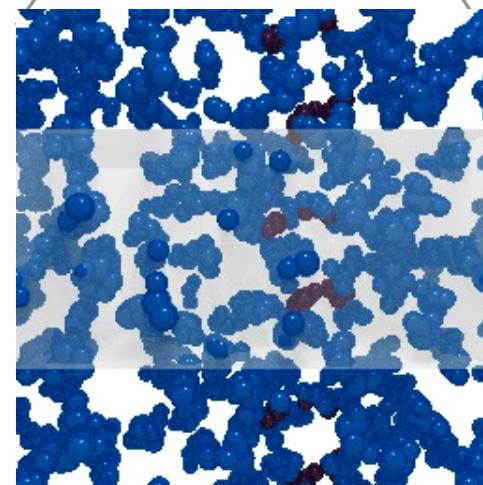


Direct shock MD method:
Exact hydrodynamics, but requires
cheap (poor) atomic potentials.
Computational work $\sim t^2$ at best



Reed, Fried, Joannopoulos, *Phys. Rev. Lett.* **90**, 235503 (2003).

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.

A DESCRIPTION OF THERMODYNAMIC STATES BEHIND THE SHOCK FRONT



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

$$\begin{aligned}\frac{d\rho}{dt} + \rho \frac{\partial u}{\partial x} &= 0 \\ \frac{du}{dt} + \tilde{v} \frac{\partial}{\partial x} \left(p - \mu \frac{\partial u}{\partial x} \right) &= 0 \\ \frac{d\tilde{e}}{dt} + \left(p - \mu \frac{\partial u}{\partial x} \right) \frac{d\tilde{v}}{dt} &= 0\end{aligned}$$

Steady solutions are:

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

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

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).

Reed, Fried, Joannopoulos, “Tractable dynamical studies of single and double shock compression,”
Phys. Rev. Lett. **90**, 235503 (2003).

MSST EQUATIONS OF MOTION



Computational cell volume:

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

shock speed
is specified

Atom positions (scaled):

$$\ddot{\vec{s}}_i = \frac{-1}{m_i} A^{-1} \frac{\partial \phi}{\partial \vec{r}_i} - G^{-1} \dot{G} \dot{\vec{s}}_i + M \frac{\mu \dot{\tilde{v}}^2}{m_i \tilde{v}} \frac{\dot{\vec{s}}_i}{\sum_j |A \dot{\vec{s}}_j|^2}$$

Diagram illustrating the components of the MSST equations of motion:

- thermal stress**: arrow pointing down from the first term.
- cold stress**: arrow pointing down from the second term.
- Hugoniot external potential**: arrow pointing down from the third term.
- damping (empirical viscosity)**: arrow pointing down from the fourth term.
- interatomic forces**: arrow pointing up from the fifth term.
- fictitious force due to computational cell motion**: arrow pointing up from the sixth term.
- energy from volume damping**: arrow pointing up from the seventh term.

A DESCRIPTION OF THERMODYNAMIC STATES BEHIND THE SHOCK FRONT



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

Steady solutions are:

$$\begin{aligned} \frac{d\rho}{dt} + \rho \frac{\partial u}{\partial x} &= 0 \\ \frac{du}{dt} + \tilde{v} \frac{\partial}{\partial x} \left(p - \mu \frac{\partial u}{\partial x} \right) &= 0 \\ \frac{d\tilde{e}}{dt} + \left(p - \mu \frac{\partial u}{\partial x} \right) \frac{d\tilde{v}}{dt} &= 0 \end{aligned}$$

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

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

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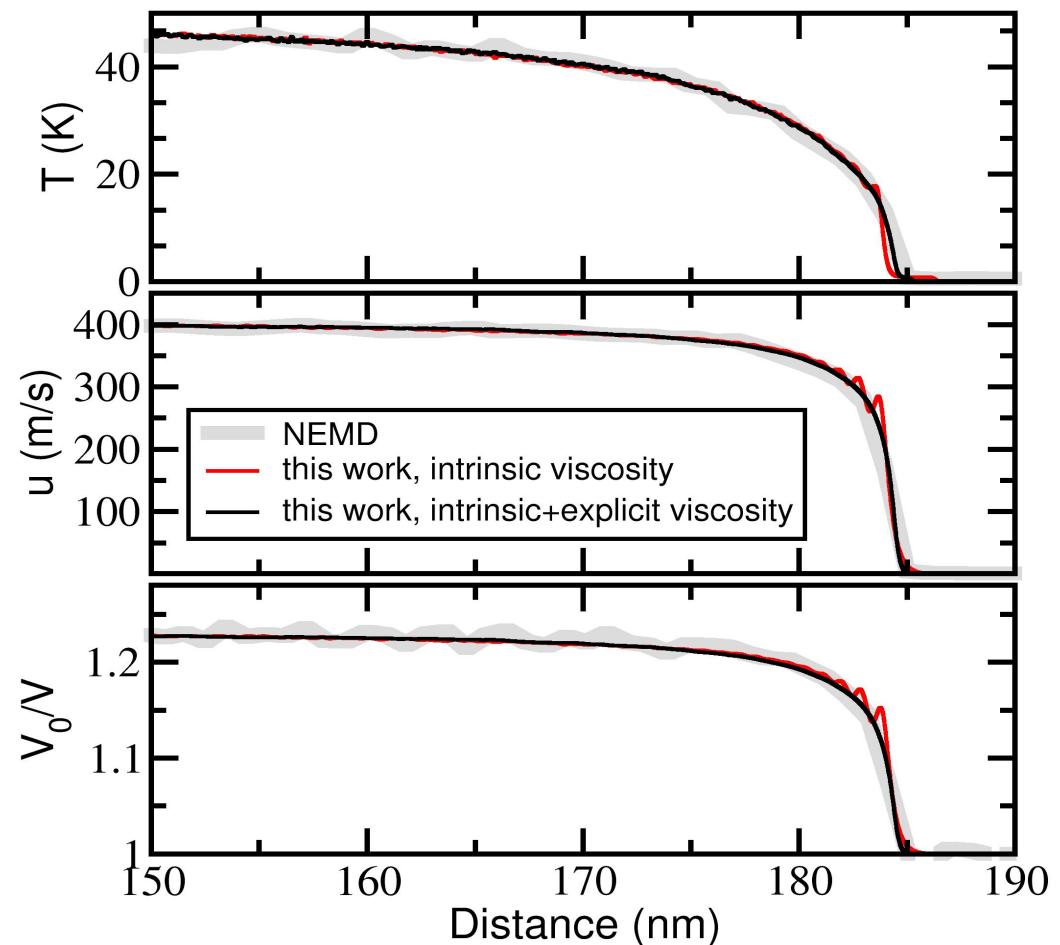
Reed, Fried, Joannopoulos, “Tractable dynamical studies of single and double shock compression,”
Phys. Rev. Lett. **90**, 235503 (2003).

MSST AGREES WITH DIRECT METHOD IN AMORPHOUS LENNARD-JONES

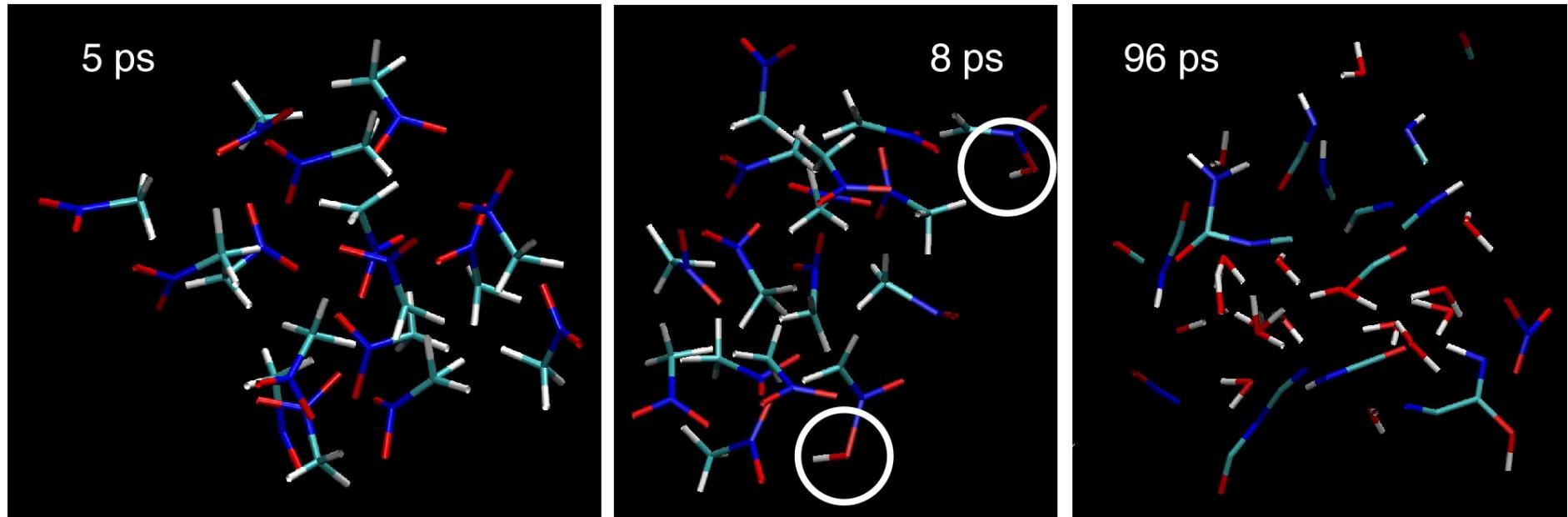


Reed, Maiti, Fried, *Phys. Rev. E* **81**, 016607 (2010).

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



FIRST MICROSCOPIC PICTURE OF DETONATION: NITROMETHANE



5 ps:
Hot unreacted liquid.

8 ps:
Hydrogen transfer occurs, consistent with density functional theory simulations at similar thermodynamic conditions: M. R. Manaa, et al., J. Chem. Phys. 120, 10146 (2004).

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

Reed, Manaa, Fried, Glaesemann, Joannopoulos," *Nature Physics* **4**, 72 (2008).

ARE THE NUCLEI PARTICLES OR WAVES



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.

SOME DE BROGLIE WAVELENGTH ESTIMATES



atom	mass	temperature	de Broglie wavelength (Angstroms)
H	1	300	1.44 Quantum!
He	4	300	0.72
Li	7	300	0.55
Si	28	300	0.27
U	238	300	0.09
Liquid states:			
H	1	20	5.59 Quantum!
He	4	4	6.25 Quantum!
Electron	0.000535294	300	62.37 Quantum!
Electron	0.000535294	3000	19.72 Quantum!
Electron	0.000535294	100000	3.42 Quantum!

- Typical distances between atoms range from 1 to 3 Angstroms (H_2 bond length is ~ 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

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

THERE IS A NEED FOR INCORPORATION OF QUANTUM NUCLEAR EFFECTS IN SHOCK CALCULATIONS



Water

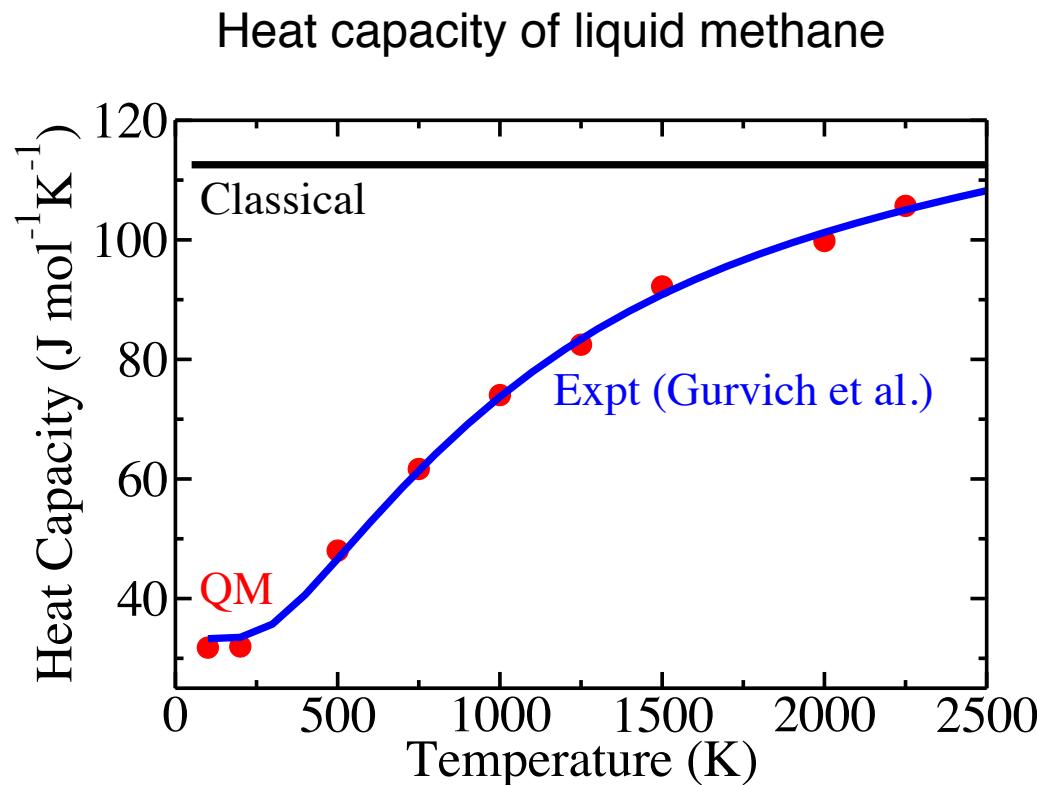
Shock velocity (km/s)	Pressure (GPa)	T_{Cl} (K)	T_{QM} (K)
5	8.3 ± 0.1	434 ± 14	609
6.5	18.2 ± 0.2	791 ± 7	1064
7.5	26.5 ± 0.4	1167 ± 4	1531
9	42.0 ± 0.3	1995 ± 8	2478
10	53.8 ± 0.3	2744 ± 10	3284
11	67.8 ± 0.2	3654 ± 6	4234

Post classical MD corrections of shock temperatures for quantum nuclear effects show temperature shifts of hundreds of K for organic molecular liquids.

Methane

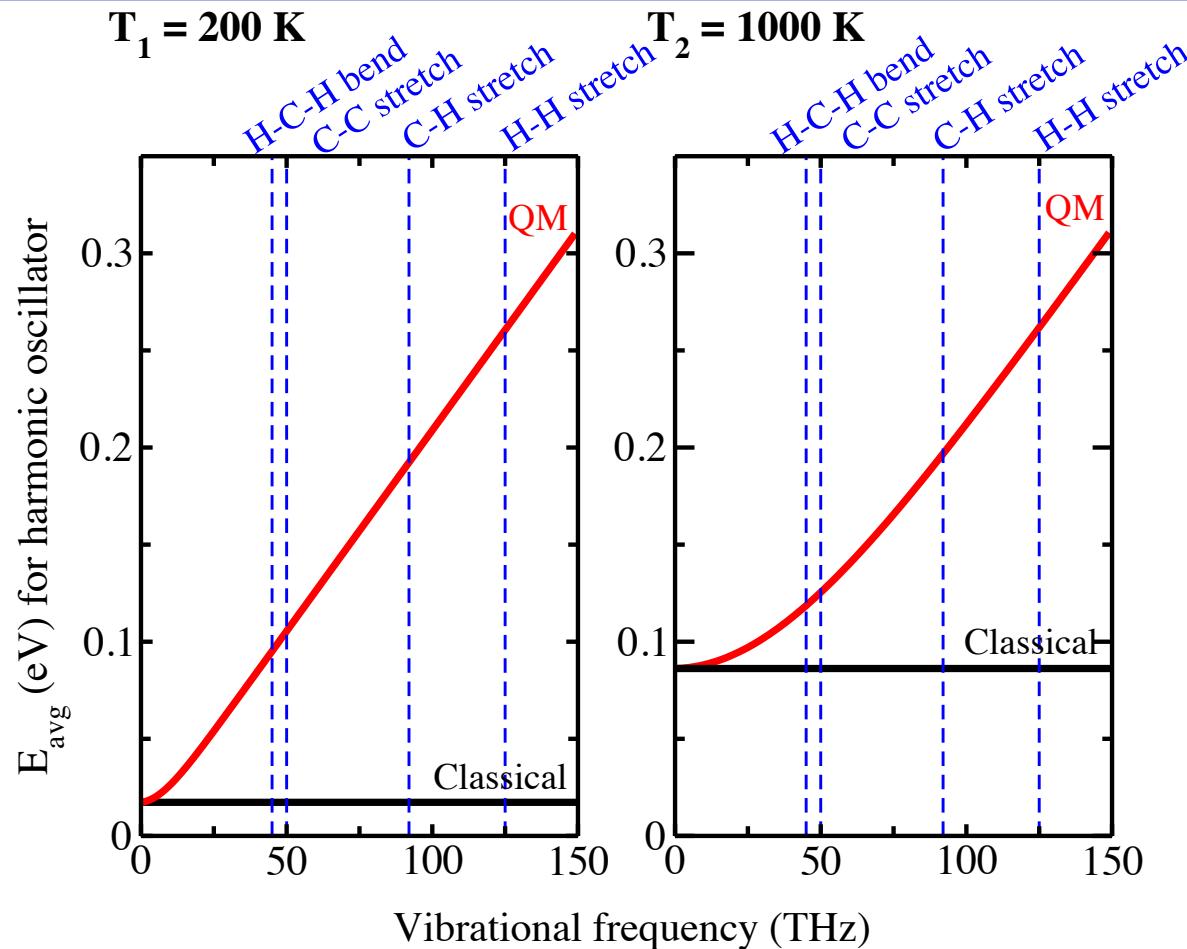
Shock velocity (km/s)	Pressure (GPa)	Density (g/cm ³)	T_{Cl} (K)	T_{QM} (K)
11	32.4 ± 0.4	1.12 ± 0.01	2448 ± 10	3243
12.2	42.2 ± 0.3	1.2 ± 0.01	3229 ± 8	4063

QUANTUM NUCLEAR EFFECTS SIGNIFICANTLY IMPACT HEAT CAPACITY



- Heat capacity may differ from classical values by over 50%
 - This alters Hugoniot temperatures from classical values

QUANTUM NUCLEAR EFFECTS CAN IMPACT MOL. AND PHASE STABILITY



- 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

THE QUANTUM NUCLEAR EFFECT WISH LIST



- 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:

H. Dammak, et. al. Phys. Rev. Lett. **103**: 190601, (2009).

M. Ceriotti, et. al. Phys. Rev. Lett. **103**, 030603 (2009).

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:

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

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

For classical (canonical) ensemble averages

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

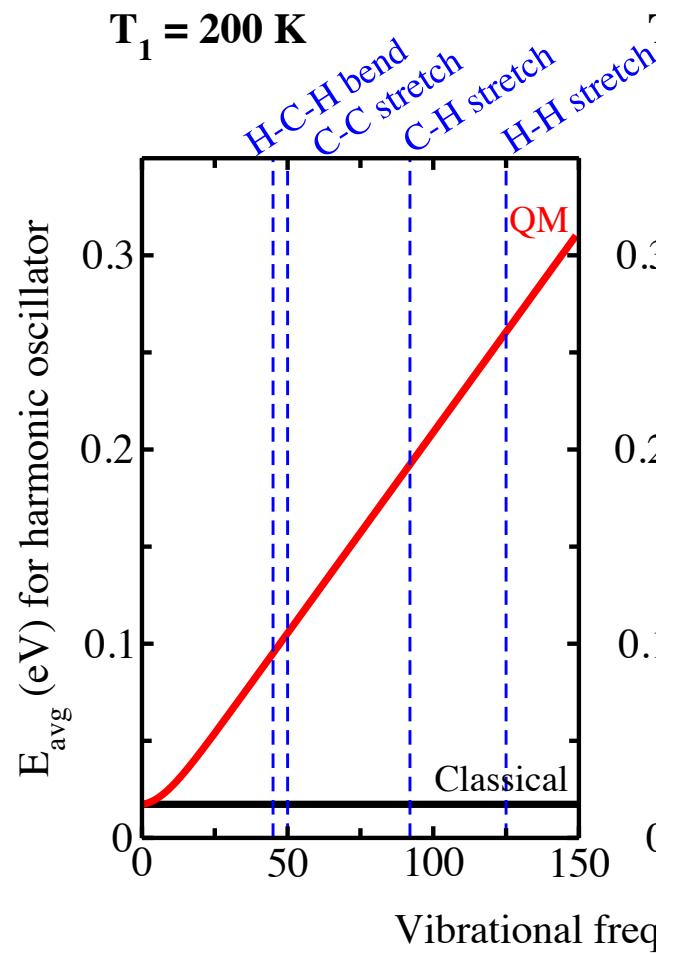
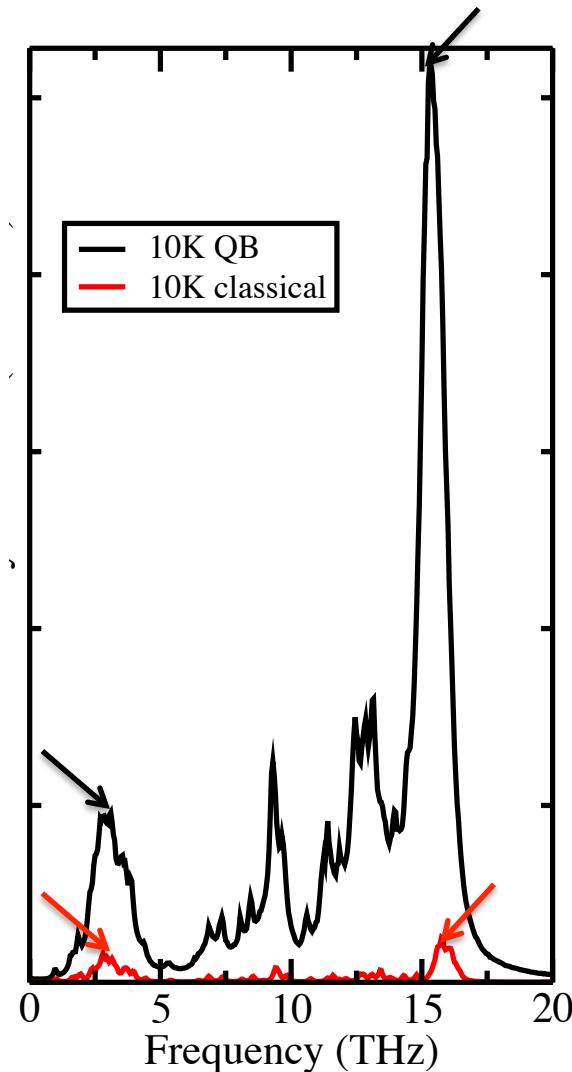
For quantum, Bose-Einstein ensemble averages

H. Dammak, et. al. Phys. Rev. Lett. **103**: 190601, (2009).

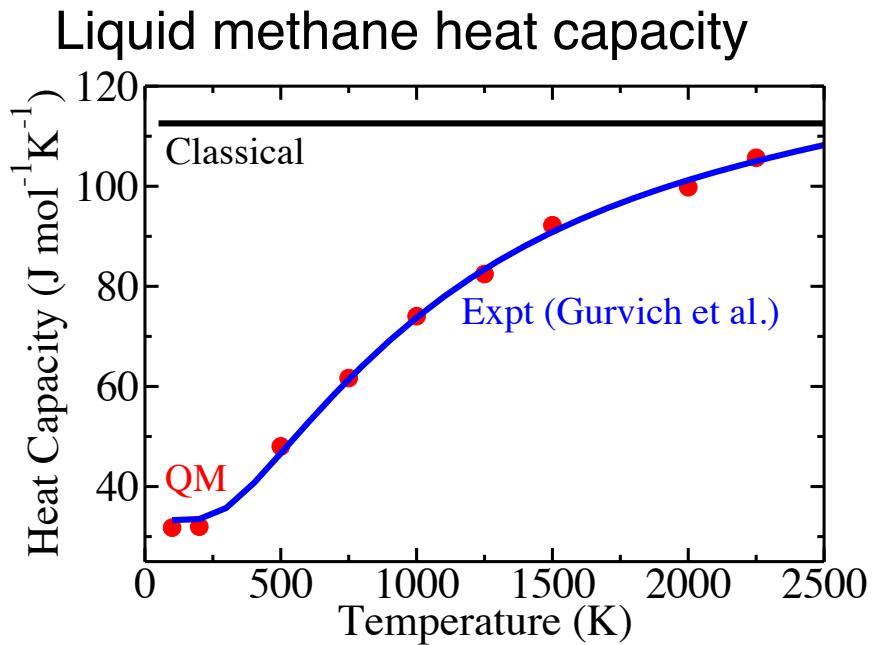
VIBRATION SPECTRUM OF LIQUID METHANE



Liquid methane vibrational velocity autocorrelation spectrum computed using classical MD (red) and the quantum bath of Dammak et al. (red).

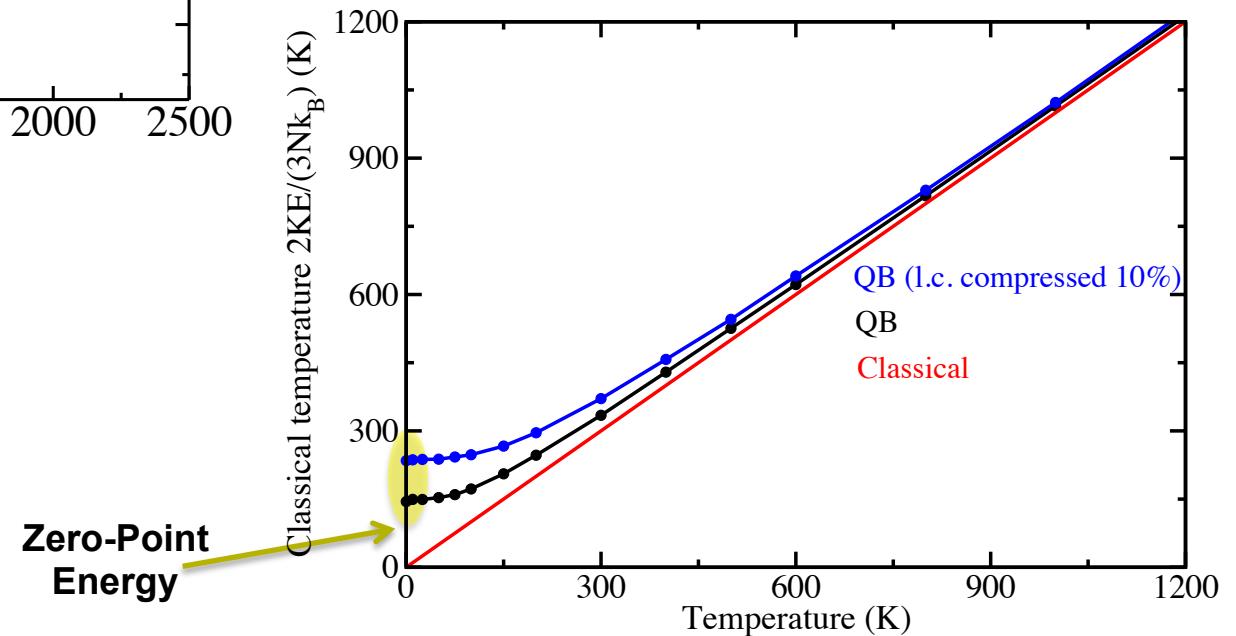


METHANE EXPERIMENTAL HEAT CAPACITY IS REPRODUCED BY QUANTUM BATH



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

EAM Aluminum exhibits pressure-dependent zero-point energy



(QB)MSST EQUATIONS OF MOTION



Volume EOM

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

Atom EOM

$$\ddot{\vec{s}_i} = \frac{-1}{m_i} A^{-1} \frac{\partial \phi}{\partial \vec{r}_i} - G^{-1} \dot{G} \dot{\vec{s}_i} + M \frac{\mu \dot{\tilde{v}}^2}{m_i \tilde{v}} \frac{\dot{\vec{s}_i}}{\sum_j |A \dot{\vec{s}_j}|^2} + \frac{-1}{m_i} A^{-1} \vec{R}_i - \gamma \dot{\vec{s}_i}$$

Constraint
quantity

$$\tilde{e} = \sum_i \frac{1}{2M} m_i |A \dot{\vec{s}_i}|^2 + \frac{1}{M} \phi(\{\vec{r}_i\}) - p_0 (\tilde{v}_0 - \tilde{v}) - \frac{v_s^2}{2} \left(1 - \frac{\tilde{v}}{\tilde{v}_0}\right)^2 + \frac{1}{2} Q \dot{\tilde{v}}^2$$

Quantum
temperature
EOM

$$\dot{T}^{\text{QM}}(t) = \gamma \eta \frac{M(\tilde{e}(t) - \tilde{e}_0)}{3Nk_B}$$

γ and η are new parameters to be chosen.

EFFICIENT GENERATION OF COLORED NOISE



J. Barrat, et. al. J. Stat. Phys. **144**: 679, 2011

$$\theta(t) \equiv \frac{R_{ik}(t)}{\sqrt{2m_i\gamma}}$$

Random force

$$\tilde{\theta}(\omega) = \tilde{H}(\omega)\tilde{r}(\omega)$$

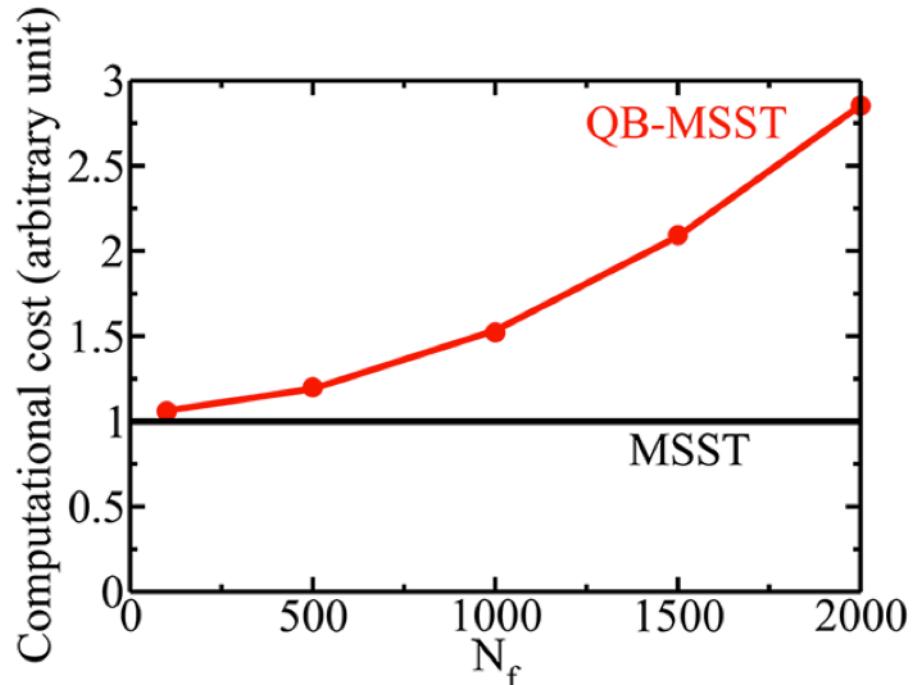
White noise

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

Spectral filter

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

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



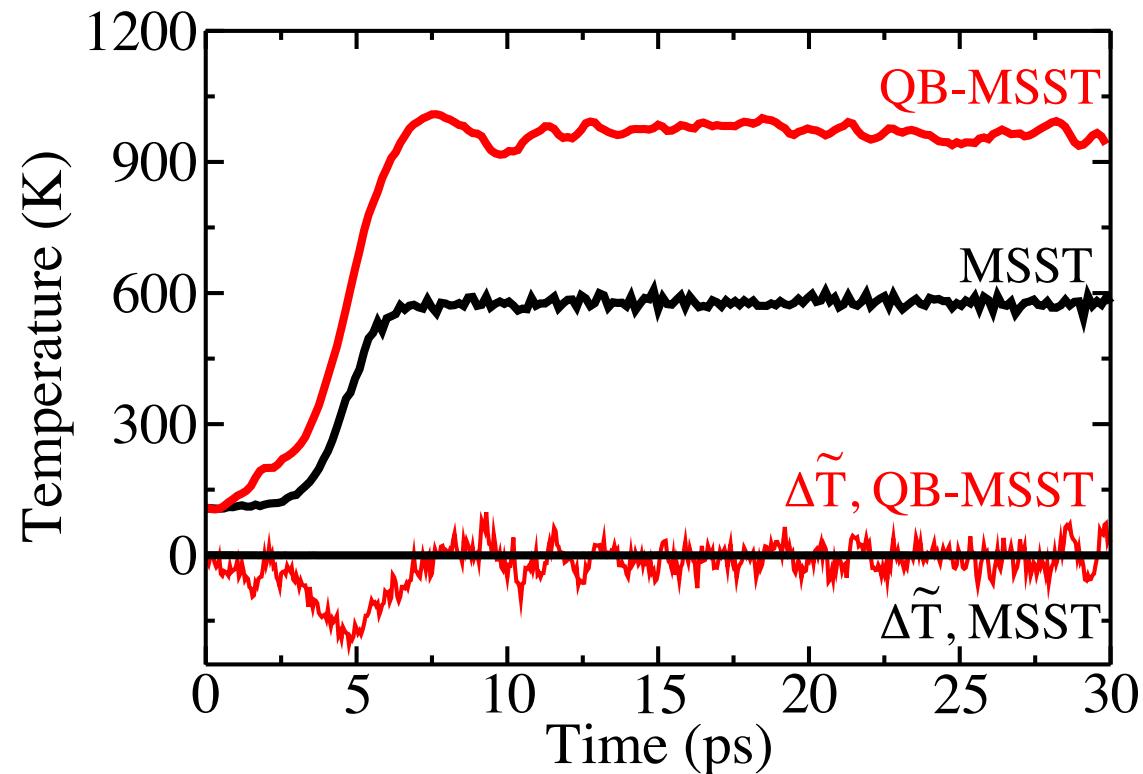
N_f is the number of discrete points used to represent the Bose-Einstein spectrum

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

6 KM/S SHOCK IN LIQUID METHANE

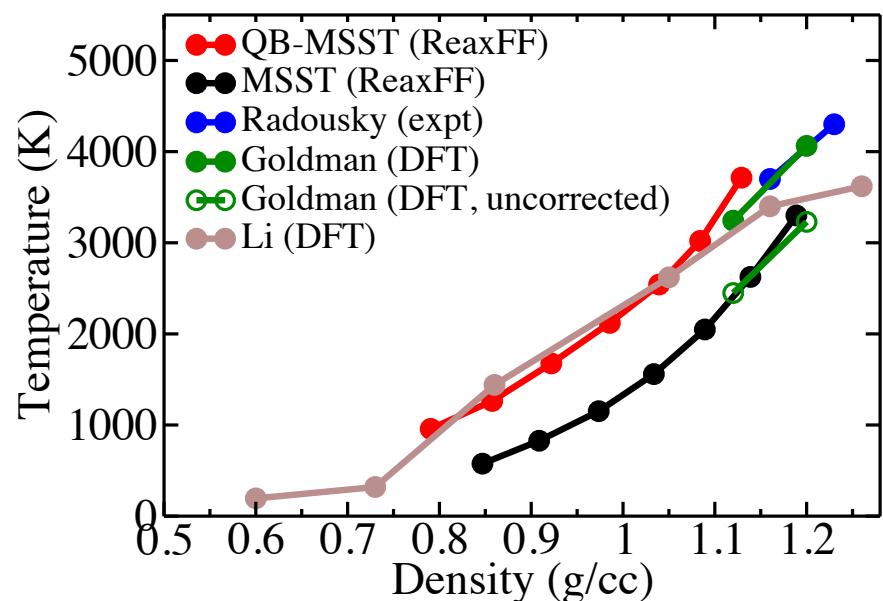
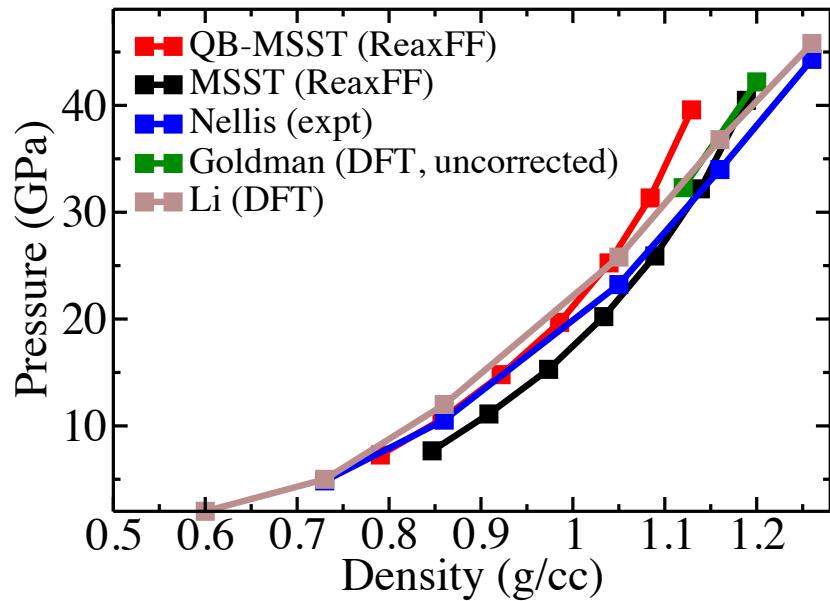


ReaxFF potential of Mattson et al, 216-molecules, 6 km/s shock speed,
initial temperature: 111K, initial density: 0.432 g/cc.



**Deviation from the constraint energy (ΔT) fluctuates around zero
for QBMSST.**

QBMSST LIQUID METHANE HUGONIOT COMPARISON



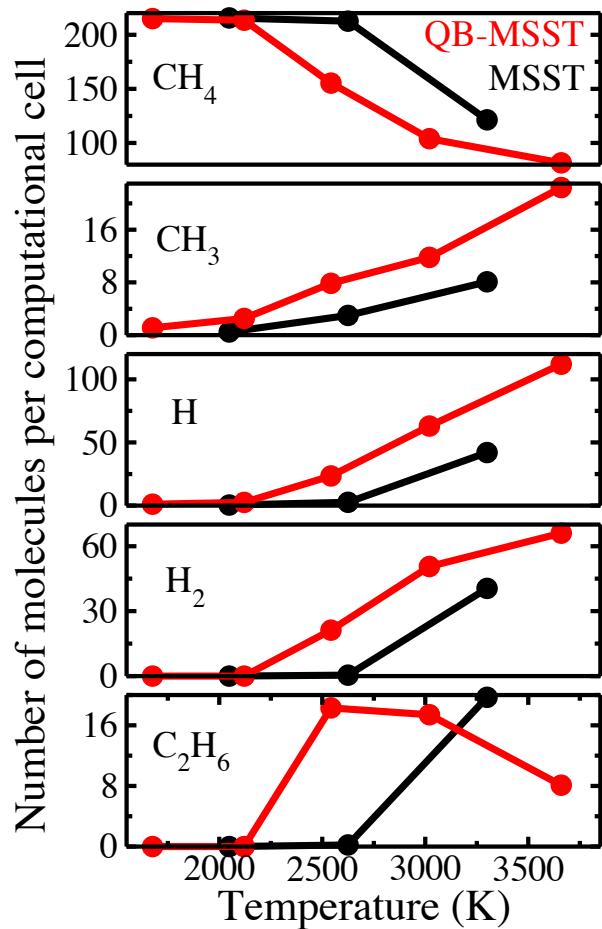
QBMSST and MSST simulation durations of 300 ps

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

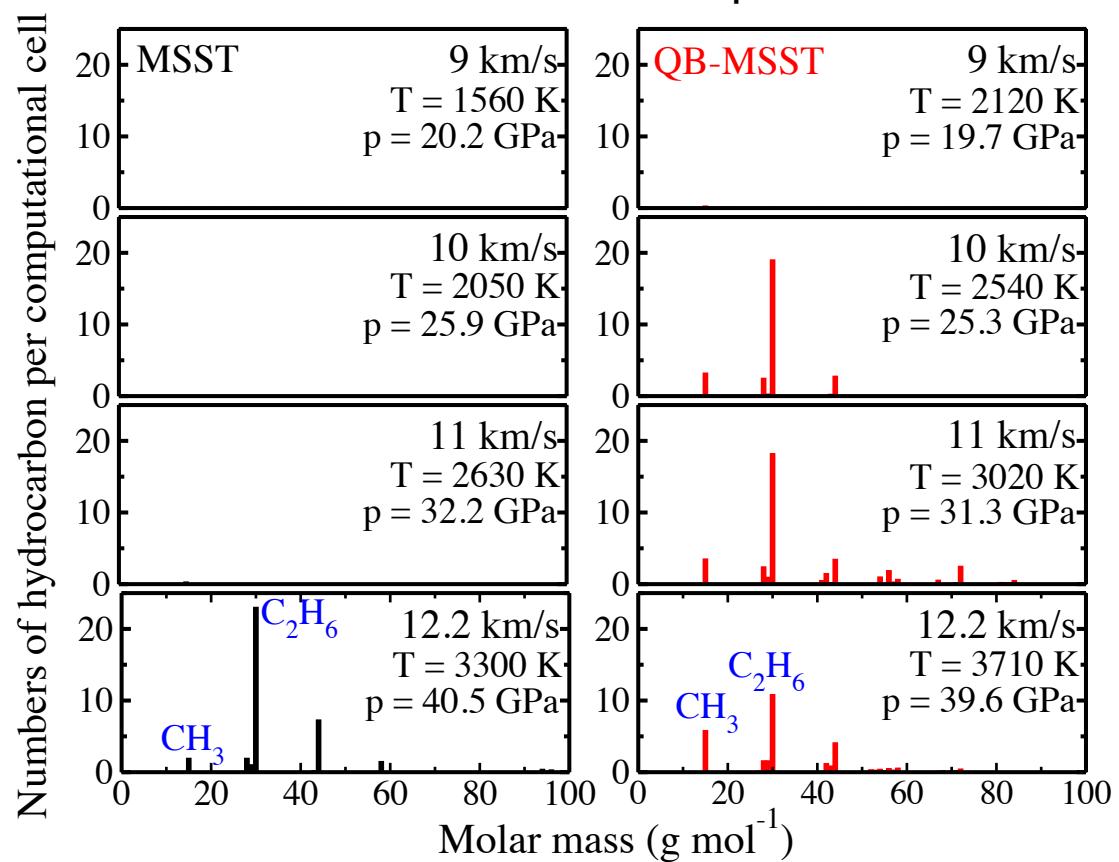
T. Qi, E. J. Reed, J. Phys. Chem. A **116**, 10451 (2012).

Experimental data from: W. Nellis, et al., J. Chem. Phys. **75**: 3055, 1981; H. Radousky, et al., J. Chem. Phys. **93**: 8235, 1990

SELF-CONSISTENT NATURE OF QBMSST CAN SHIFT CHEMICAL EQUILIBRIUM



QBMSST and MSST simulation durations of 300 ps

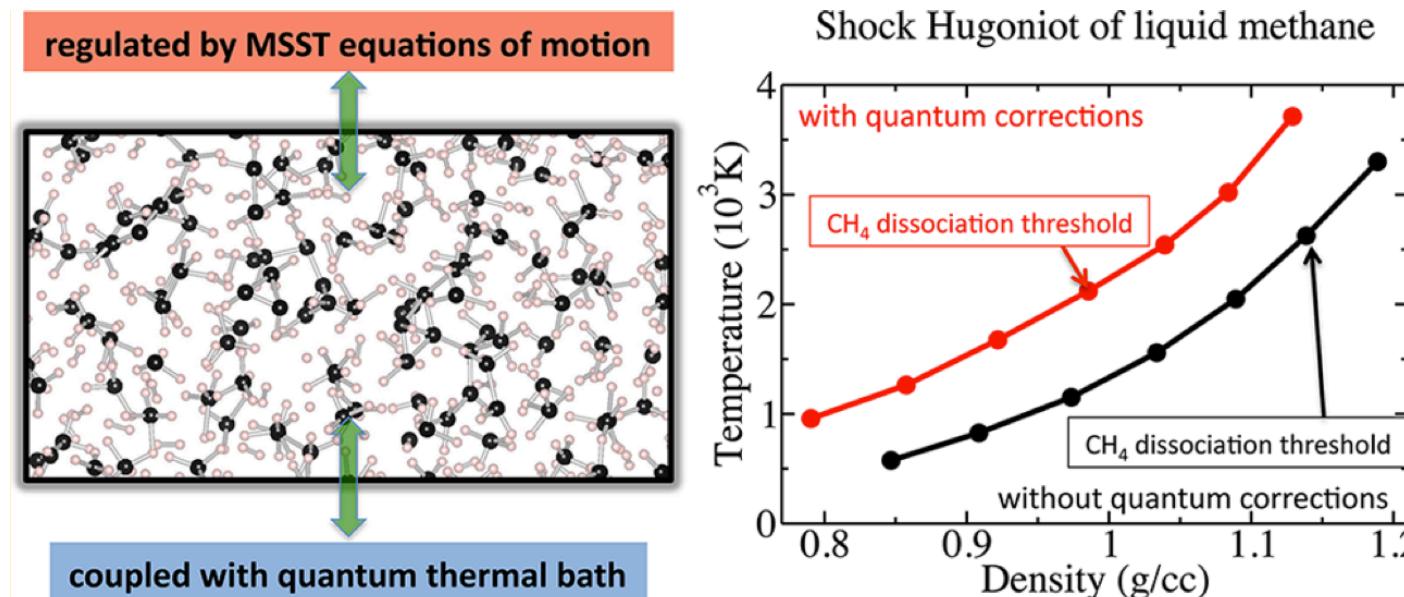


The onset of methane dissociation occurs 15 GPa (~35%) lower pressure and 800 K lower T for QBMSST.

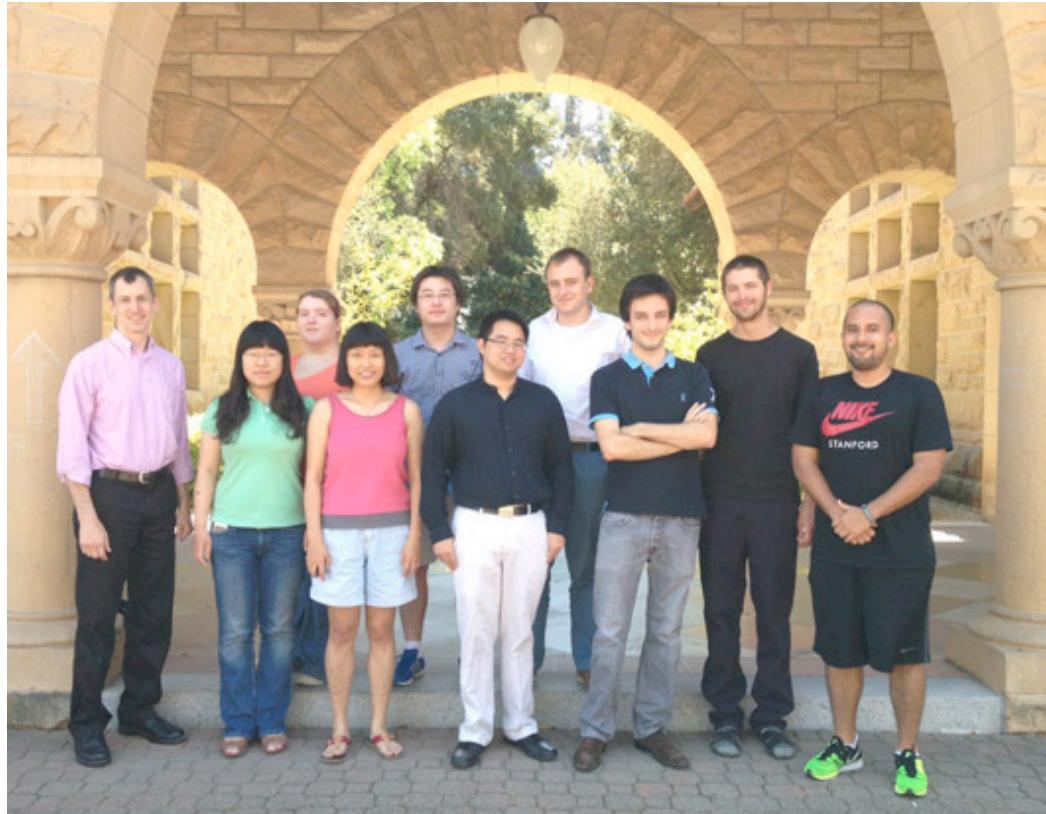


SUMMARY

- 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)



Computational resources for this work:

- National Energy Research Science Computing Center (NERSC)
- National Nanotechnology Infrastructure Network (NNIN)