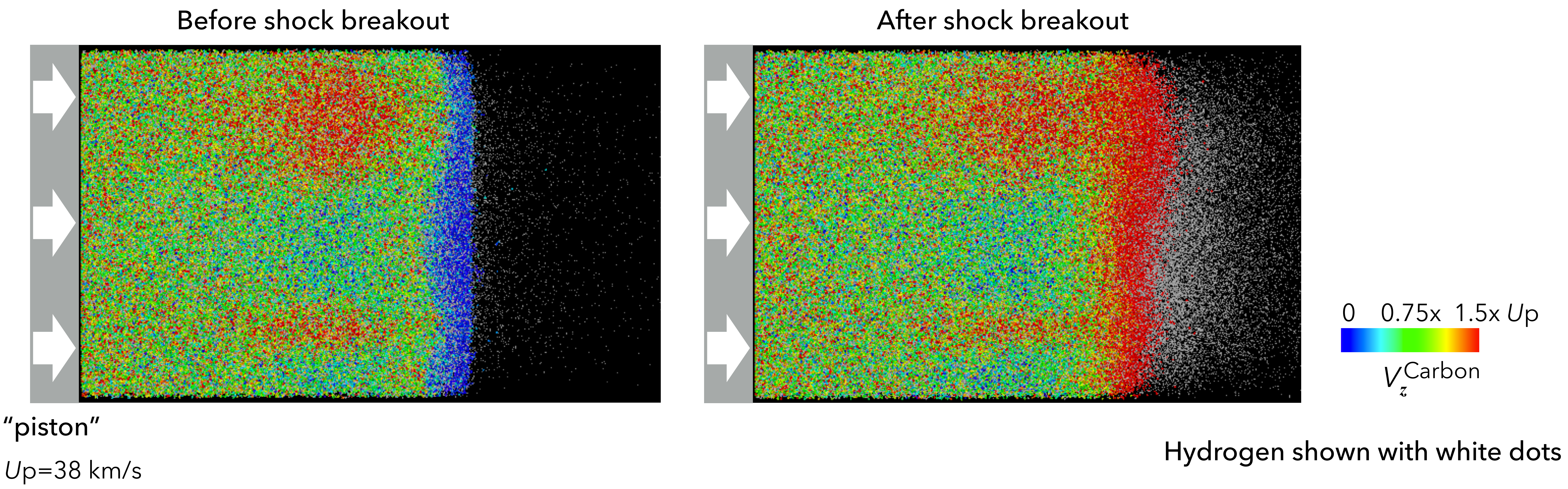
# Large-Scale Molecular-Dynamics Studies on the Release of Shocked Polystyrene Under Inertial Confinement Fusion Conditions




**Shuai Zhang, Suxing Hu**
University of Rochester
Laboratory for Laser Energetics

APS DPP Meeting
November 11, 2020

SUMMARY

# Large-scale non-equilibrium MD simulations of CH show species separation and hydrogen streaming upon release of strong shock

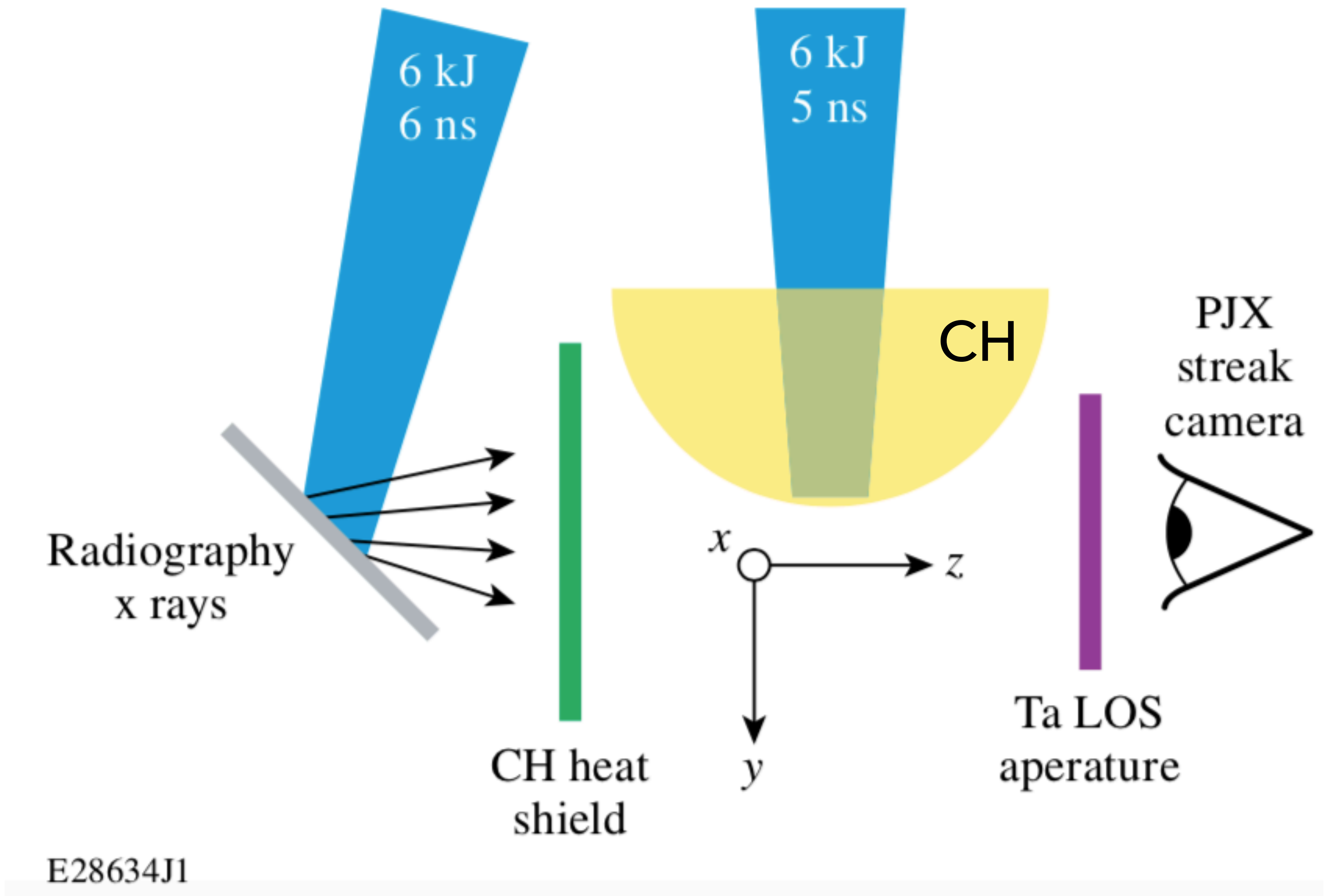
- Streamed hydrogen generates low-density plasmas that provide a possible explanation to the discrepancy between recent experiments‡ and regular hydro simulations‡
- Accurate Hugoniot EOS is obtained (3–20% error compared to DFT) for CH shocked to 25+ Mbar (10+ times the highest previous record), which sets an benchmark for the simulations
- The microscopic physics can happen in compounds (such as plastics and DT ice/fuel) used in ICF and HED experiments, but is currently missing in single-fluid hydro simulations

‡D. Haberberger et al, Phys. Rev. Lett. 123, 235001 (2019)

***Ref:*** S. Zhang & S. X. Hu, *Phys. Rev. Lett.* **125**, 105001 (2020)

# *Shock release poses grand challenges to hydro simulations*

- Recent experiments shows low-density plasmas generated by shock released CH move far ahead of what regular hydro predicts
- Agreement is reached when *assuming* **pre-expansion** (**due to radiation preheat**) at the rear surface of CH before shock arrival (ref: following talk by A. Shvydky)
- **Q**: any other explanation on the inconsistency between expt and regular hydro?

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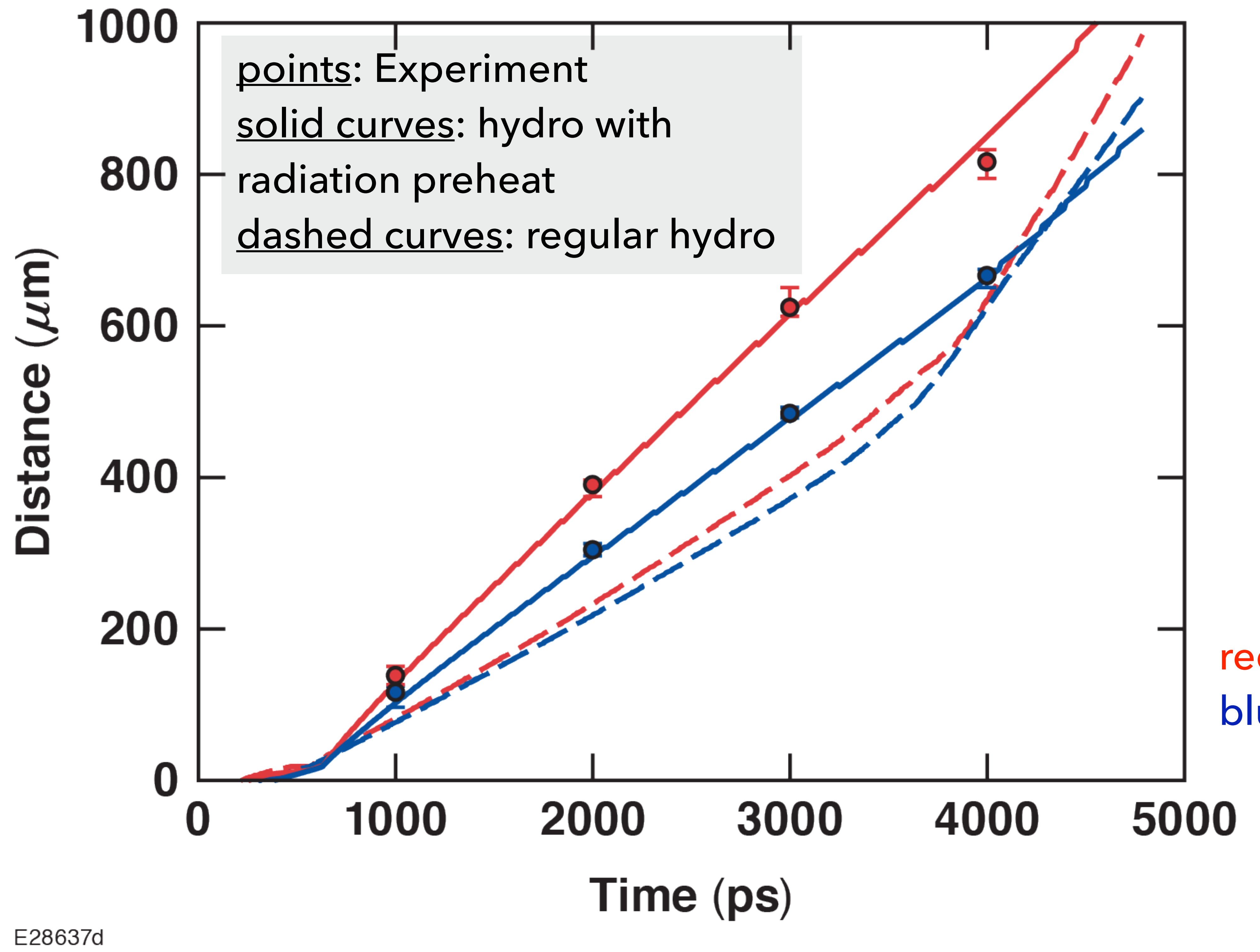


red: $10^{19}$ cm$^{-3}$
blue: $10^{20}$ cm$^{-3}$

# *We use classical molecular dynamics to simulate CH shock release*

- We prepare a structure that resembles real CH samples
- A momentum-mirror technique to simulate piston
- Up=38 km/s (corresponding Us~50 km/s, similar to the experiment‡)

- $1.35\times10^6$ atom cell
- $\rho_0$: 1.05 g/cm$^3$
- LAMMPS
- AIREBO-M, dt=0.05 fs
- periodic(x,y)/open(+z) boundaries

‡ D. Haberberger et al, Phys. Rev. Lett. 123, 235001 (2019)

# *We monitor the shock propagation*

- Hot spot formation when shock front passes the voids
- Higher-velocity particles ⇨ Nonuniformity of the shock front


Hydrogen shown with white dots

# We calculate the Hugoniot EOS to set a benchmark for the simulations

- Shock front position vs time ⇨ Shock velocity $U_s = dz/dt$
- Kinetic + virial contribution ⇨ Pressure $P = P_{kin} + P_{virial} = \frac{Nk_BT}{V} + \frac{\langle W \rangle}{3V}$
- Kinetic **+ ionization/energy partition** ⇨ Temperature $T_{ei} = \frac{T}{1 + \langle Z \rangle}$, $T = \sum_i \frac{m_i v_i^2}{3Nk_B}$

Up=38 km/s
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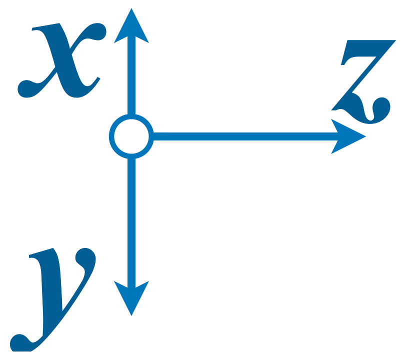


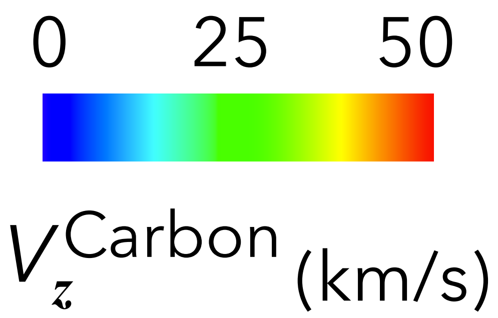


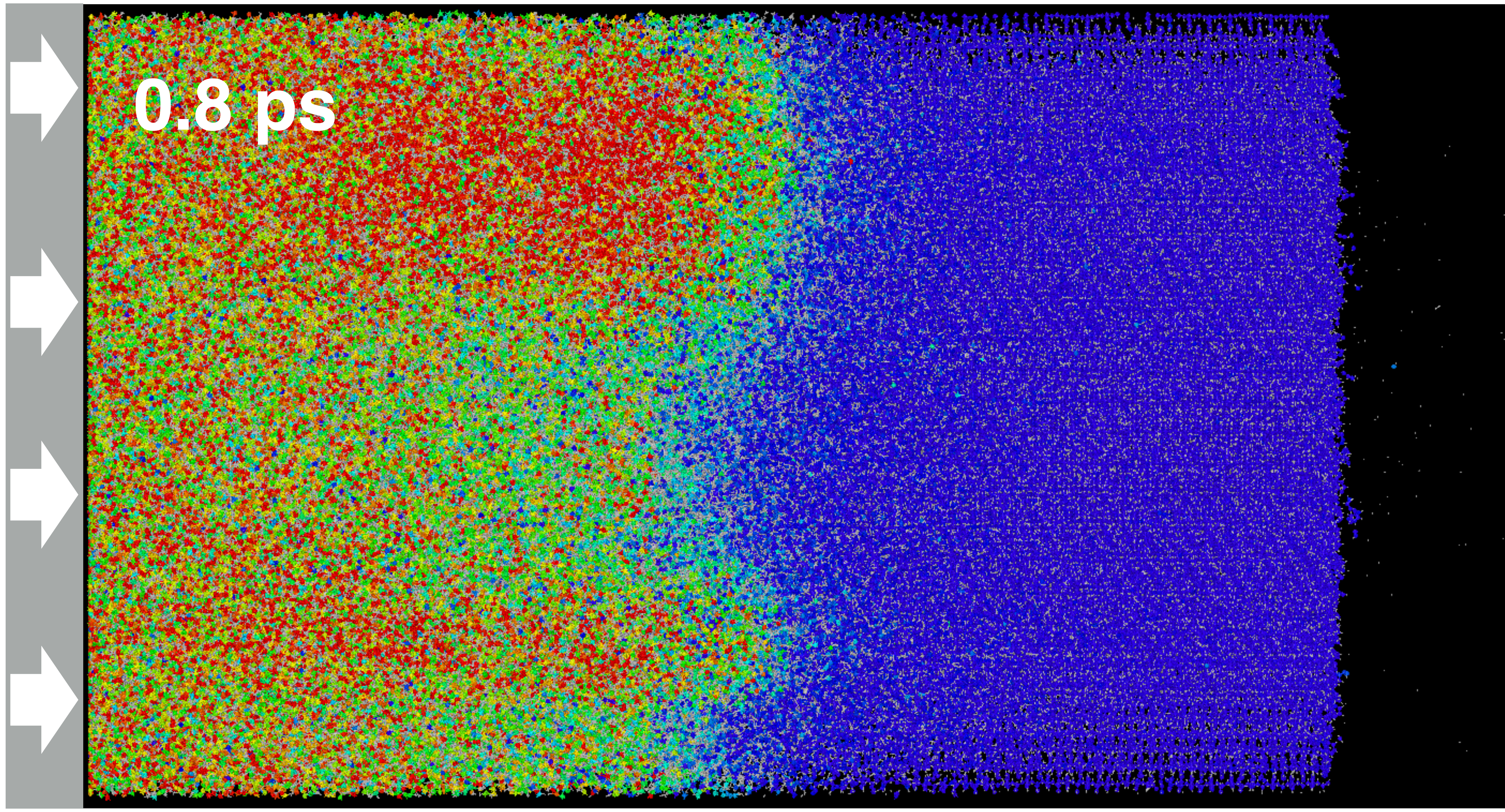


"Piston"

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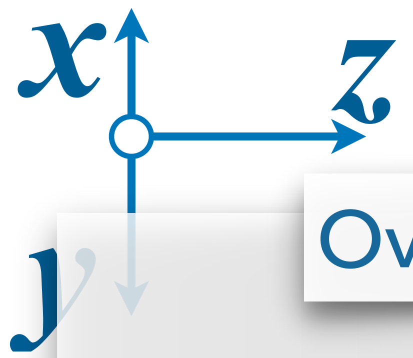
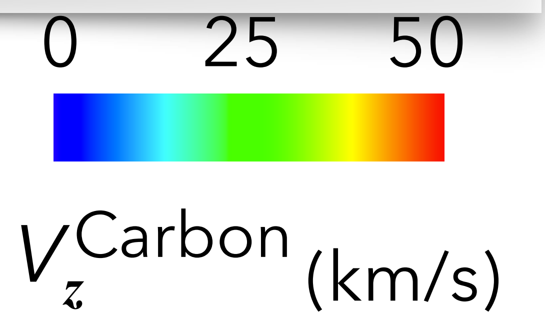
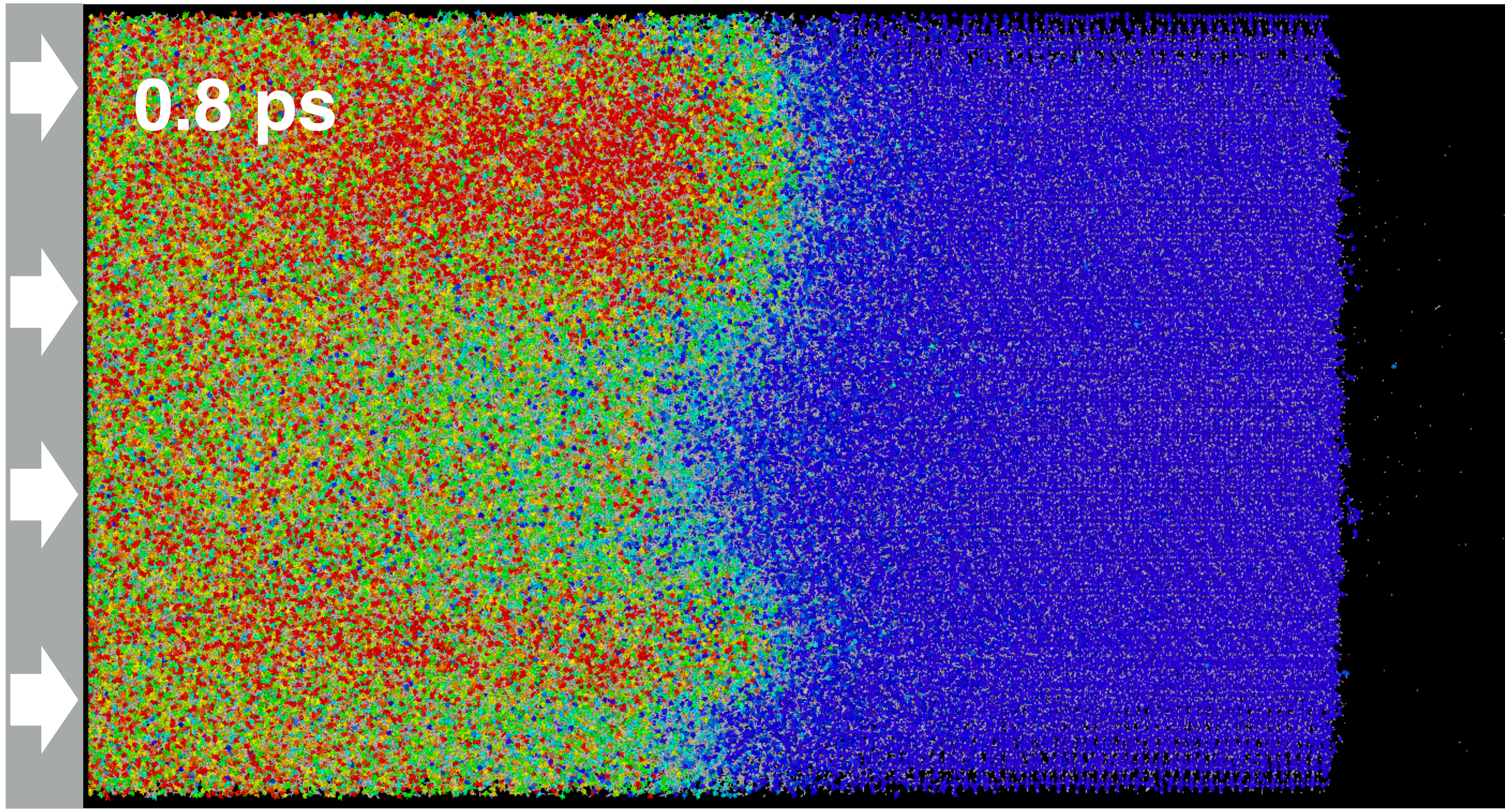



Overall differences (relative to DFT-MD): 3-20%

| | Us (km/s) | ρ (g/cc) | P (GPa) | $T_{ei}$ (x$10^5$K) |
|---|---|---|---|---|
| DFT | 52.5 | 3.8 | 2096 | 1.49 |
| CMD | 58.0 ± 1.2 | 3.0 ± 0.42 | 2022 ± 222 | 1.54 ± 0.36 |

* According to a DFT-based average-atom model for ionization‡, <Z>=1.45 at this temperature and density. ‡S. X. Hu et al., Phys. Plasmas 23, 042704 (2016).



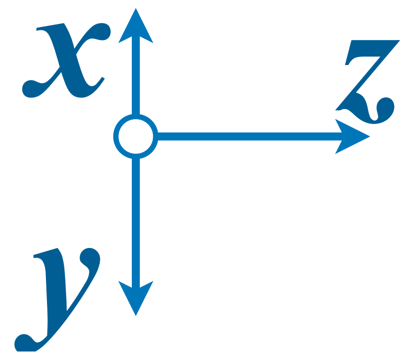




"Piston"

Hydrogen shown with white dots

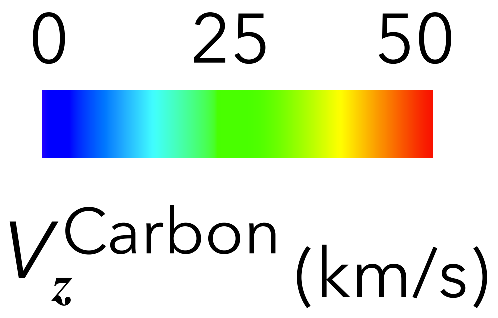
# We observe species separation and hydrogen streaming upon shock breakout

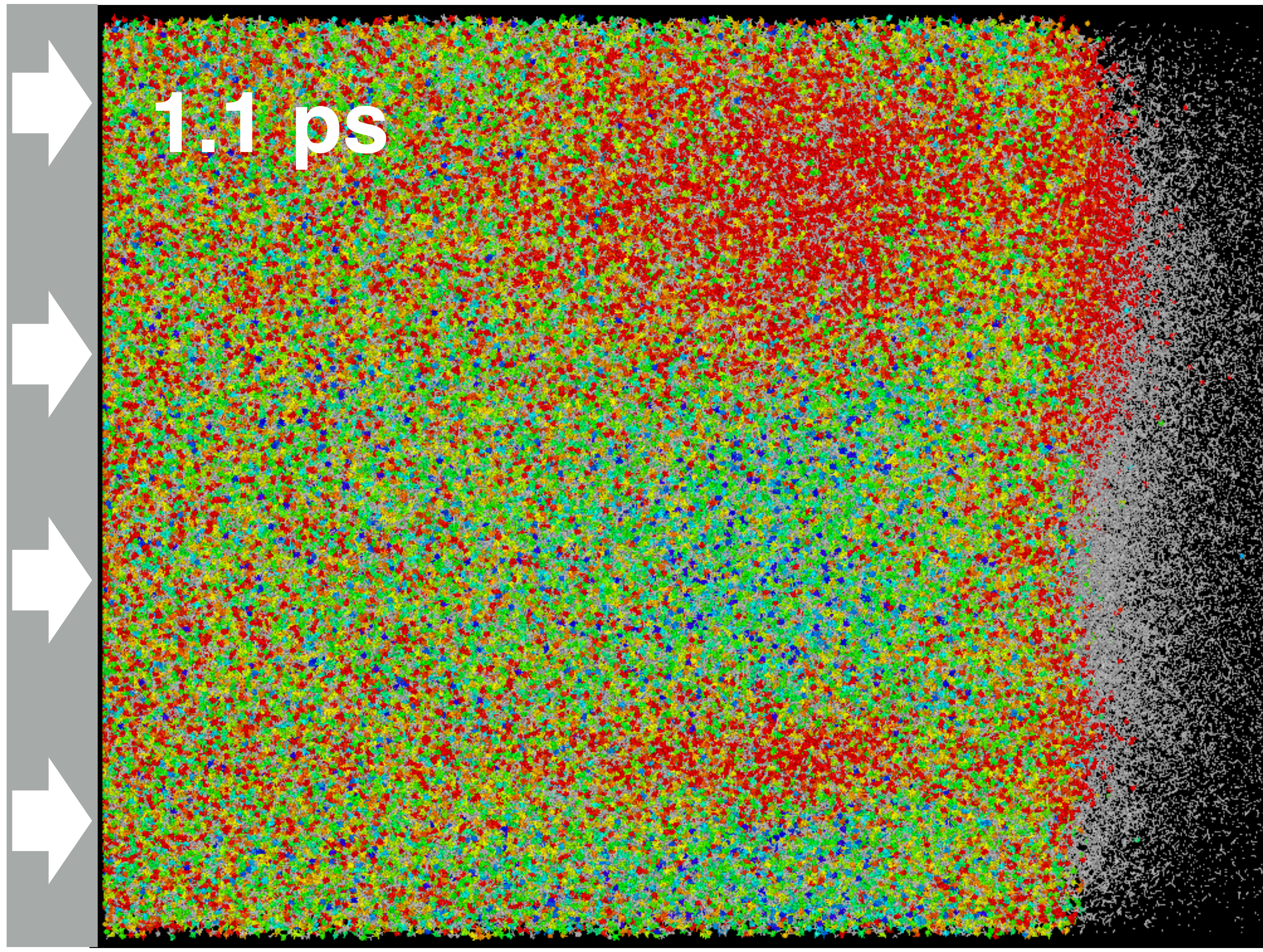
- Atom velocities dramatically increase upon shock breakout
- A significant amount of hydrogen stream ahead of carbon




## Reasons for species separation:

- Dissociation when being shocked
- Conservation of momentum and energy upon shock breakout
- Velocity distribution of H is broader than C
- Particle thermal energy and kinetics exceeds the dragging force due to chemical bonding




"Piston"

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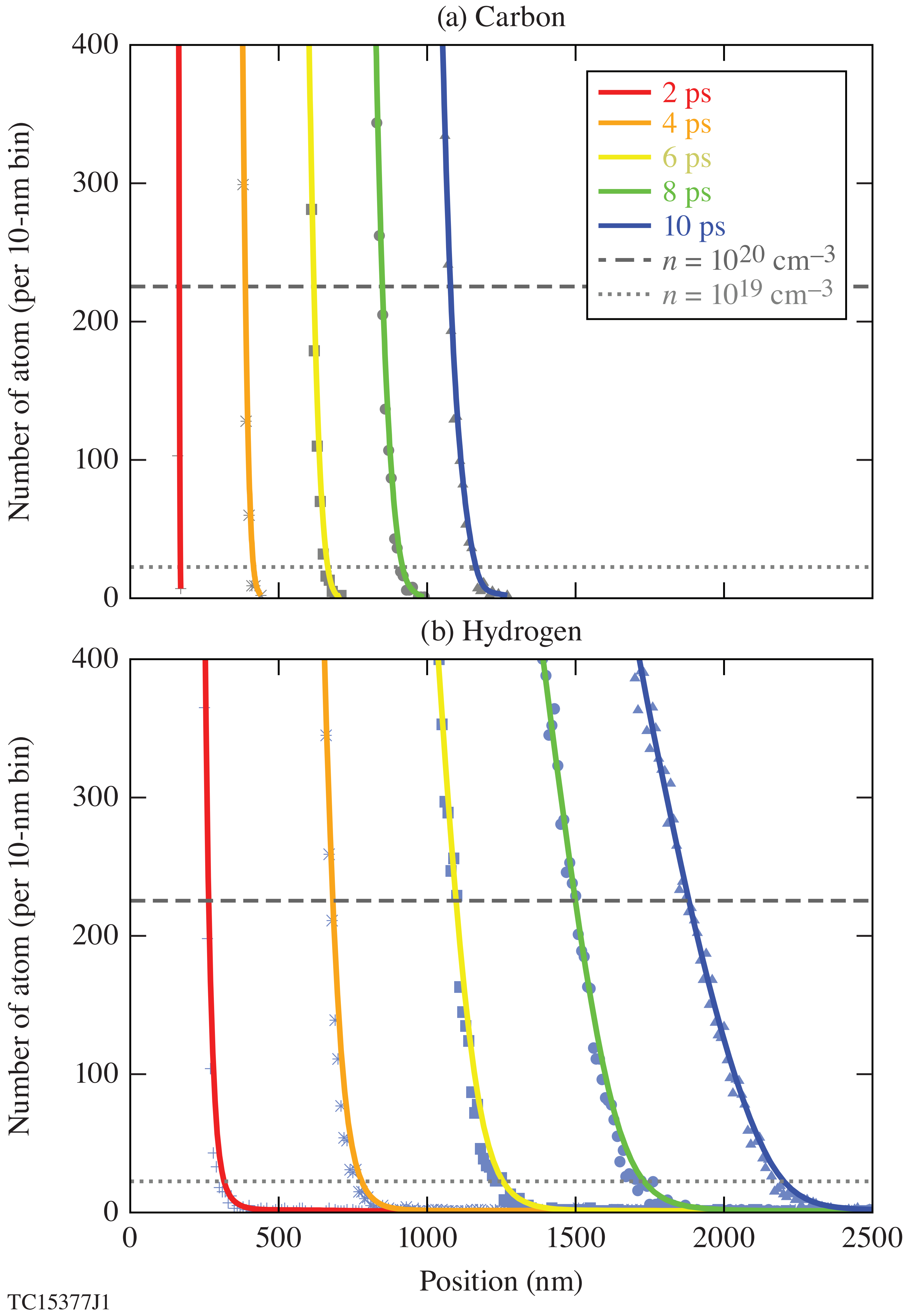
# Faster hydrogen streams ahead of carbon after shock release

- Hydrogen atoms travel far ahead of carbon, more so at lower densities




points: histogram
curves: fits with Bézier curves

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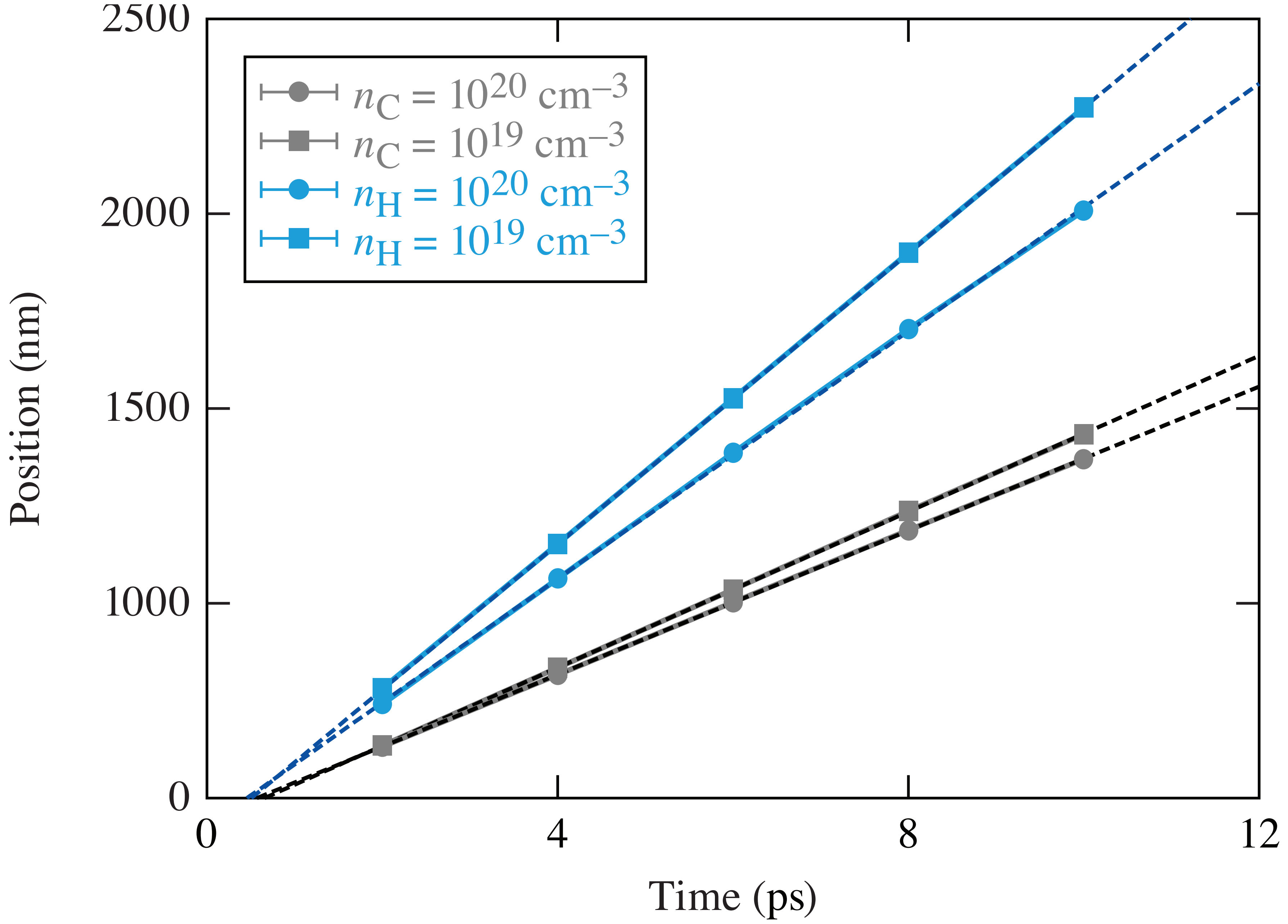
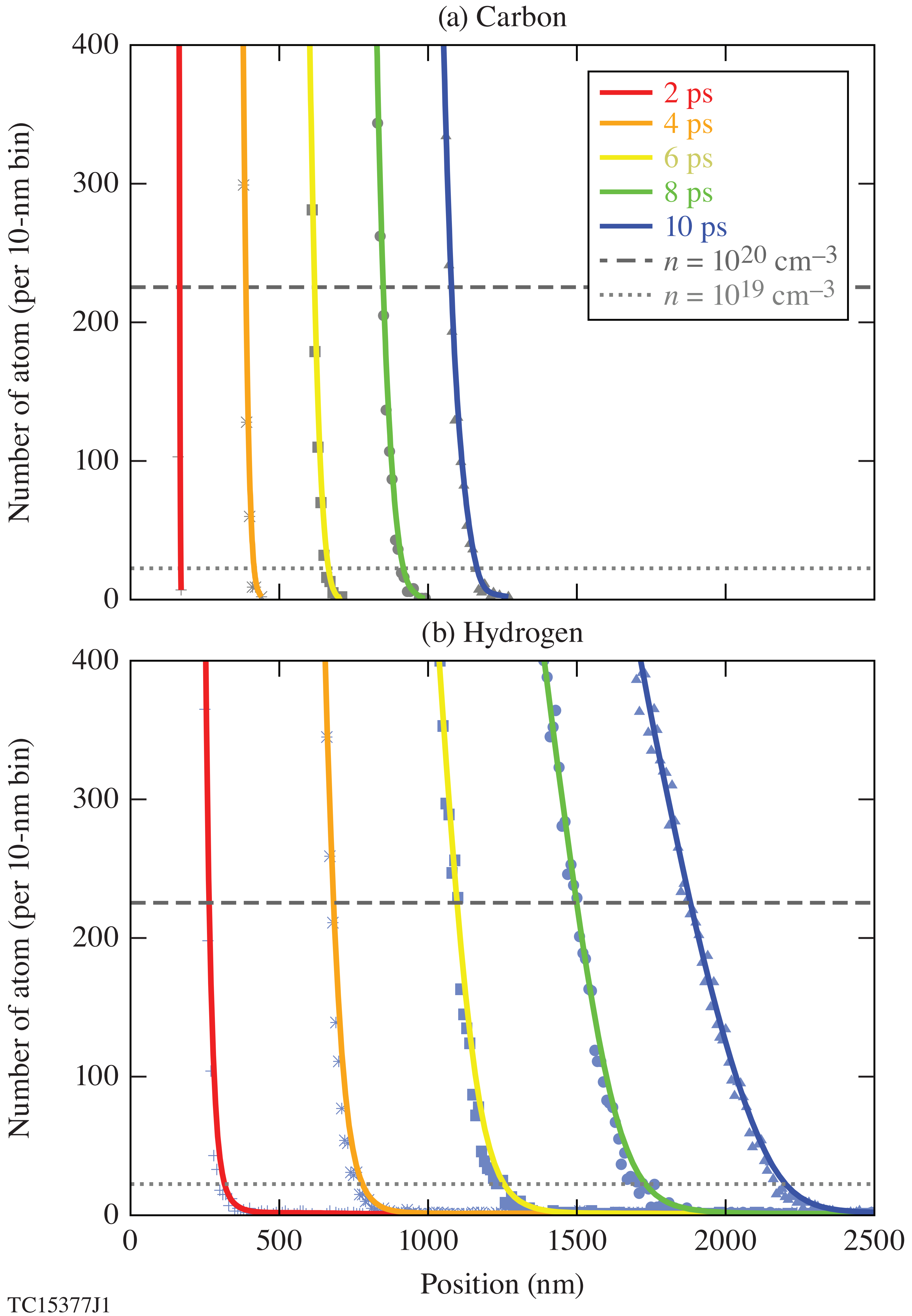


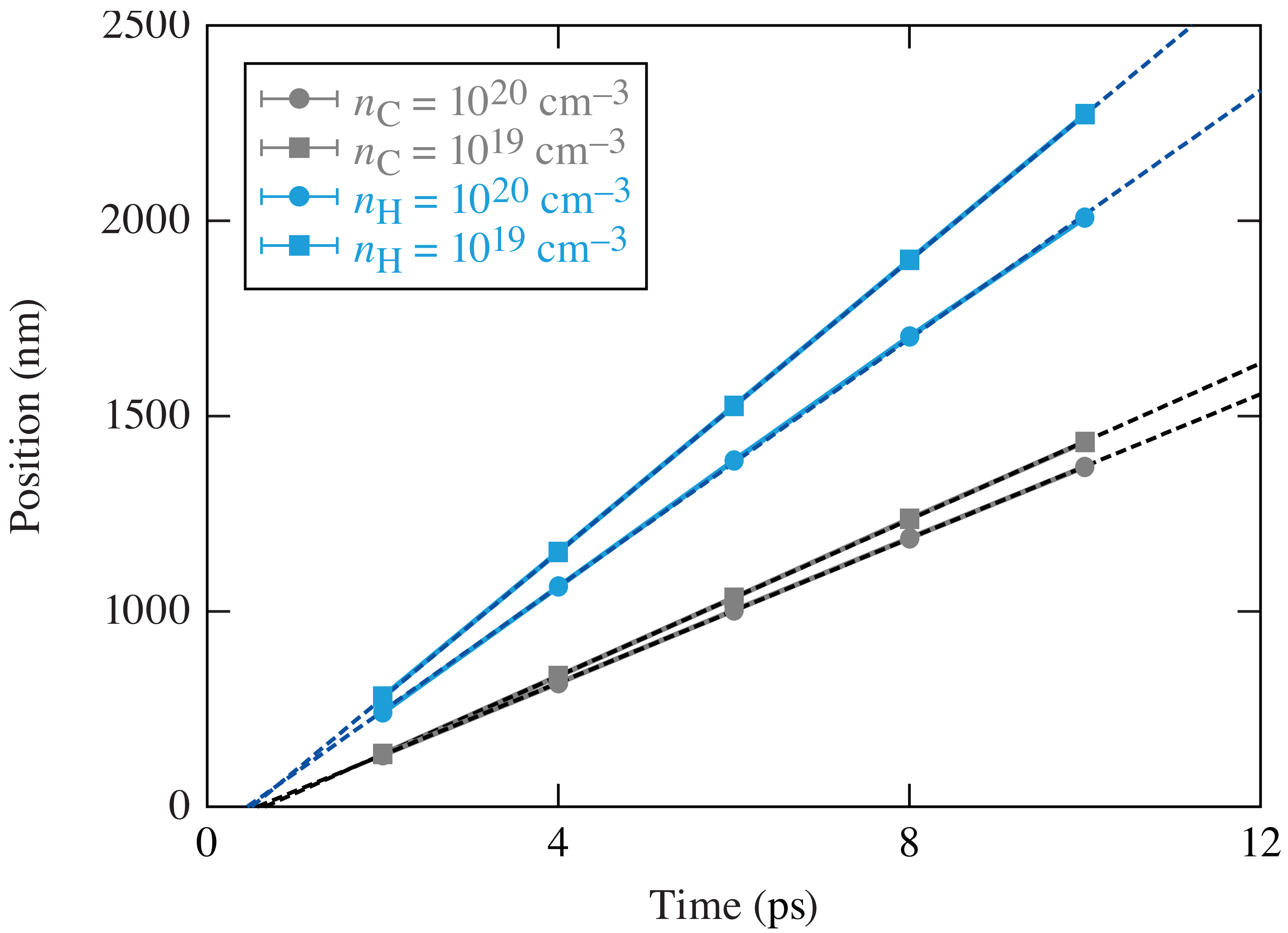



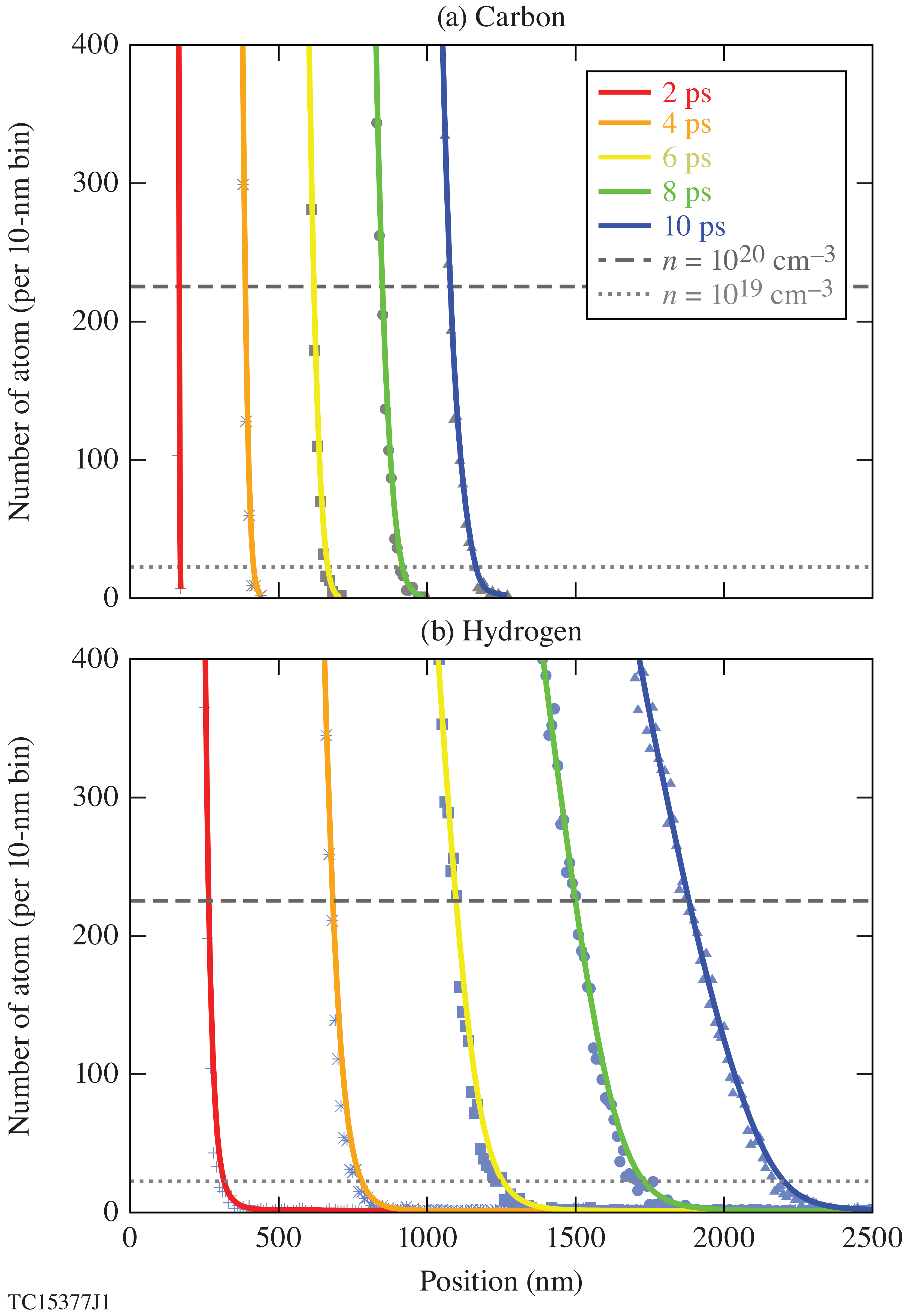

TC15377J1

points: histogram
curves: fits with Bézier curves

# *Faster hydrogen streams ahead of carbon after shock release*

- Hydrogen atoms travel far ahead of carbon, more so at lower densities
- Motion of both species is linear
- Hydrogen travels much faster than carbon, more so at the lower density



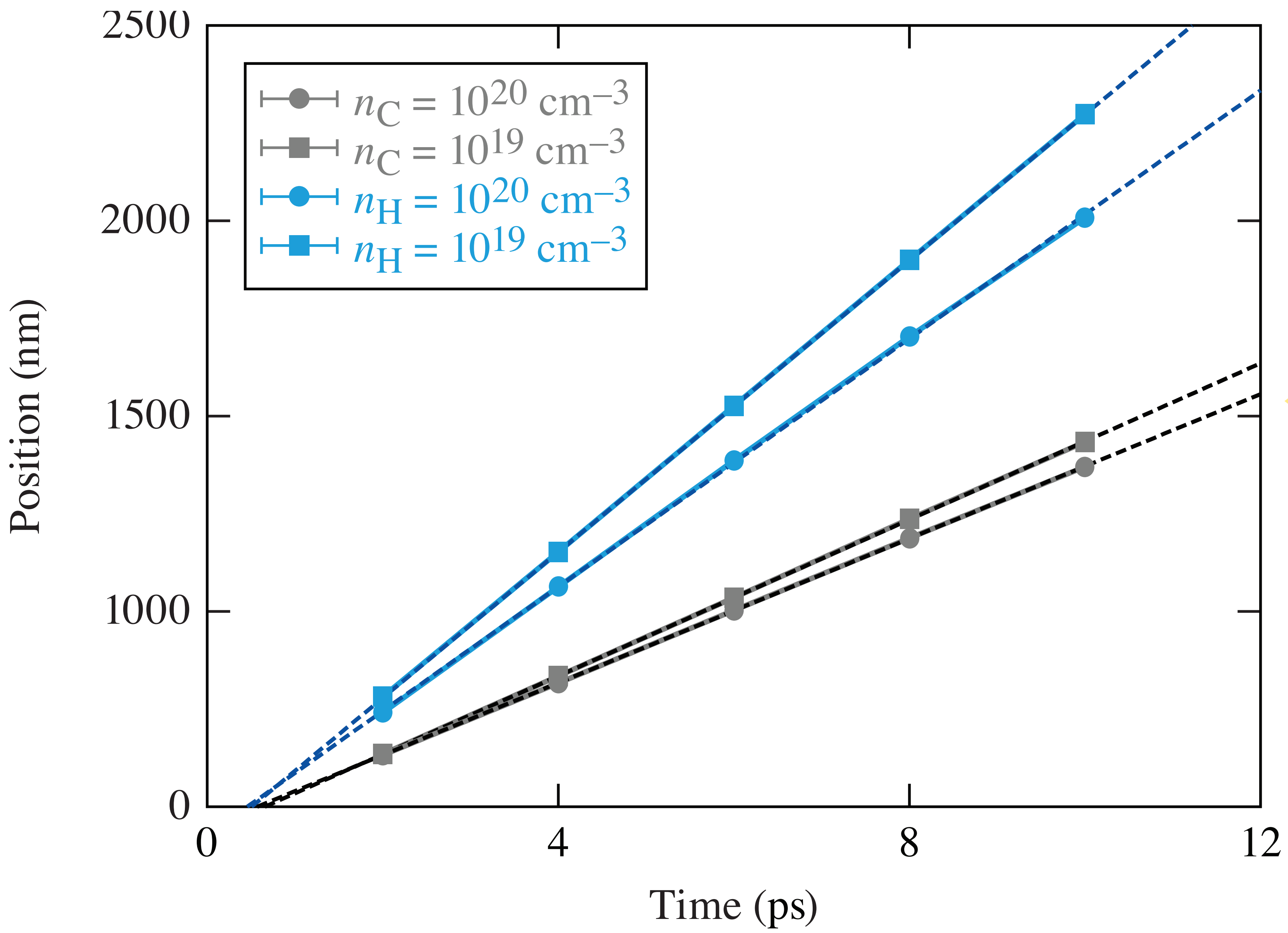

points: histogram
curves: fits with Bézier curves

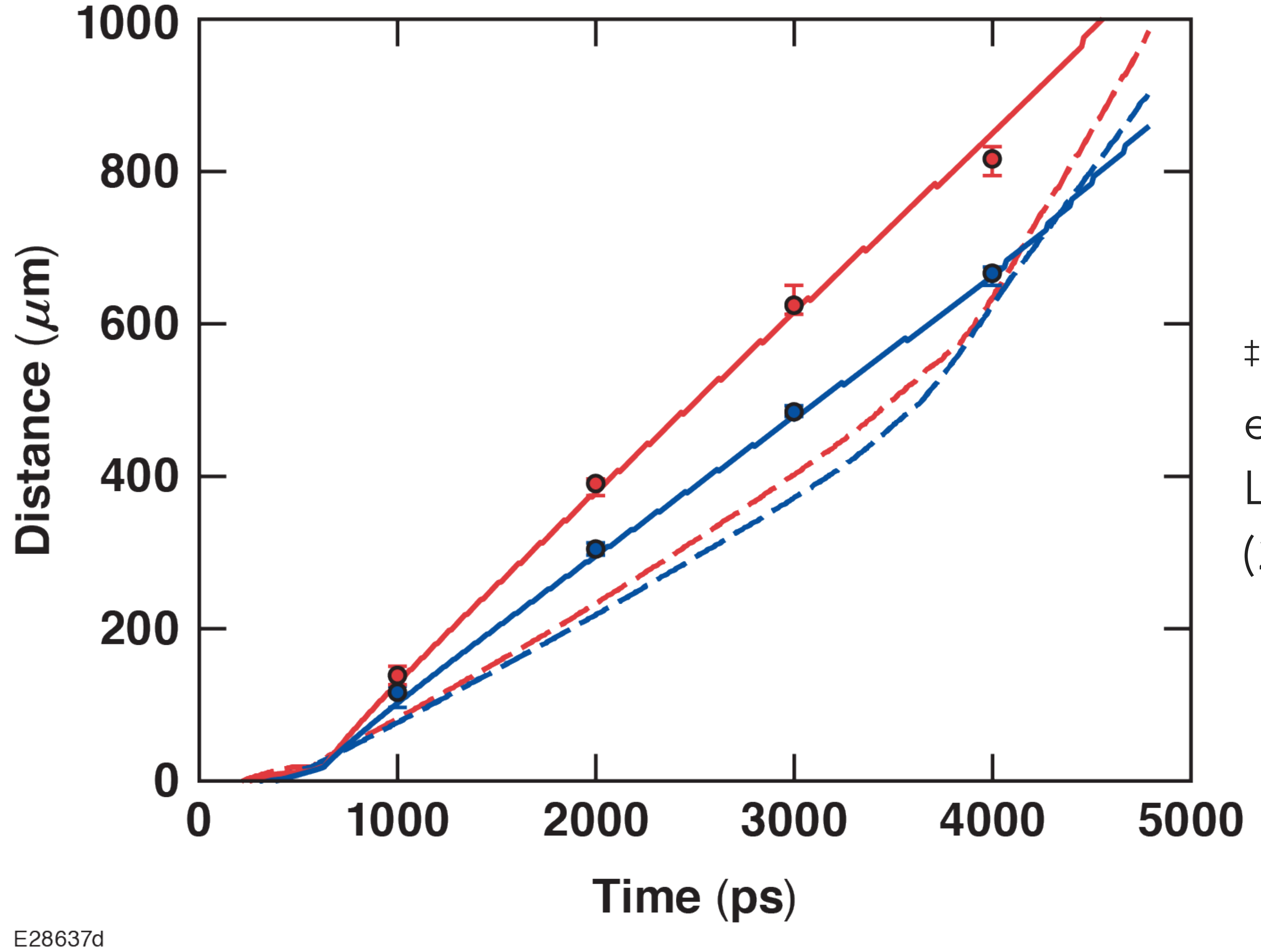
# *Still two challenges to be tackled before comparing calculation to expt.*

**Challenge#0** How to compare atomic velocities to plasma velocities?

**Challenge#1** Sample size is smaller and the simulation time is shorter by orders of magnitude in CMD than in experiment!

| CMD simulation (this work) | | Experiment‡ |
|---|---|---|
| 61.7 nm | Sample thickness $z_0$ | 37 $\mu$m |
| 1.1 ps | Shock duration $t_0$ | 580 ± 40 ps |




‡D. Haberberger et al, Phys. Rev. Lett. 123, 235001 (2019)

# We tackle Challenge#0 by ionization considerations

**Challenge#0** How to compare atomic velocities to plasma velocities?

- Comparing atomic velocities to plasma (electron) velocities is effectively assuming <Z>=1
- Released plasmas remain hot ($T>10^4$–$3\times10^4$ K) until after 10 ps and may not sufficiently recombine to reach equilibrium*
- <Z>~0.5 according to DFT-based average-atom calculations for C and H plasmas at $2\times10^4$ K and $10^{19}$–$10^{20}$ $cm^{-3}$

Therefore, we consider the range of <Z>=0.5 to 1

* According to collisional-radiative models‡, it can take several ns for shock generated C and H plasmas (<Z>=1.45) at $10^{20}$ $cm^{-3}$ density and 2 eV temperature to recombine and reach <Z>=1

‡J. J. MacFarlane, NLTERT–A Collisional-Radiative Code for Computing the Radiative Properties of Non-LTE Plasmas (Fusion Technology Institute, University of Wisconsin-Madison, 1997). p. 99.

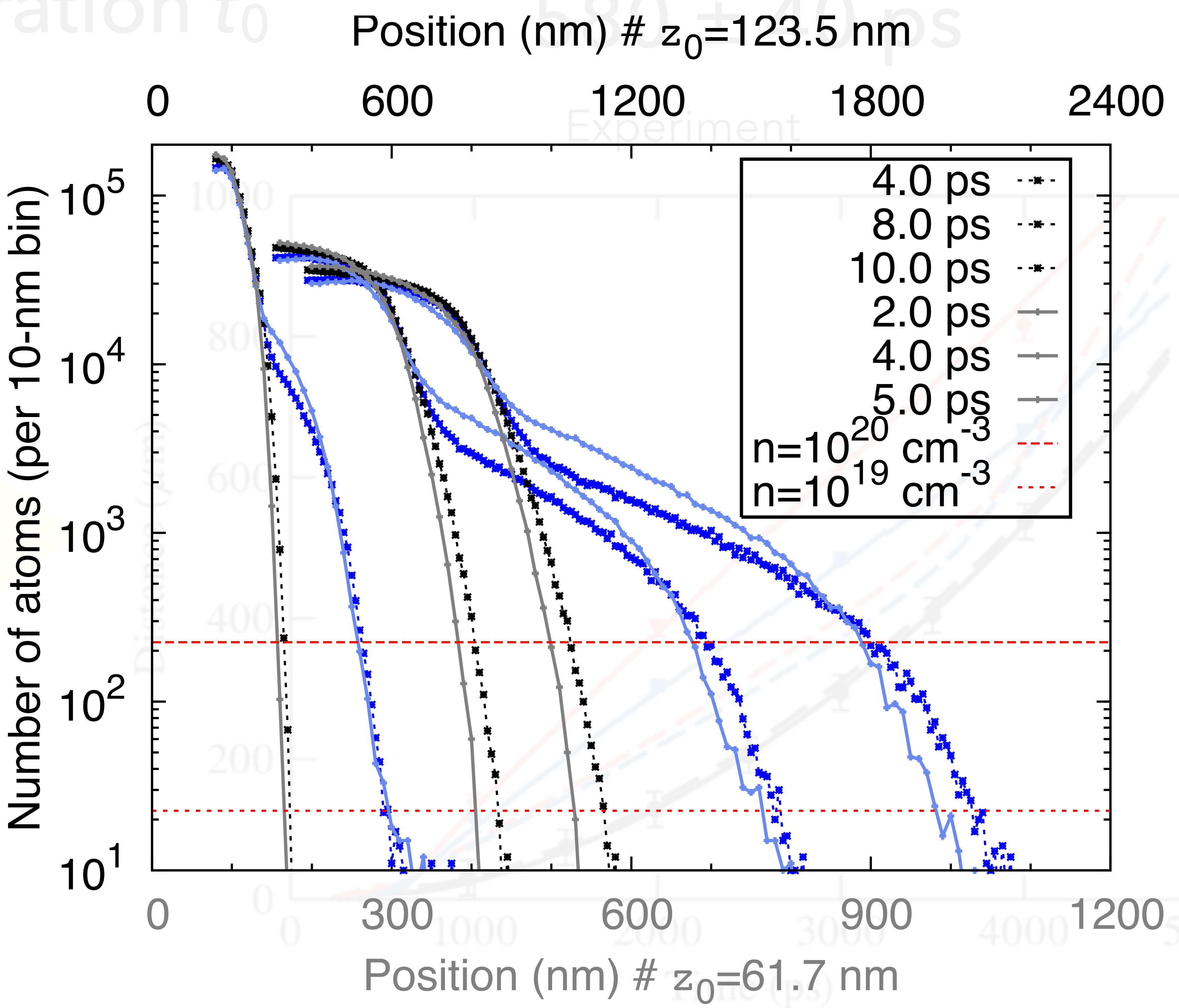
# We tackle Challenge#1 by hydrodynamic scaling

**Challenge#0** How to compare atomic velocities to plasma velocities?

**Challenge#1** Sample size is smaller and the simulation time is shorter by orders of magnitude in CMD than in experiment!

Solution#0 Consider the range of <Z> = 0.5 to 1

- Two CMD simulations are performed with the same $U_p$ and $\rho_0$ but different cell sizes
- Atomic distribution profiles agree very well with each other by choosing sample thickness $z_0$ as the length scale and shock propagation duration $t_0$ as the time scale



# *We tackle Challenge#1 by hydrodynamic scaling*

***Challenge#0*** How to compare atomic velocities to plasma velocities?

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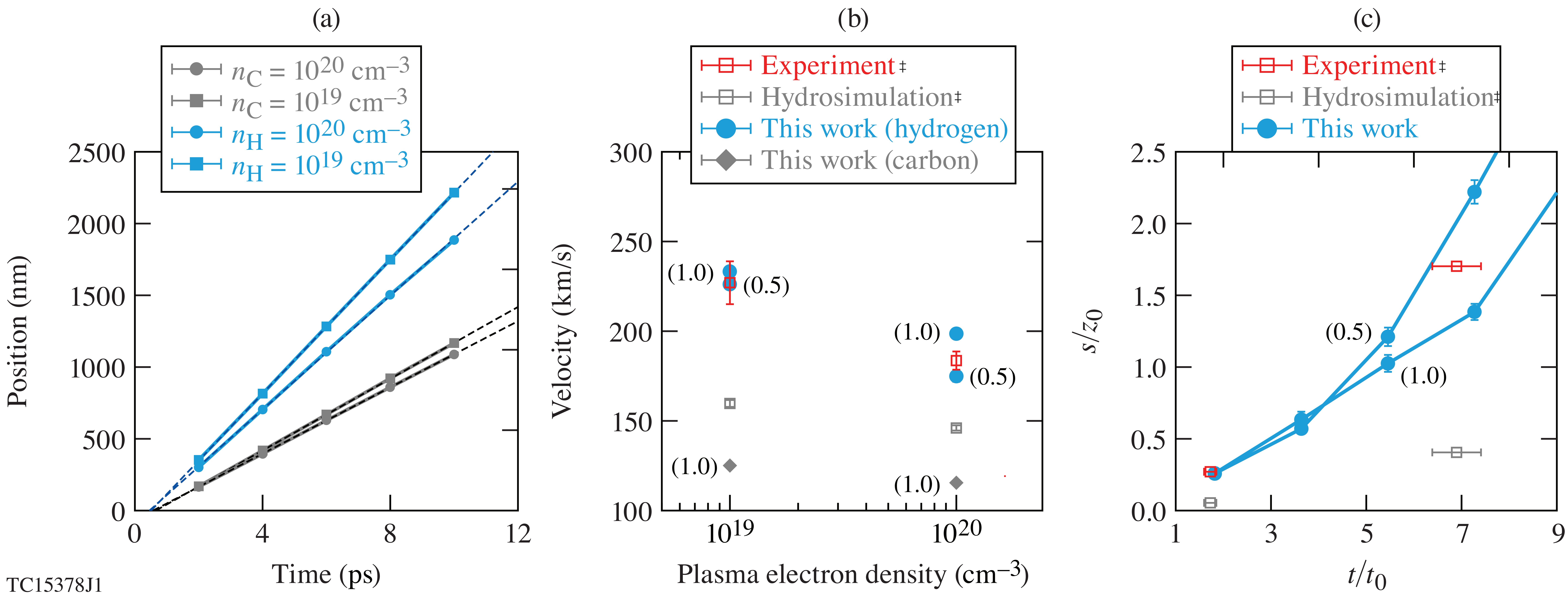
Solution#1 Hydrodynamic scaling

# Hydrogen streaming explains experimental observations

- Remarkable agreement between our calculation and experiment in both plasma velocities and scale length




TC15378J1

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***Ref:*** S. Zhang & S. X. Hu, *Phys. Rev. Lett.* **125**, 105001 (2020)

## ACKNOWLEDGEMENT

D. Haberberger, A. Shvydky, D. Harding, J. Carroll-Nellenback, V. Goncharov, A. Maximov, and V. Karasiev

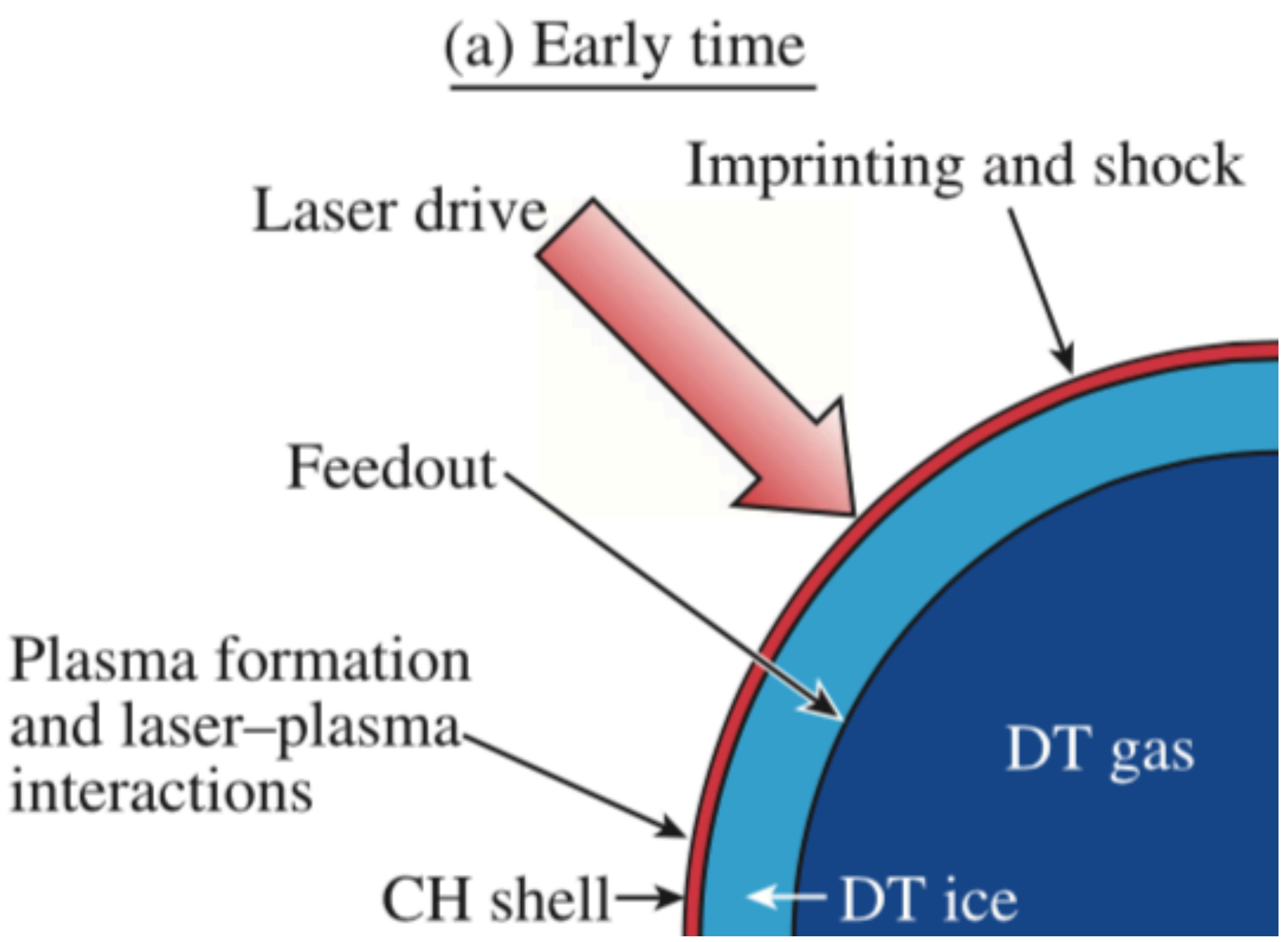
*This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003856.

# Thank you!

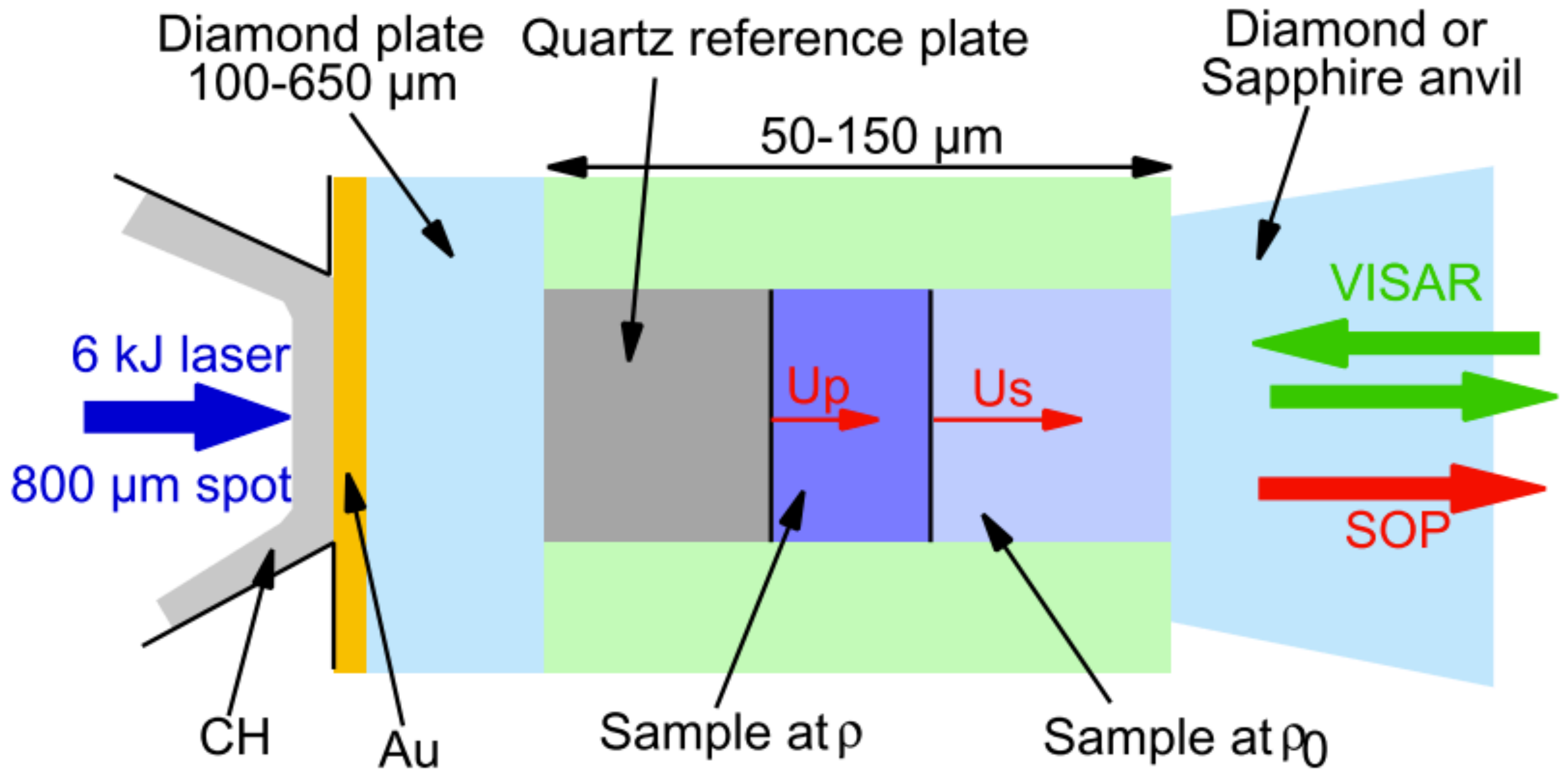
# CH: an important material for HEDP and ICF experiments

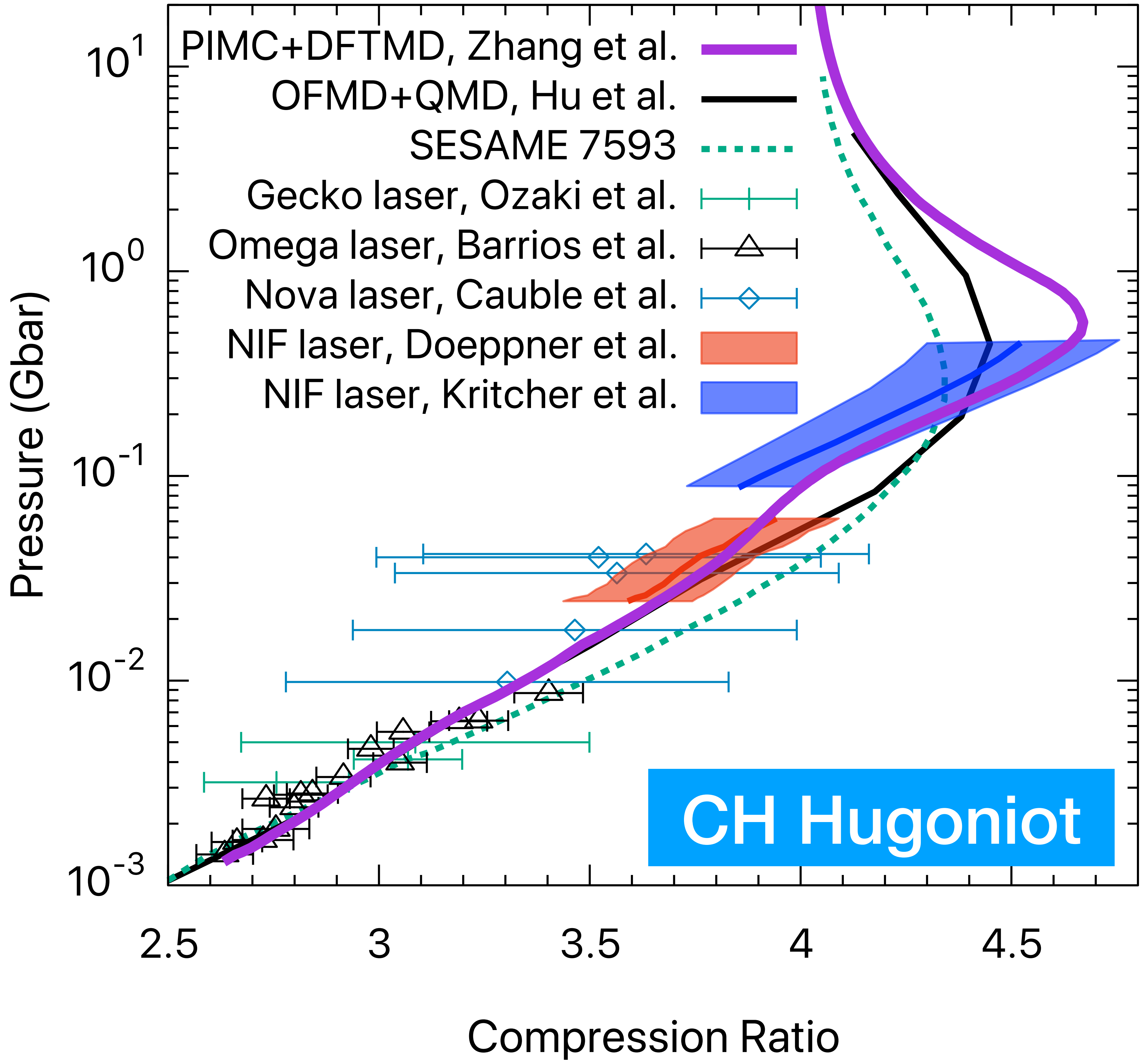
- CH is widely used as an ablator material
- Its EOS and properties under shock well studied

S. Craxton et al., Phys. Plasmas (2015)




S. Brygoo et al., J. Appl. Phys. (2015)



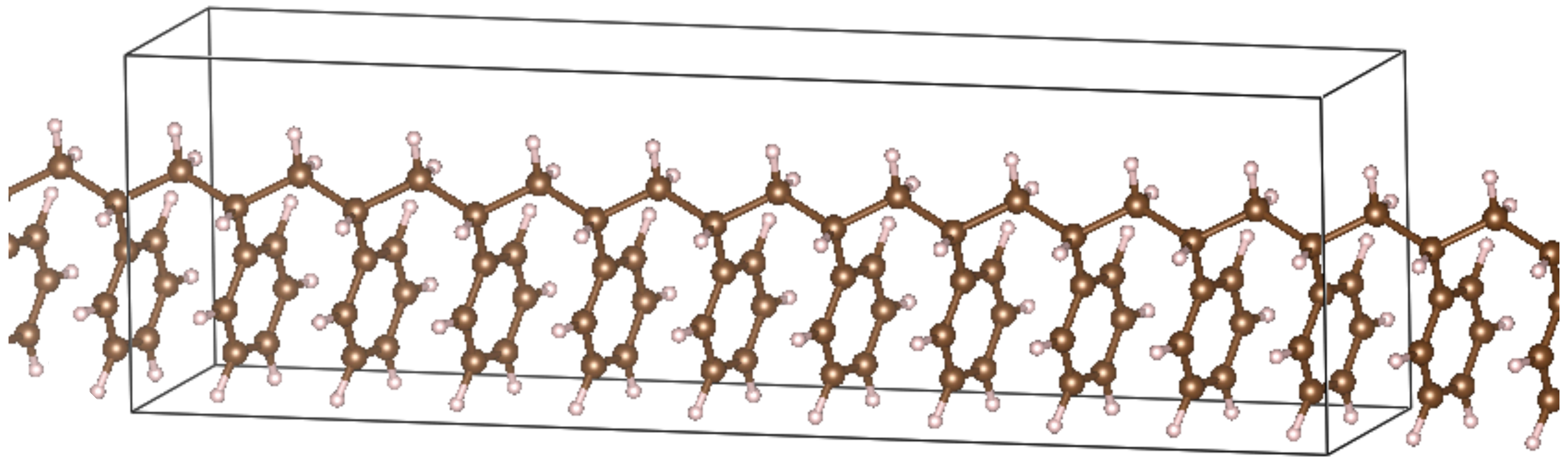




S. Zhang et al., J. Chem. Phys. (2018); Hu et al., Phys. Rev. E (2015); Ozaki et al., Phys. Plasmas (2009); Barrios et al., Phys. Plasmas (2010); Cauble et al., Phys. Plasmas (1997); Phys. Rev. Lett. (1998); Döppner et al., Phys. Rev. Lett. (2018); Kritcher et al., Nature (2020)

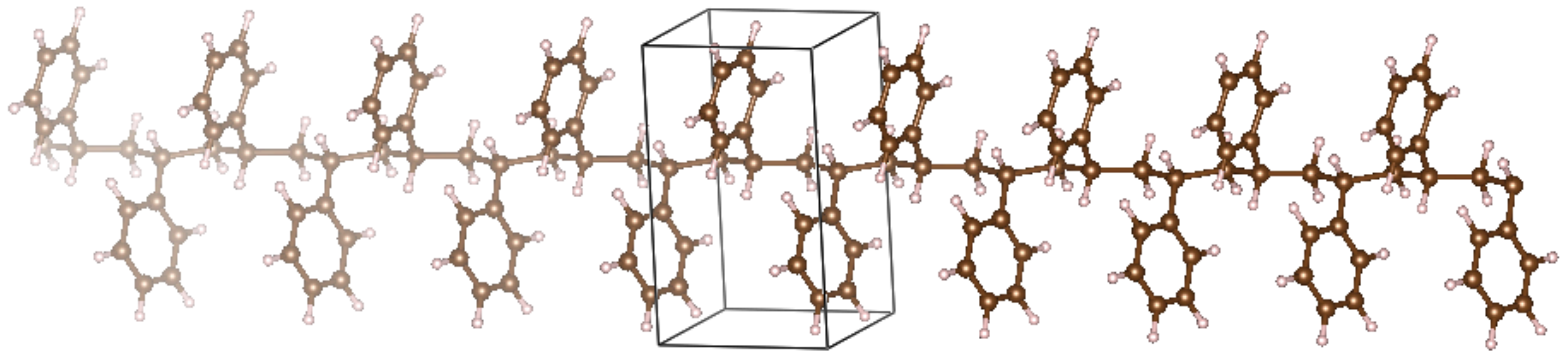
# *CMD approximates inter-atomic interactions with empirical force fields*

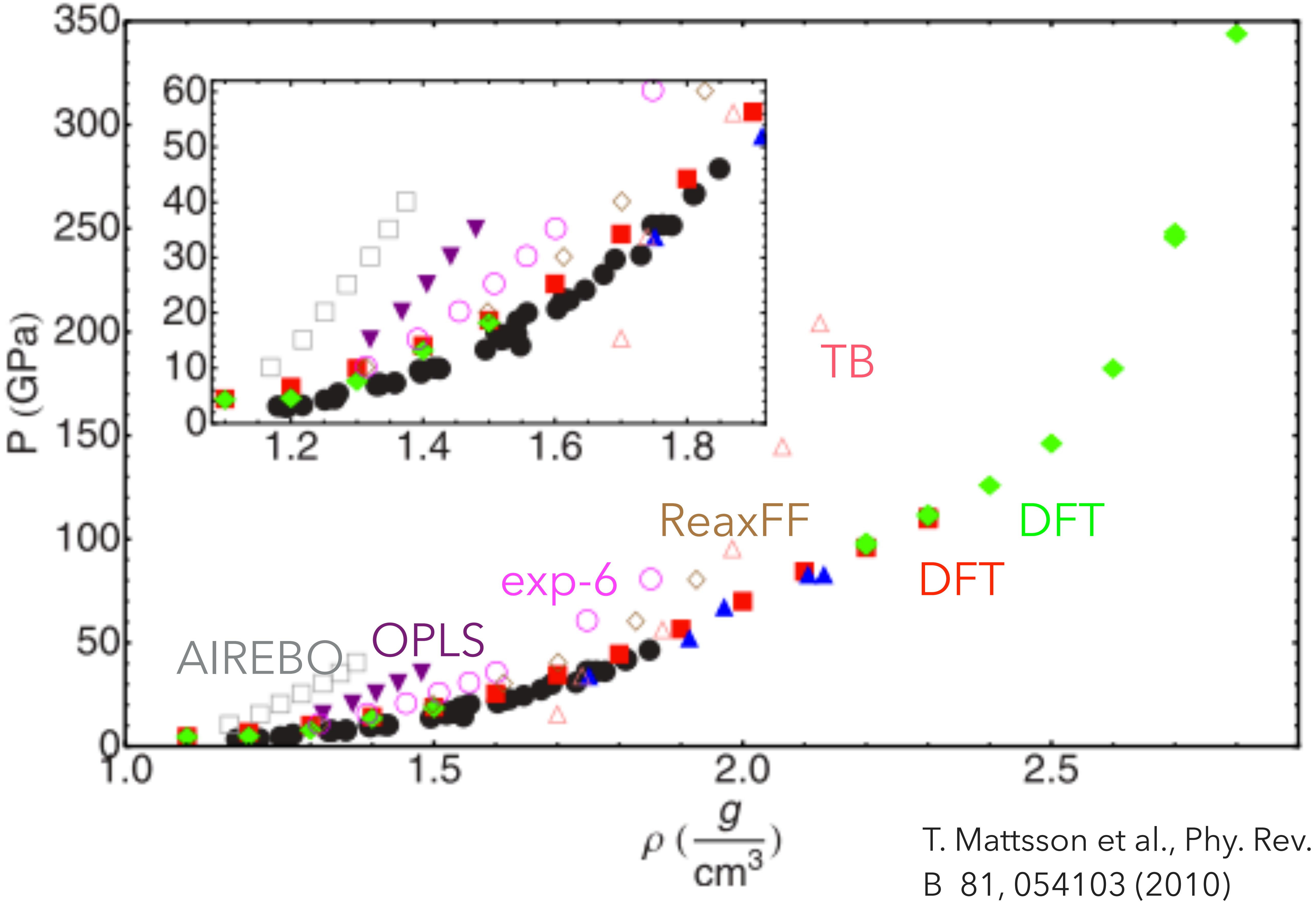
- For CH, reactive potentials were shown to be more accurate than non-reactive ones
- Highest pressure records: 200 GPa w/ ReaxFF, 40 GPa w/AIREBO-M
- 10-30% difference at up to 40-80 GPa, in comparison to DFT predicted Hugoniots

*isotactic*



*syndiotactic*

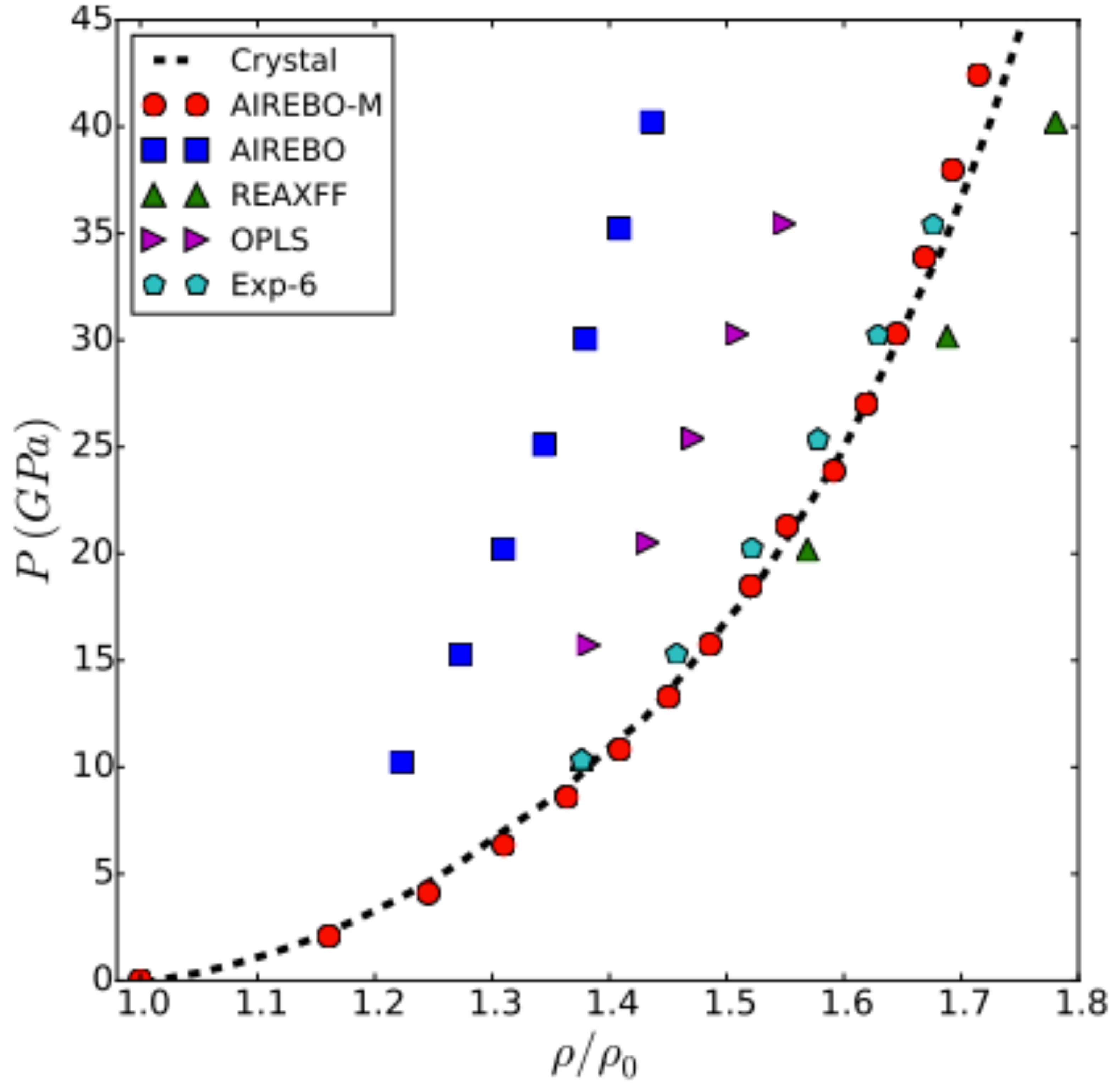





T. Mattsson et al., Phy. Rev. B 81, 054103 (2010)

# Reactive empirical bond-order potentials for applications to hydrocarbons

- We mainly use AIREBO-M, but have tested some others




O'Connor et al., J. Chem. Phys. 142, 024903 (2015)

**AIREBO**

$$E = \frac{1}{2}\sum_i \sum_{j\neq i}\left[E_{ij}^{\mathrm{REBO}} + E_{ij}^{\mathrm{LJ}} + \sum_{k\neq i,j}\sum_{l\neq i,j,k} E_{kijl}^{\mathrm{tors}}\right]$$

covalent bonding

$$E_{ij}^{\mathrm{REBO}} = V_{ij}^{R}\left(r_{ij}\right) + b_{ij}V_{ij}^{A}\left(r_{ij}\right)$$

Lennard-Jones (inter-molecular)

$$E_{ij}^{\mathrm{LJ}} = S\left(t_r\left(r_{ij}\right)\right) S\left(t_b\left(b_{ij}^{*}\right)\right) C_{ij}V_{ij}^{\mathrm{LJ}}\left(r_{ij}\right) + \left[1 - S\left(t_r\left(r_{ij}\right)\right)\right] C_{ij}V_{ij}^{\mathrm{LJ}}\left(r_{ij}\right)$$

torsion interactions

$$E^{\mathrm{tors}} = \frac{1}{2}\sum_i \sum_{j\neq i}\sum_{k\neq i,j}\sum_{l\neq i,j,k} w_{ij}\left(r_{ij}\right) w_{jk}\left(r_{jk}\right) w_{kl}\left(r_{kl}\right) \times V^{\mathrm{tors}}\left(\omega_{ijkl}\right)$$

**AIREBO-M**

$$U_{ij}^{\mathrm{LJ}}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

⇩

$$U_{ij}(r) = -\epsilon_{ij}\left[1 - \left(1 - e^{-\alpha_{ij}\left(r - r_{ij}^{eq}\right)}\right)^{2}\right]$$

Replace LJ with a Morse potential

S. J. Stuart et al., J. Chem. Phys. 112, 6472 (2000)

O'Connor et al., J. Chem. Phys. 142, 024903 (2015)

# *We calculate the Hugoniot EOS to set a benchmark for the simulations*

- Shock front position vs time ⇨ Shock velocity $U_s = dz/dt$
- Kinetic + virial contribution ⇨ Pressure $P = P_{kin} + P_{virial} = \frac{Nk_BT}{V} + \frac{\langle W \rangle}{3V}$
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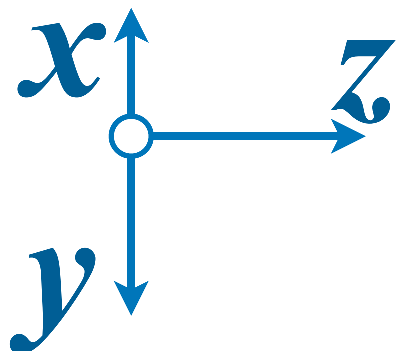
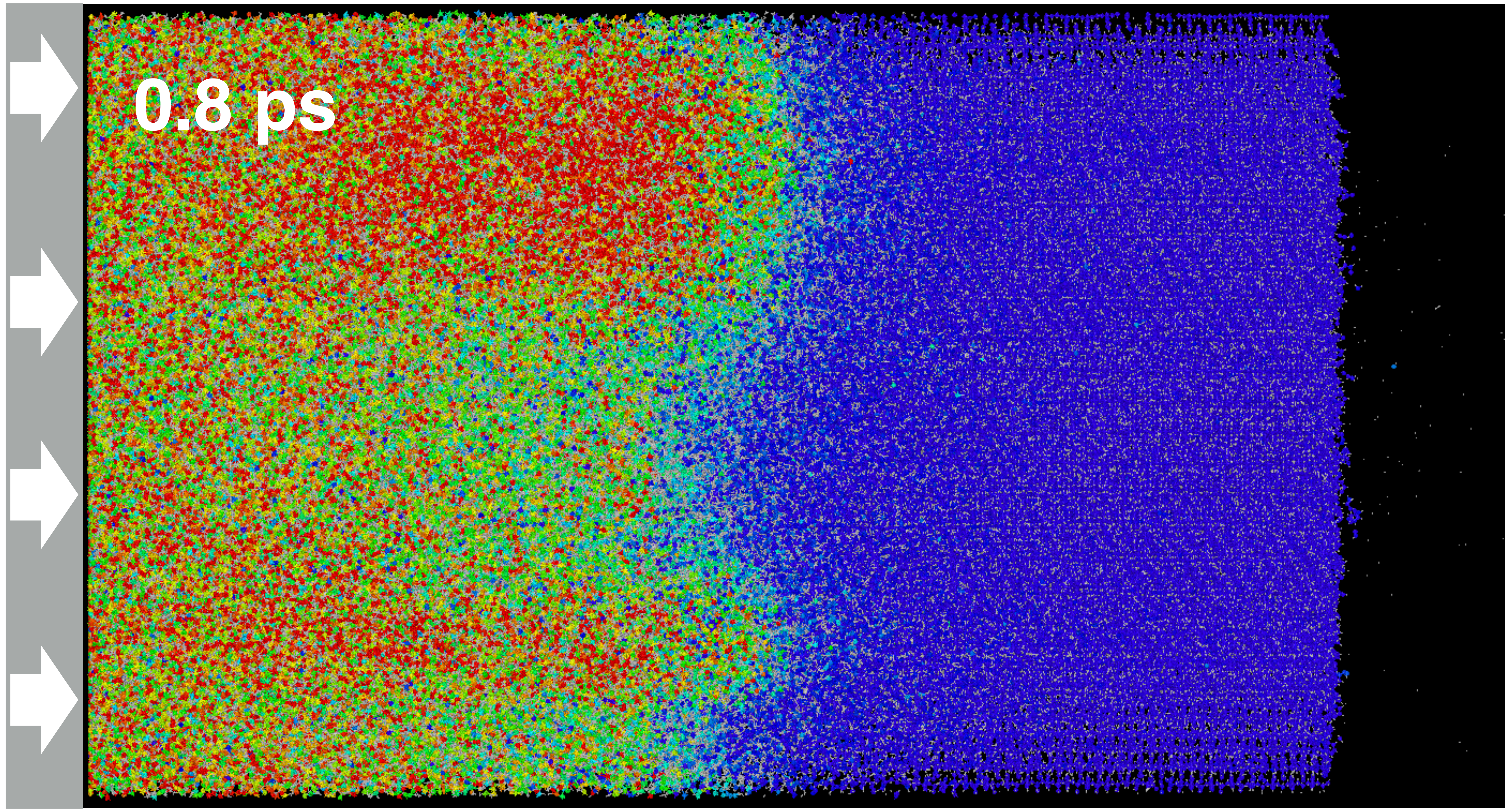



0 25 50

$V_z^{Carbon}$ (km/s)

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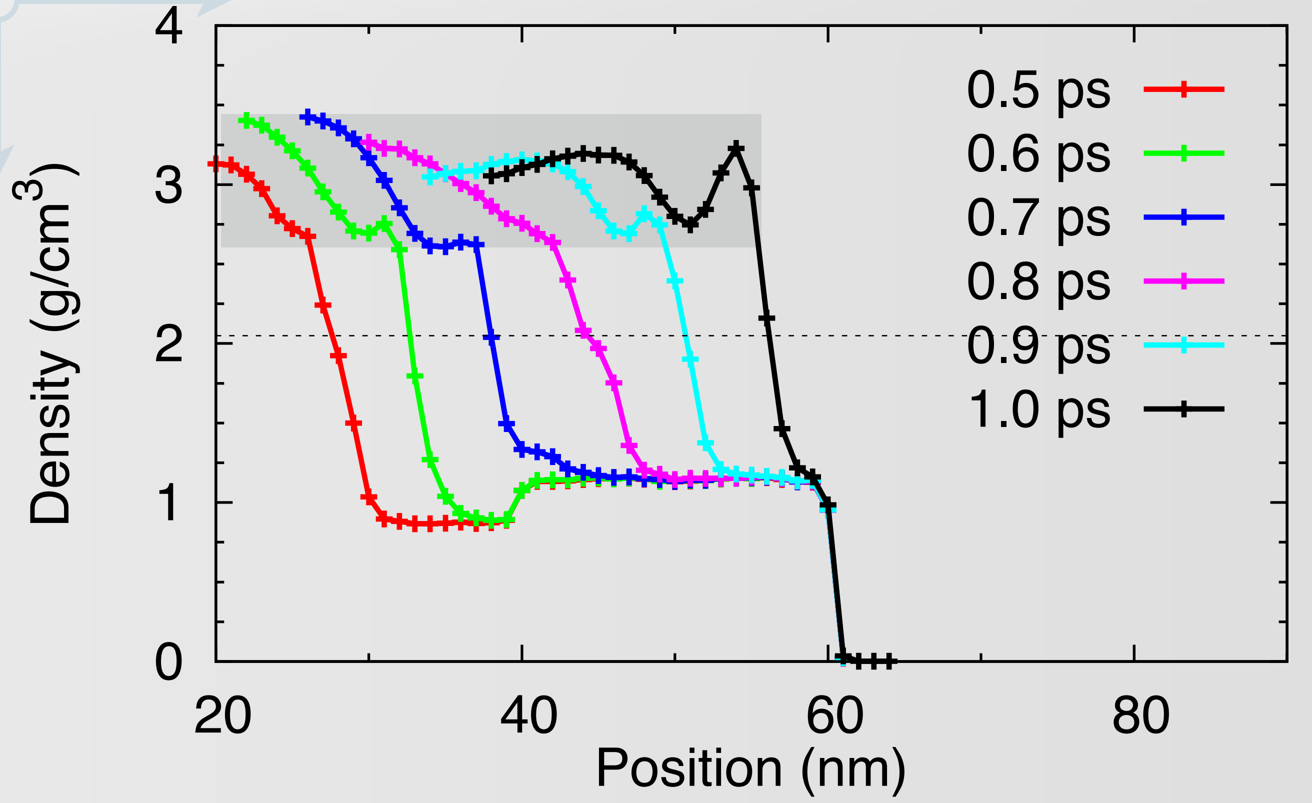


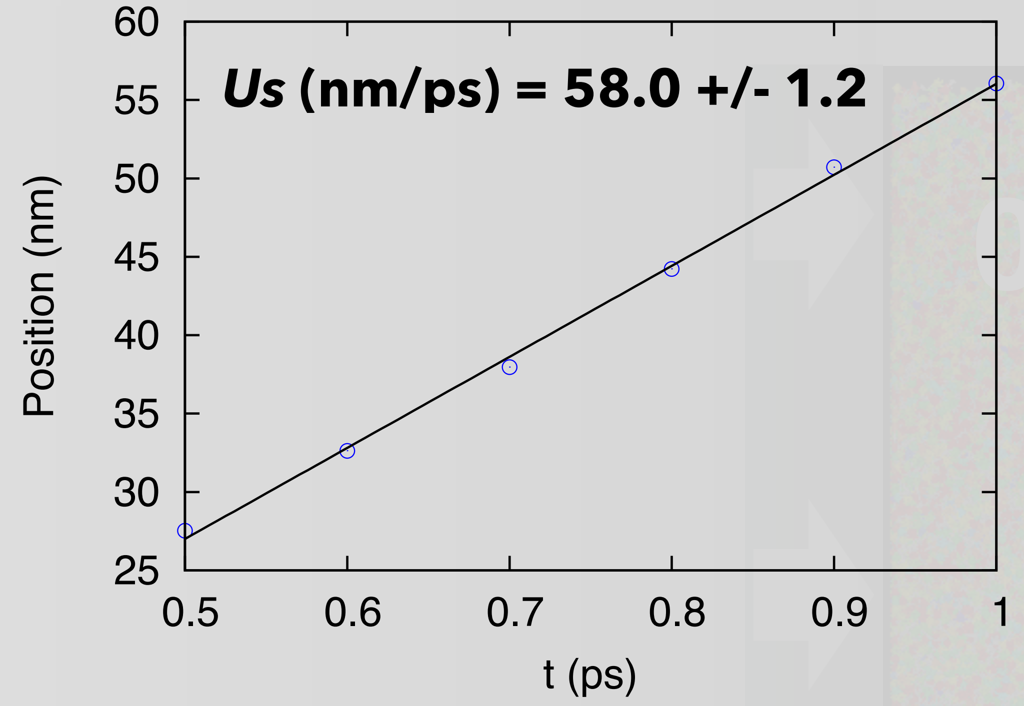


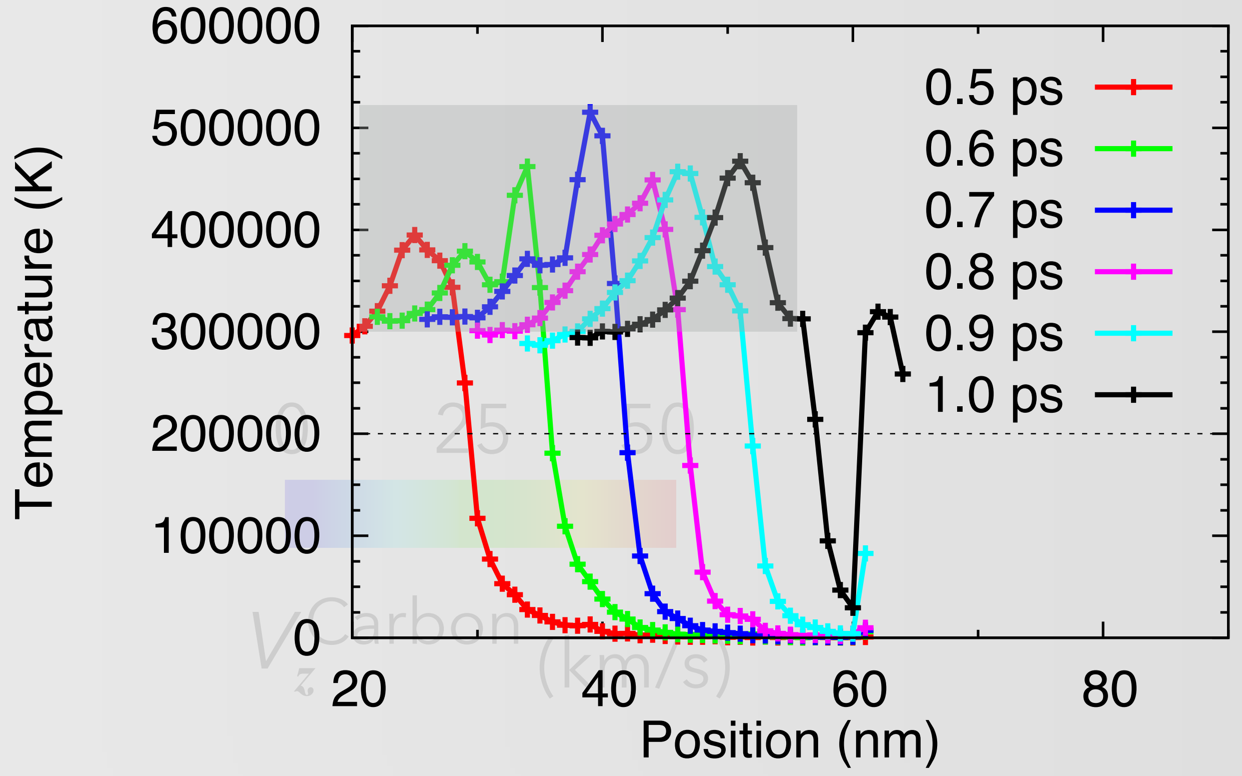


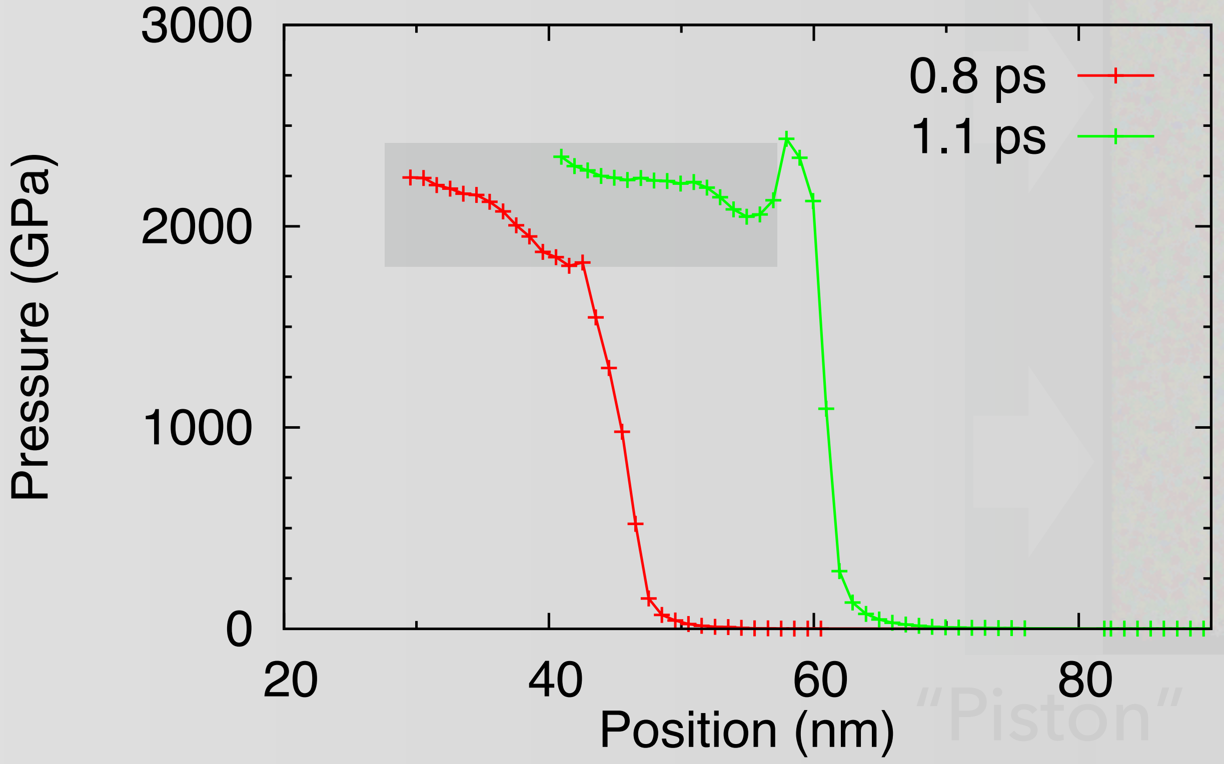


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| CMD | 58.0 ± 1.2 | 3.0 ± 0.42 | 2022 ± 222 | 1.54 ± 0.36 |

* According to a DFT-based average-atom model for ionization‡, <Z>=1.45 at this temperature and density.

‡S. X. Hu et al., Phys. Plasmas 23, 042704 (2016).

# Hugoniot EOS from CMD agrees with DFT-MD to within 3%–20%

- Results are similar from calculations of samples with different density, structure, shock direction, and sizes and simulations with different time steps
- Results are overall similar when using AIREBO or REBO2 potentials

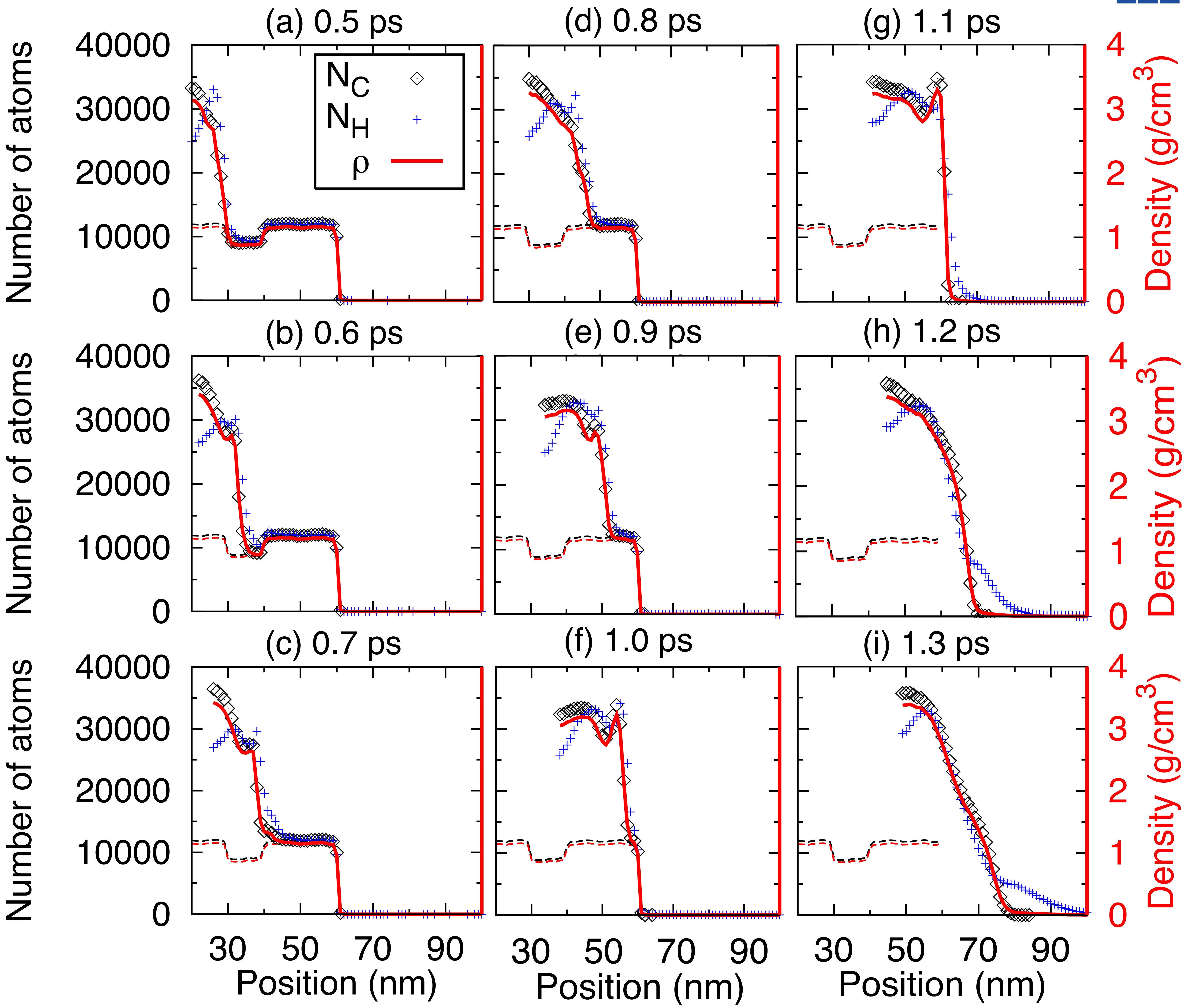
| | $u_p$ (km/s) | $u_s$ (km/s) | $\rho$ (g/cm$^3$) | $T$ ($\times 10^5$ K) | $P$ (GPa) |
|---|---|---|---|---|---|
| $\rho_0$=0.77 g/cm$^3$ | | | | | |
| DFT | 38 | 51.4 | 2.96 | 1.470 | 1503 |
| CMD[a] | 38 | $54.1 \pm 0.20$ | $2.57 \pm 0.03$ | $1.36 \pm 0.01$ | $1633 \pm 18$ |
| $\rho_0$=1.29 g/cm$^3$ | | | | | |
| DFT | 38 | 53.2 | 4.50 | 1.483 | 2602 |
| CMD[b] | 38 | $58.2 \pm 0.15$ | $3.69 \pm 0.03$ | $1.19 \pm 0.03$ | $2878 \pm 20$ |
| CMD[c] | 38 | $58.4 \pm 0.15$ | $3.71 \pm 0.04$ | $1.19 \pm 0.02$ | $2876 \pm 24$ |
| CMD[d] | 38 | $56.5 \pm 0.78$ | $3.80 \pm 0.15$ | $1.27 \pm 0.07$ | $2855 \pm 35$ |
| CMD[e] | 38 | $56.4 \pm 0.20$ | $3.78 \pm 0.16$ | $1.30 \pm 0.09$ | $2796 \pm 55$ |
| $\rho_0$=1.31 g/cm$^3$ | | | | | |
| DFT | 38 | 53.3 | 4.56 | 1.484 | 2651 |
| CMD[f] | 38 | $58.3 \pm 0.03$ | $3.75 \pm 0.03$ | $1.19 \pm 0.02$ | $2928 \pm 24$ |
| CMD[g] | 38 | $58.1 \pm 0.16$ | $3.81 \pm 0.02$ | $1.18 \pm 0.02$ | $2904 \pm 48$ |
| CMD[h] | 38 | $57.2 \pm 0.00$ | $3.86 \pm 0.13$ | $1.19 \pm 0.01$ | $2882 \pm 45$ |
| $\rho_0$=1.05 g/cm$^3$ | | | | | |
| DFT | 38 | 52.5 | 3.80 | 1.492 | 2096 |
| CMD[i] | 38 | $58.0 \pm 1.2$ | $3.02 \pm 0.42$ | $1.54 \pm 0.36$ | $2022 \pm 222$ |
| CMD[j] | 38 | $57.0 \pm 0.7$ | $3.04 \pm 0.38$ | $1.51 \pm 0.43$ | $2290 \pm 324$ |
| CMD[k] | 38 | $57.9 \pm 1.4$ | $3.03 \pm 0.42$ | $1.51 \pm 0.36$ | $2222 \pm 246$ |
| CMD-REBO2[i] | 38 | $57.7 \pm 1.1$ | $2.99 \pm 0.35$ | $1.32 \pm 0.12$ | $2050 \pm 360$ |
| CMD-AIREBO[i] | 38 | $59.2 \pm 1.8$ | $3.28 \pm 0.48$ | $1.37 \pm 0.18$ | $2300 \pm 202$ |

Overall differences (relative to DFT-MD):
~14% in shock velocity
12%–20% in density
7%–20% in temperature
3%–10% in pressure

[a] Amorphous polystyrene (PS). 1.35 million atoms.
[b] Syndiotactic (Synd.) PS. 1.47 million atoms. Shock ⊥ chain.
[c] Synd. PS. 3.69 million atoms. Shock || chain.
[d] Synd. PS. 61.44 thousand atoms. Shock || chain.
[e] Synd. PS. 61.44 thousand atoms. Shock ⊥ chain.
[f] Isotactic (Isot.) PS. 1.73 million atoms. Shock || chain.
[g] Isot. PS. 4.15 million atoms. Shock ⊥ chain.
[h] Isot. PS. 86.4 thousand atoms. Shock ⊥ chain.
[i] Synd. PS with voids. 1.35 million atoms. Shock || chain.
[j] Synd. PS with voids. 2.70 million atoms. Shock || chain.
[k] Synd. PS with voids. 1.35 million atoms. Shock || chain. Time step 0.005 fs.

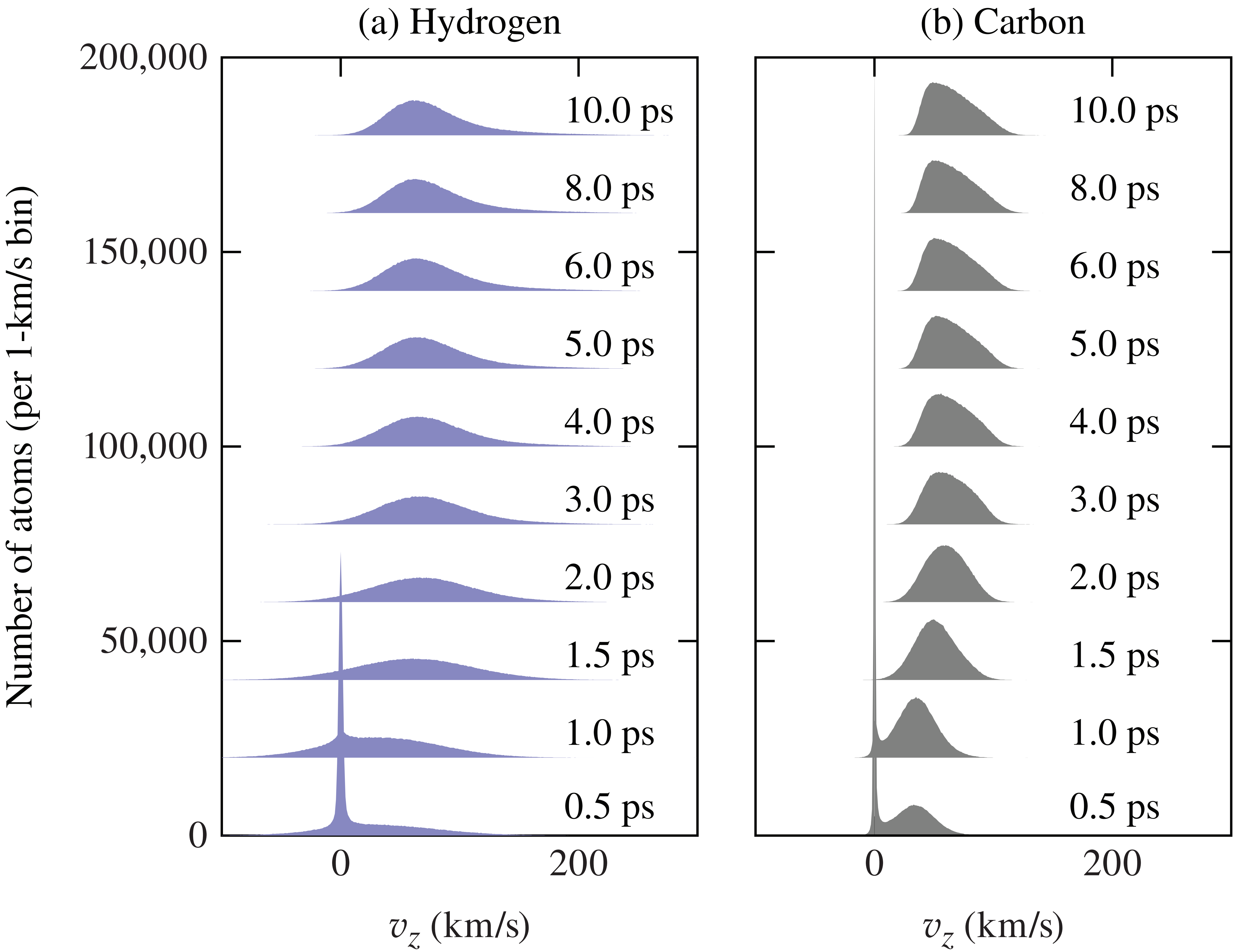
# Atomic distribution and density profiles around shock breakout

- Three-stage feature before shock breakout (at 1.1 ps)
- Less hydrogen than carbon next to the piston
- More hydrogen than carbon at the shock front (more so at the void), and in released CH after shock breakout

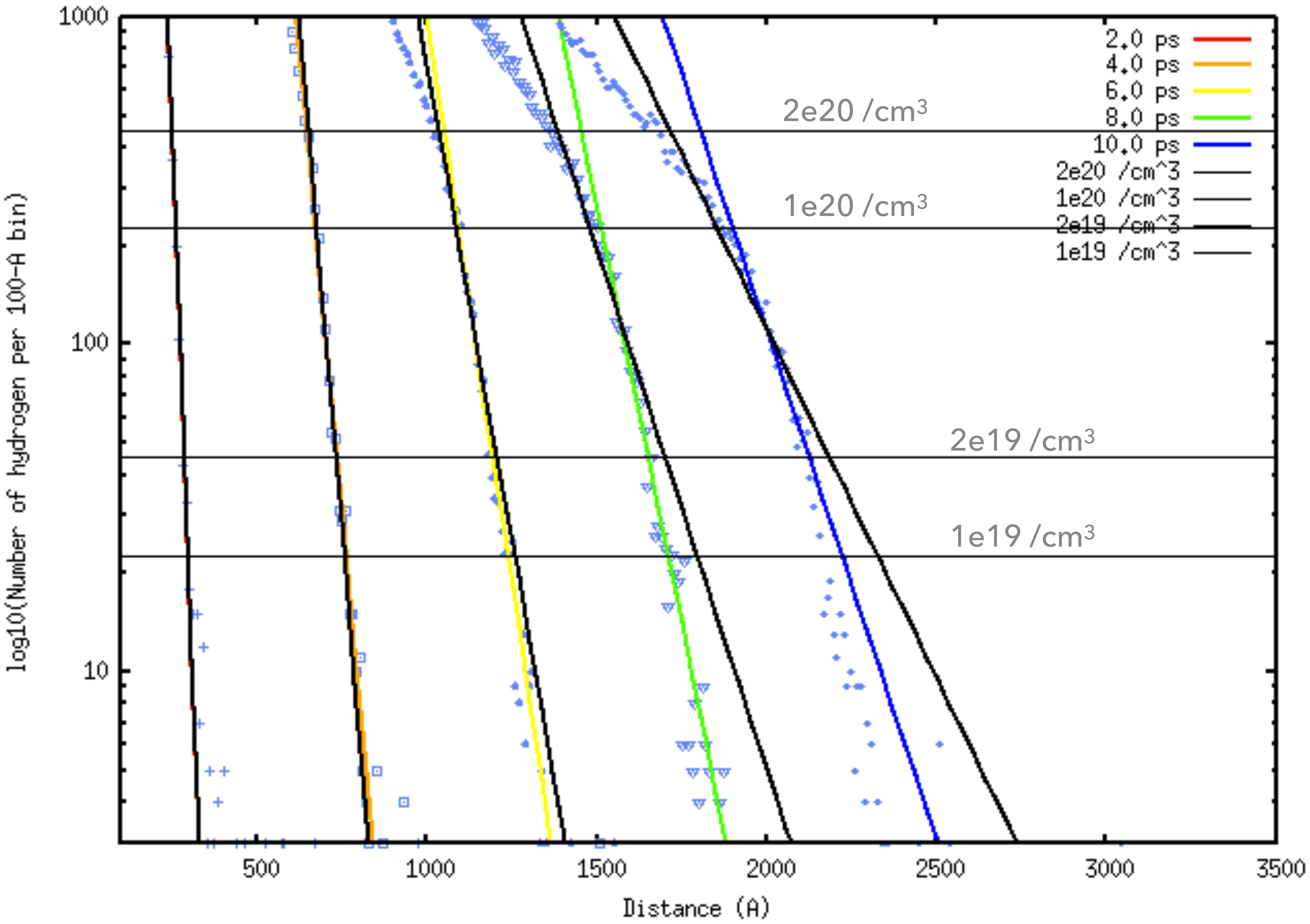


# *Velocity distributions of carbon in comparison to hydrogen*

- Before shock breakout, both C and H follow the Maxwell–Boltzmann distribution (broadness characterized by $m/2k_BT$, centered at $U$p)
- H profiles broader than C
- Peak velocity increases after shock breakout
- Distribution stabilizes to non-Maxwell after 2 ps



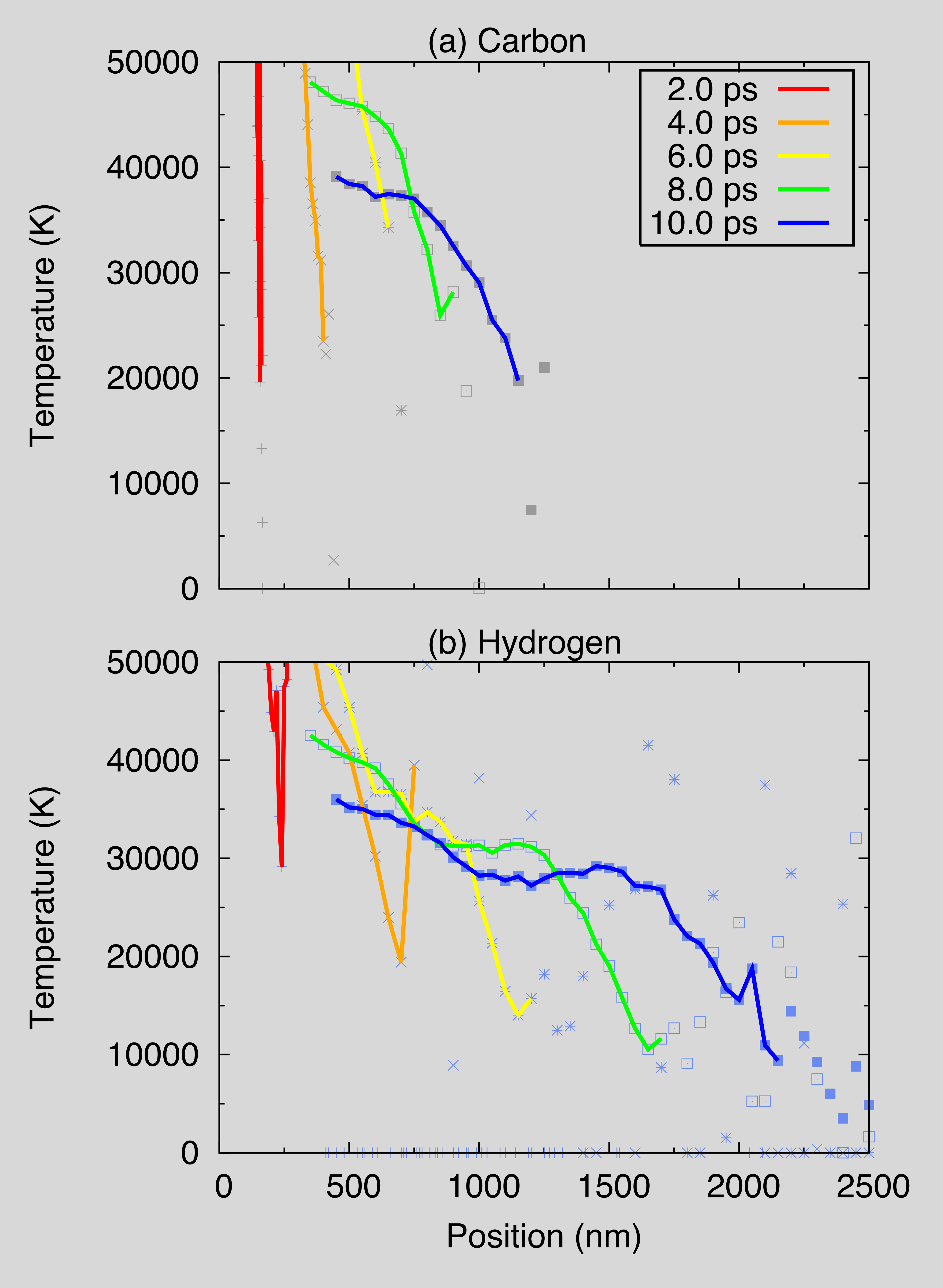

# Sensitivity of scale length to range of exponential fitting

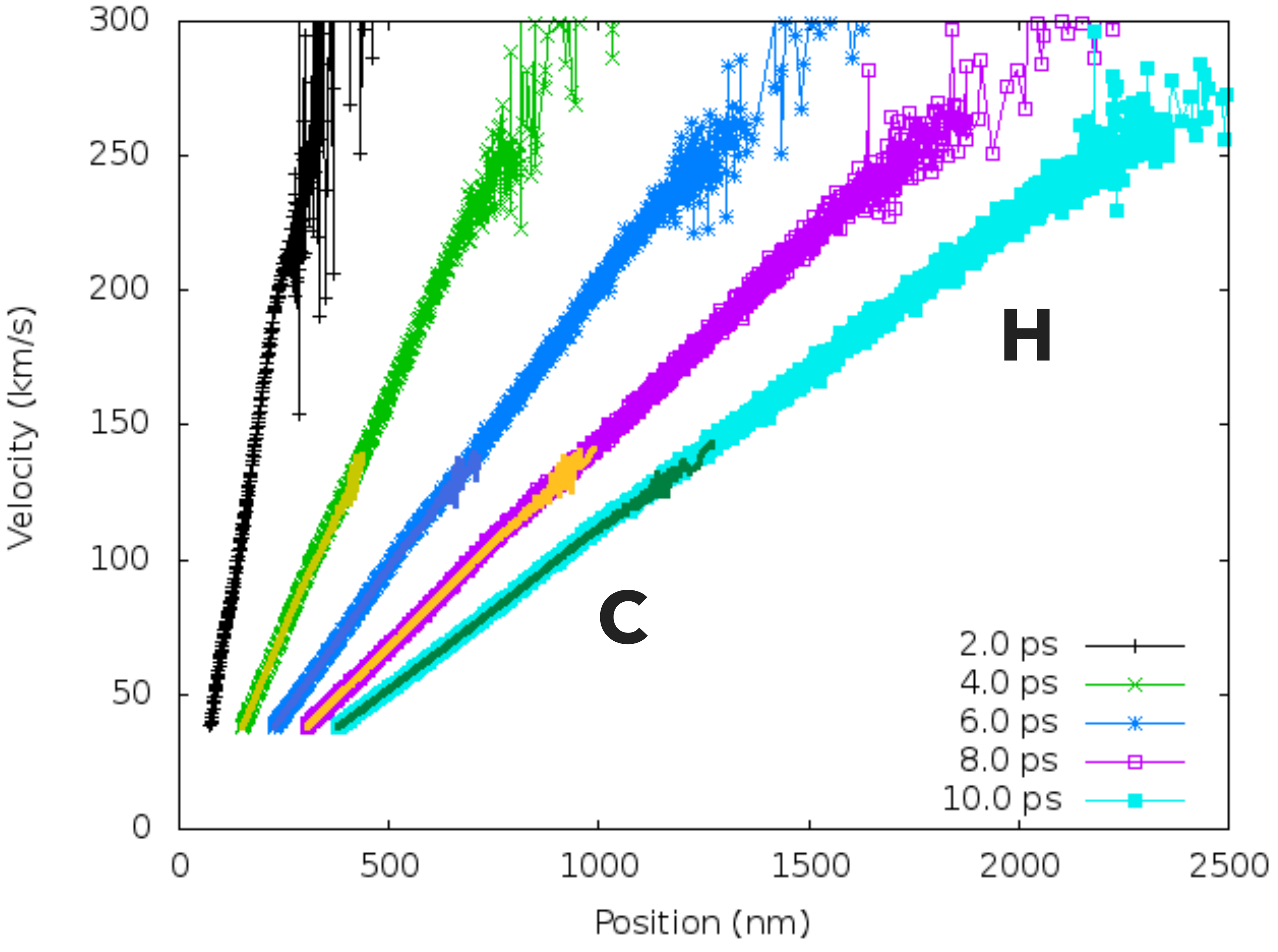



$$n_e = n_0 e^{-z/s}$$

- Slope prop to -1/*s*

# Temperature and velocity profiles of released CH



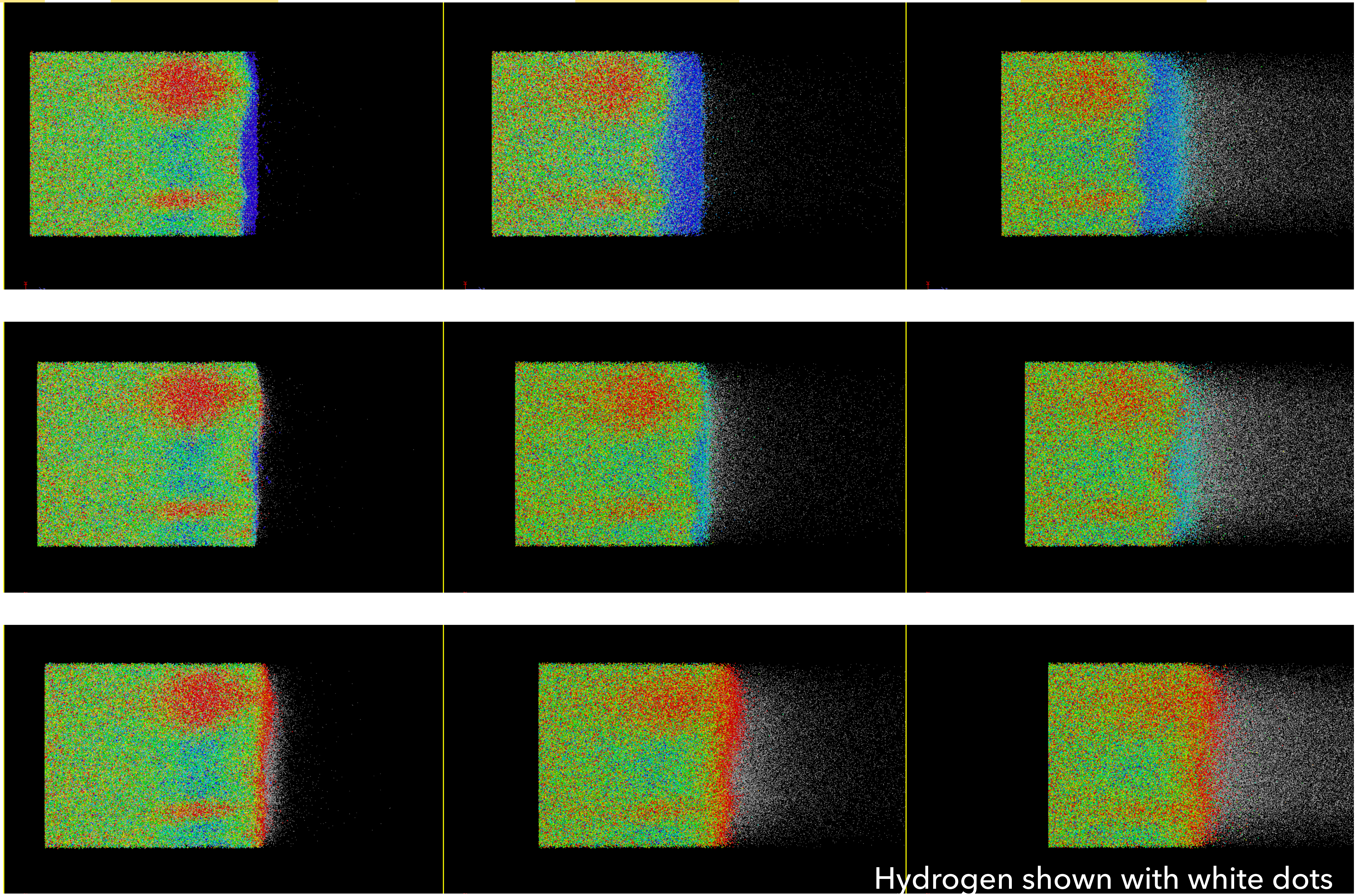
# *Hydrogen streaming disappears under weak shock (<5.9 Mbar)*

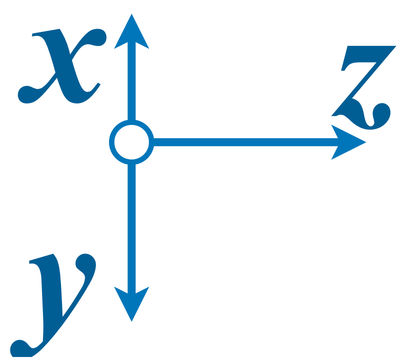
| | | | |
|---|---|---|---|
| Piston Velocity (*Up*) | 20 km/s | 50 km/s | 100 km/s |
| Hugoniot Pressure | 5.9 Mbar | 34 Mbar | 132 Mbar |

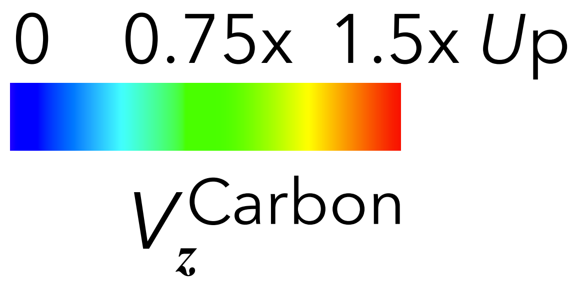
Before shock breakout

Shock breakout

After shock breakout



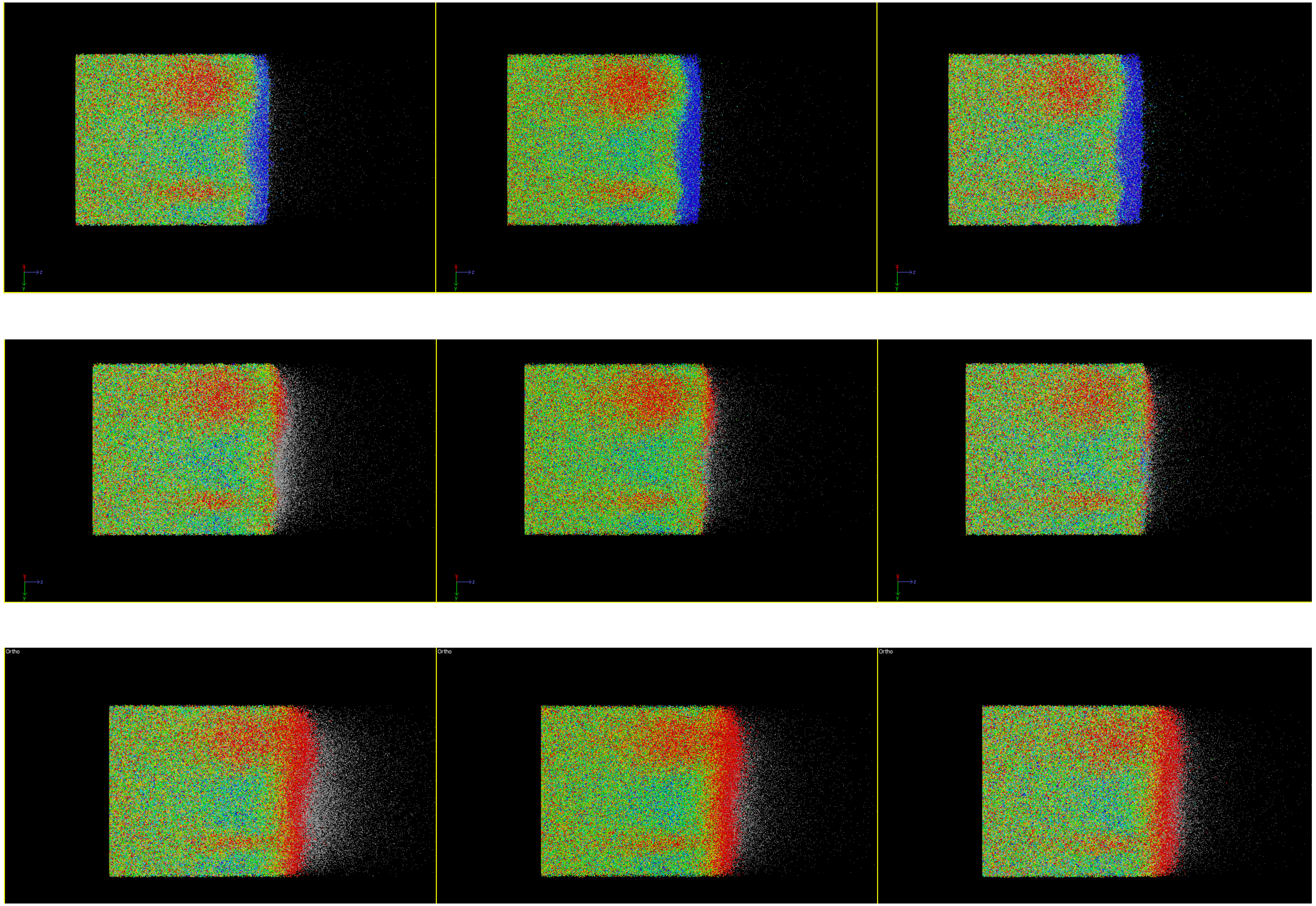



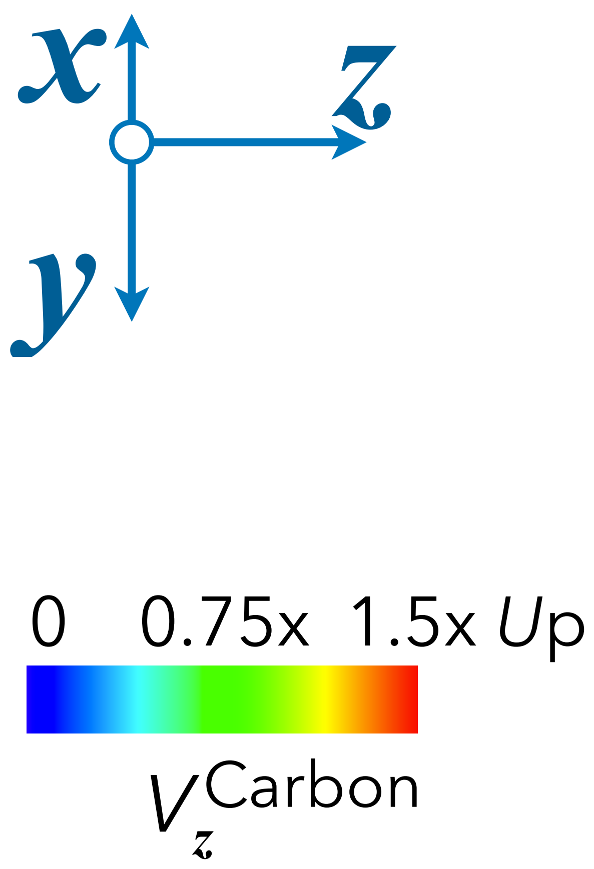



# *Heavier hydrogen isotope shows weaker streaming upon shock release*

**Piston Velocity**
***Up*=38 km/s**

| | **CH** | **CD** | **CT** |
|---|---|---|---|
| Before shock breakout | | | |
| Shock breakout | | | |
| After shock breakout | | | |






Hydrogen shown with white dots