Application of First Principles Langiven Molecular Dynamics to Hot Dense Plasmas

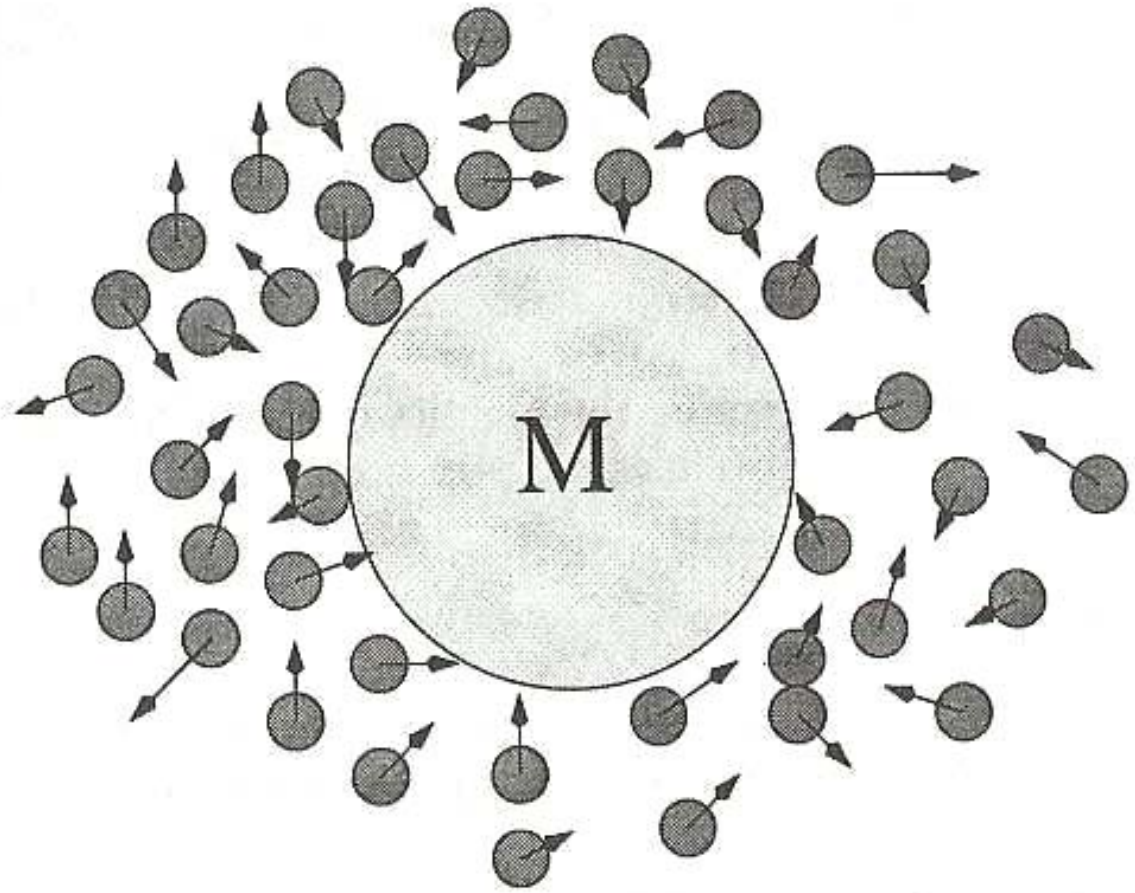
Jianmin Yuan
Department of Physics, National University of Defense Technology
Changsha 410073, China

Workshop: Computational Challenges in Hot Dense Plasmas
March 29, 2012, IPAM,UCLA

Outline

- **Introduction**
- **Quantum Langevin Molecular Dynamics (QLMD)**
- **Applications**
  - **Electronic structure and EOS of Iron**
  - **Electric and thermo conductivity**
  - **Carbon embedded in dense hydrogen**
  - **EOS of solar materials**
  - **EOS of D, T and the mixture**
- **Conclusion**

Brownian Motion: Langevin Equation



A large Brownian particle with mass M immersed in a fluid of much smaller and lighter particles.

Brownian Motion: Langevin Equation

According to Einstein's theory, the diffusion constant

$$D = \frac{RT}{N_A 6\pi\eta a} = \frac{k_B T}{6\pi\eta a}$$

According Newton's law

$$m\frac{d\vec{v}(t)}{dt} = \vec{F}(t)$$

$$\frac{d\vec{x}(t)}{dt} = \vec{v}(t)$$

Langevin Equation

$$\frac{d\vec{v}(t)}{dt} = -\frac{\gamma}{m}\vec{v}(t) + \frac{1}{m}\vec{\xi}(t)$$

$$\frac{d\vec{v}(t)}{dt} = -\frac{\gamma}{m}\vec{v}(t)$$

and

$$\vec{v}(t) = e^{-t/\tau_B}\vec{v}(0)$$

$$\tau_B = \frac{m}{\gamma}$$

$$\left\langle \vec{\xi}(t) \right\rangle_\xi = 0, \quad \left\langle \vec{\xi}(t_1)\vec{\xi}(t_2) \right\rangle_\xi = g\delta(t_1 - t_2)$$

$$\vec{v}(t) = e^{-t/\tau_B}\vec{v}(0) + \frac{1}{m}\int_0^t ds e^{-(t-s)/\tau_B}\vec{\xi}(s)$$

Brownian Motion: Langevin Equation

For a Gaussian Process

$$\left\langle \left\langle v^2(t) \right\rangle_\xi \right\rangle_{eq} = \left[\left\langle v_0^2 \right\rangle_{eq} - \frac{g\tau_B}{2m^2} \right] e^{-2t/\tau_B} + \frac{g\tau_B}{2m^2}$$

$$g = \frac{2mk_BT}{\tau_B} = 2\gamma k_BT$$

Fluctuation-Dissipation (Langevin) Theorem: The equilibrium is brought about by a dissipation force ("friction") between the particle and the bath. It is the same process that produces the random, fluctuating force on the particle. Both processes are uniquely determined by the statistical nature of the microscopic forces .

Classical Independent Oscillator Model

See: P. Hänggi, Lecture Notes in Physics 484, 15-22 (1997)

$$H = \frac{p^2}{2M} + U(x) + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{m_j \omega_j^2}{2} \left(x_j - (\alpha) x \right)^2 \right]$$

According to Hamilton Equation:

$$M\dot{x} = p \qquad\qquad m_j \dot{x}_j = p_j$$

$$\dot{p} = -\frac{\partial U(x)}{\partial x} + \sum_j m_j \omega_j^2 (x_j - x) \qquad\qquad \dot{p}_j = -m_j \omega_j^2 (x_j - x)$$

$$x_j(t) = x_j(t_0)\cos[\omega_j(t-t_0)] + \frac{p_j(t_0)}{m_j \omega_j}\sin[\omega_j(t-t_0)]$$

$$+ \omega_j \int_{t_0}^{t} ds \sin[\omega_j(t-s)]\, x(s).$$

Classical Independent Oscillator Model

$$M\ddot{x} = -\frac{\partial U(x)}{\partial x} - M\int_{t_0}^{t} ds\gamma(t-s)\dot{x}(s) - M\gamma(t-t_0)x(t_0) + F(t)$$

$$\gamma(t-s) = \frac{(\alpha^2)1}{M}\sum_j m_j\omega_j^2\cos[\omega_j(t-s)]$$

$$F(t) = (\alpha)\sum_j m_j\omega_j^2\left[x_j(t_0)\cos[\omega_j(t-t_0)] + \frac{p_j(t_0)}{m_j\omega_j}\sin[\omega_j(t-t_0)]\right]$$

$$\left\langle F(t)\right\rangle_{\rho_B} = 0$$

$$\left\langle F(t)F(s)\right\rangle_{\rho_B} = MkT\gamma(t-s)$$

$$\rho_B = Z^{-1}\exp\left\{-\beta\left[\sum_j\left(\frac{p_j^2}{2m_j} + \frac{m_j\omega_j^2}{2}x_j^2\right)\right]\right\}$$

Classical Independent Oscillator Model

$$\xi(t) \equiv F(t) - M\gamma(t-t_0)x(t_0)$$

$$= (\alpha)\sum_j \left[\left(x_j(t_0) - (\alpha)x(t_0) \right) \cos[\omega_j(t-t_0)] + \frac{p_j(t_0)}{m_j\omega_j} \sin[\omega_j(t-t_0)] \right]$$

$$\hat{\rho}(\{p_j, x_j\} \mid x(t_0) = x)$$

$$= Z^{-1} \exp\left\{ -\beta \left[\sum_j \left(\frac{p_j^2}{2m_j^2} + \frac{m_j\omega_j^2}{2} \left(x_j - (\alpha)x \right)^2 \right) \right] \right\}$$

$$\left\langle \xi(t) \right\rangle_{\hat{\rho}} = 0$$

$$\left\langle \xi(t)\xi(s) \right\rangle_{\hat{\rho}} = \left\langle \xi(t-s+t_0)\xi(t_0) \right\rangle_{\hat{\rho}} = MkT\gamma(t-s)$$

Classical Independent Oscillator Model

$$M\frac{d\vec{v}}{dt} = U'(x) - \int_{-\infty}^{t} ds[\gamma(t-s)\vec{v}(s)] + \vec{\xi}(t)$$

When the bath has dense infinite spectra distribution, with random phase approximation one has

$$\gamma(t-s) = \gamma\delta(t-s)$$

$$-\int_{-\infty}^{t} ds[\gamma(t-s)\vec{v}(s)] \to -\gamma\vec{v}(t)$$

$$M\frac{d\vec{v}}{dt} = U'(x) - \gamma\vec{v}(t) + \vec{\xi}(t)$$

Quantum corresponding Eqs. can also be obtained in Heisenberg picture [see for example: Ford and Kac, J. Stat. Phys. 46, 803(1987)]

Open Quantum System-Wavefunction

P. Gaspard and M. Nagaoka,J. Chem. Phys. 111 (1999) 5676-5690

Partitioning into system and environment

$$\hat{H}(t) = \hat{H}_S(t) \otimes \hat{I}_B + \hat{I}_S \otimes \hat{H}_B(t) + \alpha \hat{H}_{SB}(t)$$

$$\hat{H}_{SB}(t) = \sum_{j=1}^{m} \hat{S}_j(t) \otimes \hat{B}_j(t)$$

$$i\frac{d}{dt}\left|\Psi(t)\right\rangle = \hat{H}(t)\left|\Psi(t)\right\rangle$$

$$\hat{P}_q = \hat{I}_S \otimes \left|\varphi_{B,q}\right\rangle\left\langle\varphi_{B,q}\right|$$

$$\hat{H}_B \varphi_{B,n}(\vec{x}_B) = \varepsilon_n \varphi_{B,n}(\vec{x}_B)$$

$$\hat{Q}_q = \hat{I}_S \otimes \sum_{p \neq q} \left|\varphi_{B,p}\right\rangle\left\langle\varphi_{B,p}\right|$$

$$\Psi(\vec{x}_S, \vec{x}_B, t) = \sum_q \psi_{S,q}(\vec{x}_S, t)\varphi_{B,q}(\vec{x}_B)$$

Open Quantum System-Wavefunction

$$\hat{P}_q \Psi(\vec{x}_S, \vec{x}_B, t) = \psi_{S,q}(\vec{x}_S, t)\varphi_{B,q}(\vec{x}_B)$$

$$\hat{Q}_q \Psi(\vec{x}_S, \vec{x}_B, 0) = \sum_{p \neq q} \psi_{S,p}(\vec{x}_S, 0)\varphi_{B,p}(\vec{x}_B)$$

$$i\partial_t \psi_{S,q}(\vec{x}_S, t) = \hat{H}_S \psi_{S,q}(\vec{x}_S, t) + \overbrace{\hat{P}_q \hat{H} \hat{Q}_q e^{-i\hat{Q}_q \hat{H} \hat{Q}_q t} \hat{Q}_q \Psi(0)}^{F(\vec{x}_S, t, 0)}$$

$$-i\int_0^t \overbrace{\hat{P}_q \hat{H} \hat{Q}_q e^{-i\hat{Q}_q \hat{H} \hat{Q}_q (t-\tau)} \hat{Q}_q \hat{H} \hat{P}_q}^{\hat{\gamma}(t-\tau)} \psi_{S,q}(\vec{x}_S, \tau) d\tau$$

Open Quantum System-Wavefunction

By making an expansion about α and summing over the thermo distributed bath and system initial states:

$$i\partial_t \psi_S(t) = \hat{H}_S \psi_S(t) + \alpha \sum_q l_q(t) \hat{S}_q \psi_S(t)$$

$$-i\alpha^2 \sum_{pq} C_{pq}(t-\tau) \hat{S}_p^+ e^{-i\hat{H}_S(t-\tau)} \hat{S}_q \psi_S(\tau) d\tau + o(\alpha^3)$$

$$\overline{l_p(t) l_q(t')} = 0,$$

$$\overline{l_p^*(t) l_q(t')} = C_{pq}(t-t')$$

For Markovin $\overline{l_p^*(t) l_q(t)} \propto \delta_{pq} \delta(t-t')$

$$i\partial_t \psi_S(t) = \hat{H}_S \psi_S(t) + \alpha \sum_q l_q(t) \hat{S}_q \psi_S(t) - \frac{i\alpha^2}{2} \sum_{pq} \hat{S}_q^+ \hat{S}_q \psi_S(\tau) + o(\alpha^3)$$

Application in a Variety of Problem

Nuclear magnetic resonance spectroscopy

P. W. Anderson: J. Phys. Soc. Jpn. 9 (1954) 316.
R. Kubo: J. Phys. Soc. Jpn. 9 (1954) 935.
R. Kubo: in Fluctuation, Relaxation, and Resonance in Magnetic Systems, ed. D. TerHaar (Oliver and Boyd, Edinburgh, 1962) p. 23.
Yoshitaka TANIMURA, J. Phys. Soc. Jpn. 75 (2006) 082001

In the fast modulation limit:

$$\gamma >> \Delta, \qquad \gamma' = \Delta^2 / \gamma$$

$$\hat{H}_I = \Delta \Omega(t) \hat{S}$$

$$\langle \Omega(t)\Omega(0) \rangle = \exp[-\gamma |t|]$$

$$I(\omega) = \frac{2\gamma'}{\gamma'^2 + (\omega - \omega_0)^2}$$

In the slow modulation limit:

$$\gamma << \Delta$$

$$I(\omega) = \frac{2\sqrt{2}}{\Delta} \exp\left[-\frac{(\omega - \omega_0)^2}{2\Delta^2} \right]$$

Application in a Variety of Problem

Stochastic Current Density Functional Theory, and *Stochastic Quantum Molecular Dynamics*

M DiVentra and D'Agosta PRL **98,** 226403 (2007)
H Appel and Di Ventra, PRB **80**, 212303 2009;
Chem. Phys. 391, 27(2011)

Dynamical adsorption of atoms on the suface

M Evstigneev* and P Reimann, PRB **82**, 224303 2010

Laser cooling and crystallization of electron-ion plasma

A. P. Gavriliuk *et al*, PRE **80**, 056404 2009

Hot dense plasmas

Frank R Graziani *et al*,HEDP **8**, 105(2012)

Introduction: Molecular dynamics

- **Classical molecular dynamics:**
  - **large scale computation**
  - **potential is empirical**
  - **temperature and density effect is complicated**

- **Quantum molecular dynamics**
  - **more accurate for degenerate electrons and ion coupling**
  - **normally for relatively low temperature**
  - **small sizes**

Introduction: Quantum Molecular Dynamics

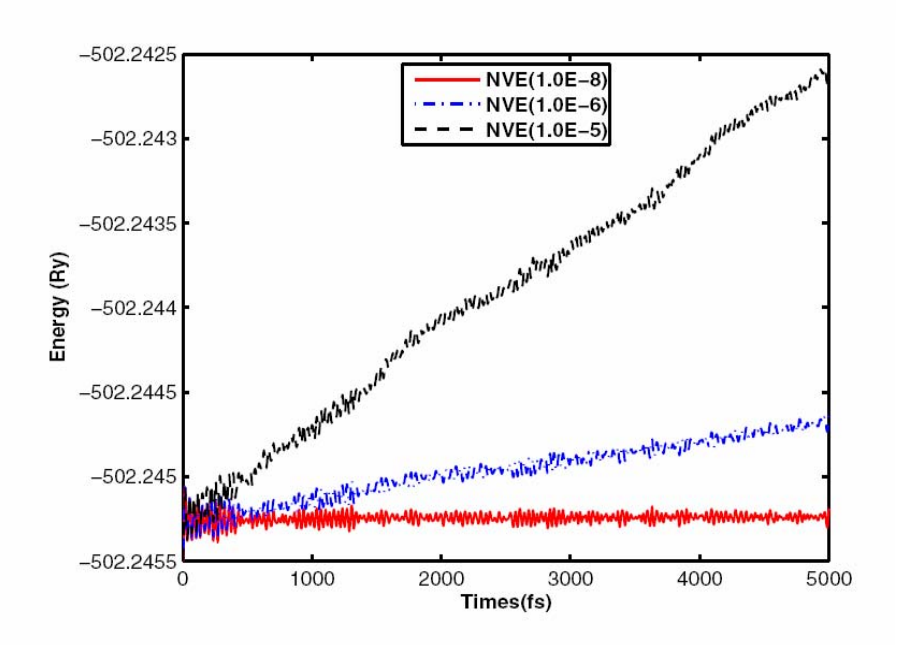
- **QMD:**
  - electrons are described using DFT
  - ions' moving on smooth potential surface is described by Newton's equation
- **Langevin molecular dynamics in condensed matter and material sciences**
  - ions in Langevin equation

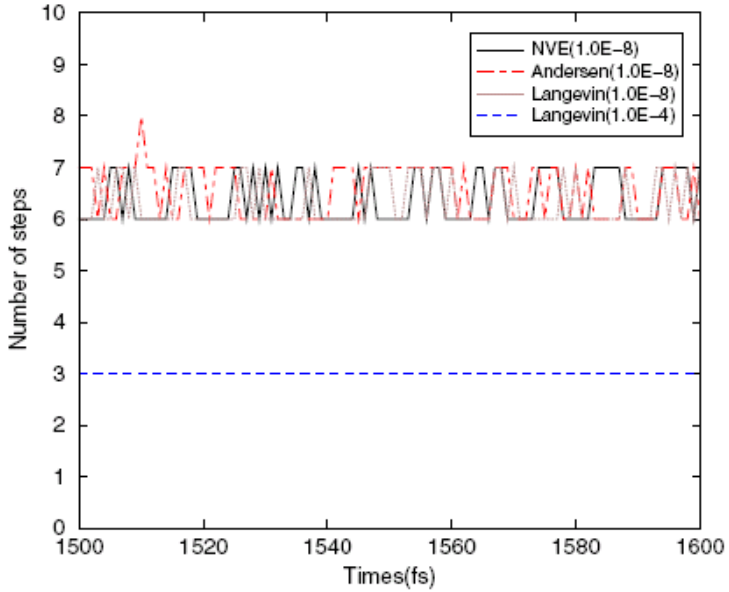
$$M_I \ddot{\mathbf{R}}_I = \mathbf{F} - \gamma_t M_I \dot{\mathbf{R}}_I + \mathbf{N}_I$$

γ_t **represents the contribution of thermostat for controlling the temperature of the system.**

Quantum Langevin Molecular dynamics

- Langevin equation combining DFT can accelerate the calculation of QMD. PRL, 98, 066401 (2007); EPL,88, 20001 (2009)





$$M_I \ddot{\mathbf{R}}_I = \mathbf{F} - (\gamma_t + \gamma_{er}) M_I \dot{\mathbf{R}}_I + \mathbf{N}_I$$

γ_{er} **represents the contribution from numerical error.**

QLMD-normally difficult for high temperatures

- Computational cost
- Partially degenerate electrons to Boltzmann distribution
- Accurate potentials → Full electrons (semi-core states)
- Numerical problems in self-consistent field calculations at high temperature

} Supercomputer

Efficient QMD

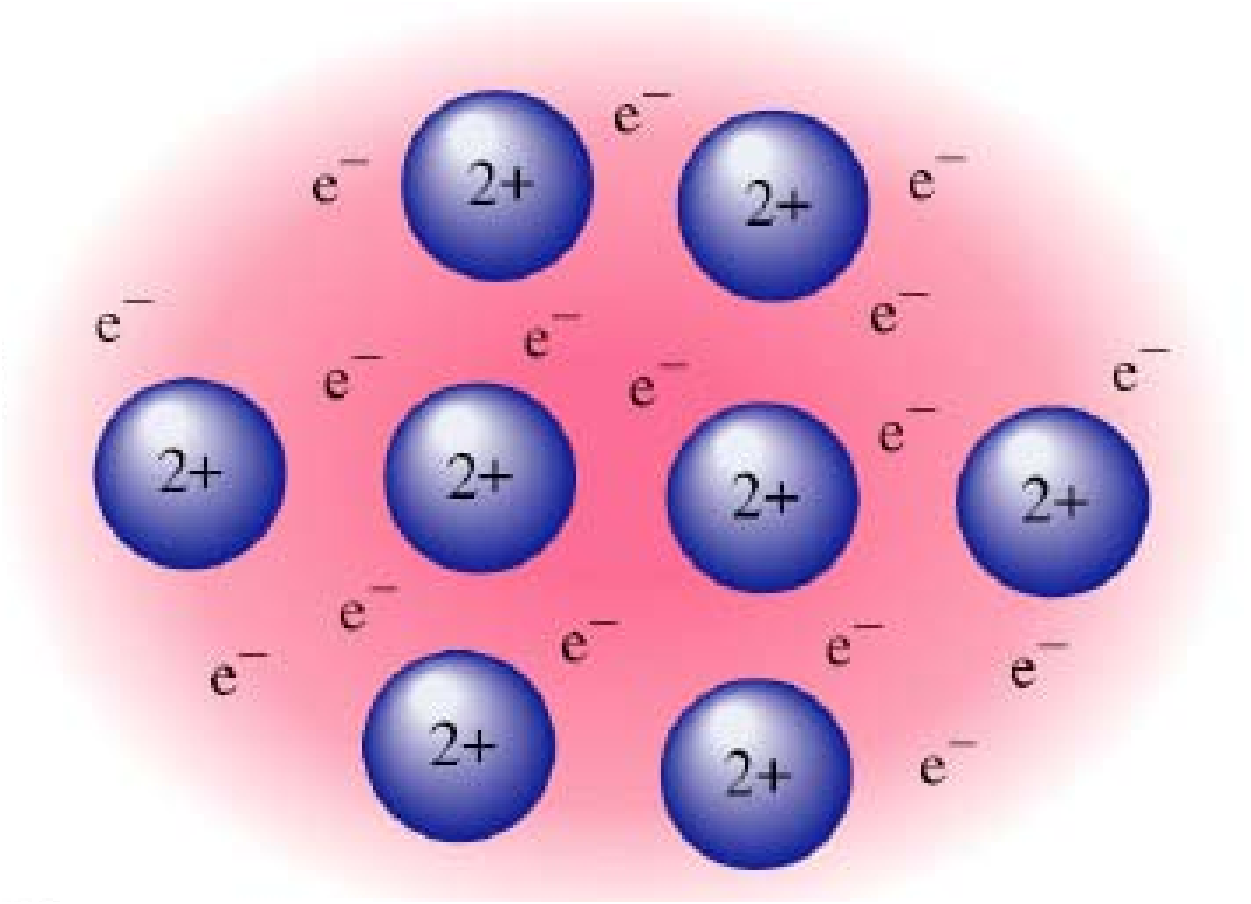
(EPL, 88 (2009) 20001)

↓ The lost physical effects

The electron-ion interactions are central to numerous phenomena

QLMD-extended to Warm (Hot) Dense Matters

Ions in a “Sea of Hot Electrons”



QLMD--Unified first principles model

- Brown motion
- Electron-ion collisions induced frinction (EI-CIF)
- Langevin equation: **Phys. Rev. Lett.** 104: 245001 (2010)

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F} - (\gamma_B + \gamma_t + \gamma_{er}) M_I \dot{\mathbf{R}}_I + \mathbf{N}_I$$

DFT

Friction coefficient

White noise

QLMD

γ_B **represents the electron-ion collisions induced friction (EICIF)**

EI-CIF: $$\gamma_B = 2\pi \frac{m_e}{M_I} Z^* \left(\frac{4\pi n_i}{3} \right)^{1/3} \sqrt{\frac{k_B T}{m_e}} \rightarrow 0.00001 - 0.01 a.u.$$

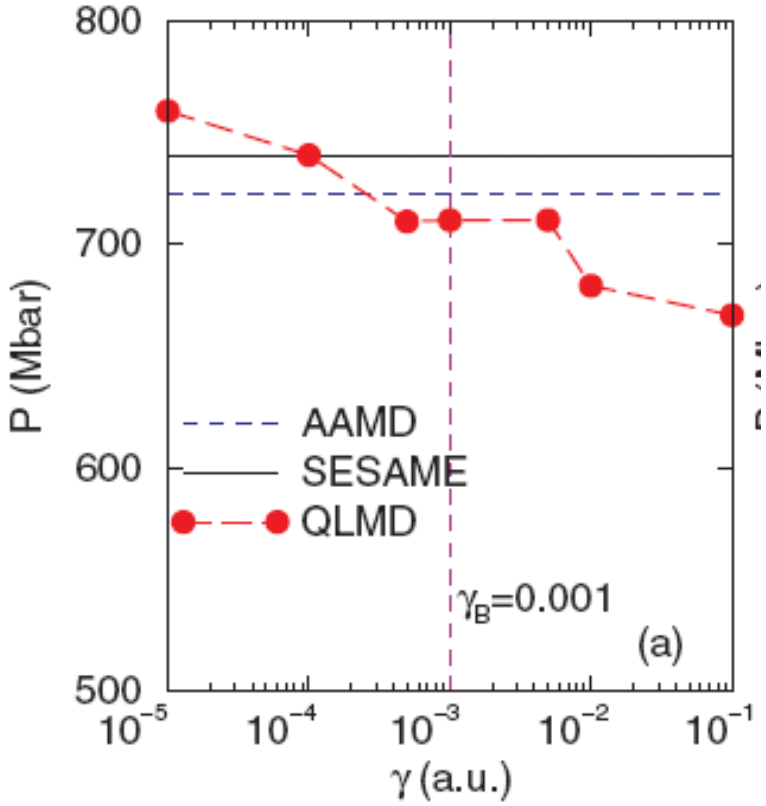
What can we do based on QLMD?

- Electronic structures based on DFT.
- Ionic structures
- Equation of state
- Transport properties for WDM: diffusion, viscosity, conductivity, x-ray absorption, opacity etc.

Electronic structure and EOS of Iron

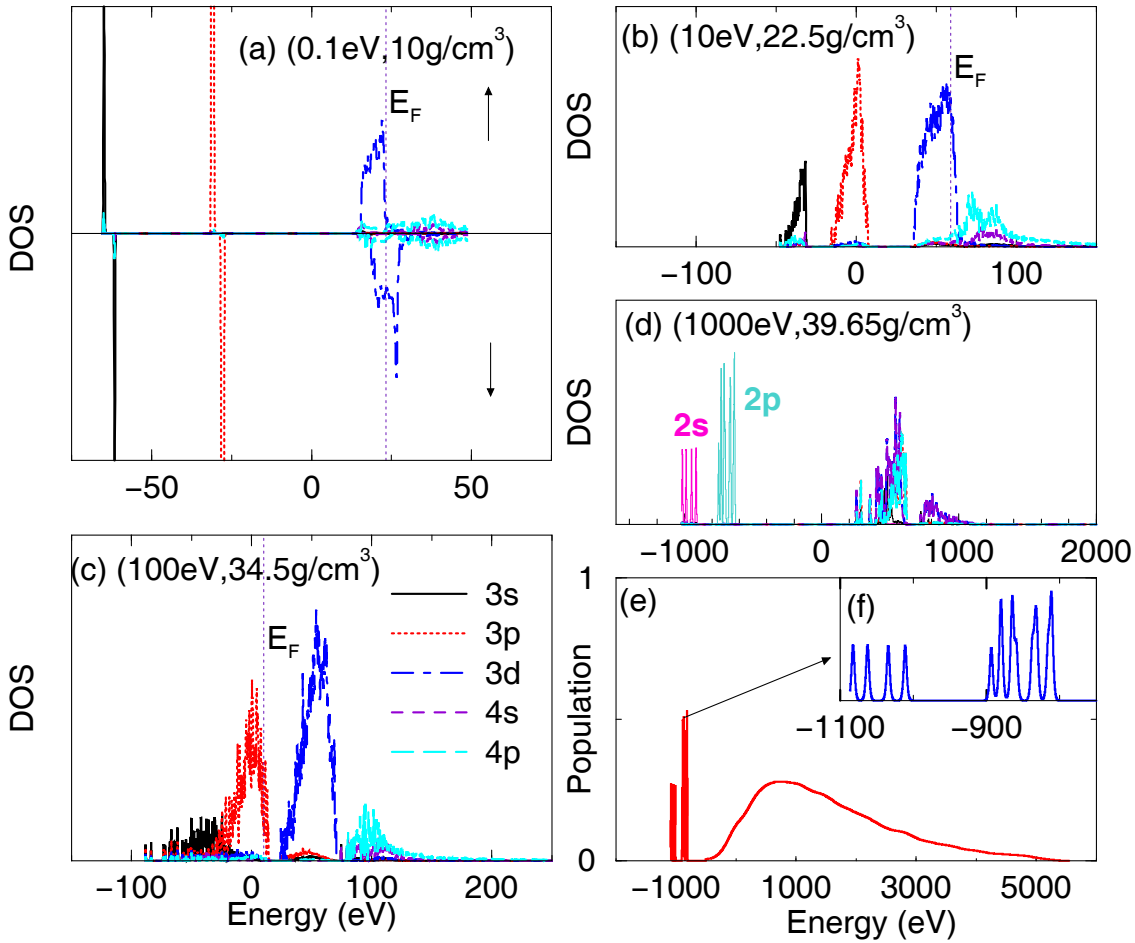
- **Earth core**
- **Hydrodynamical process**
- **DAC (relatively low temperature)**
- **Shock-wave experiments (temperature is difficult to measure)**

EOS of Iron



Influence of γ on pressure for Fe at a temperature of 100 eV.
[Phys. Rev. Lett. **104**: 245001 (2010)]

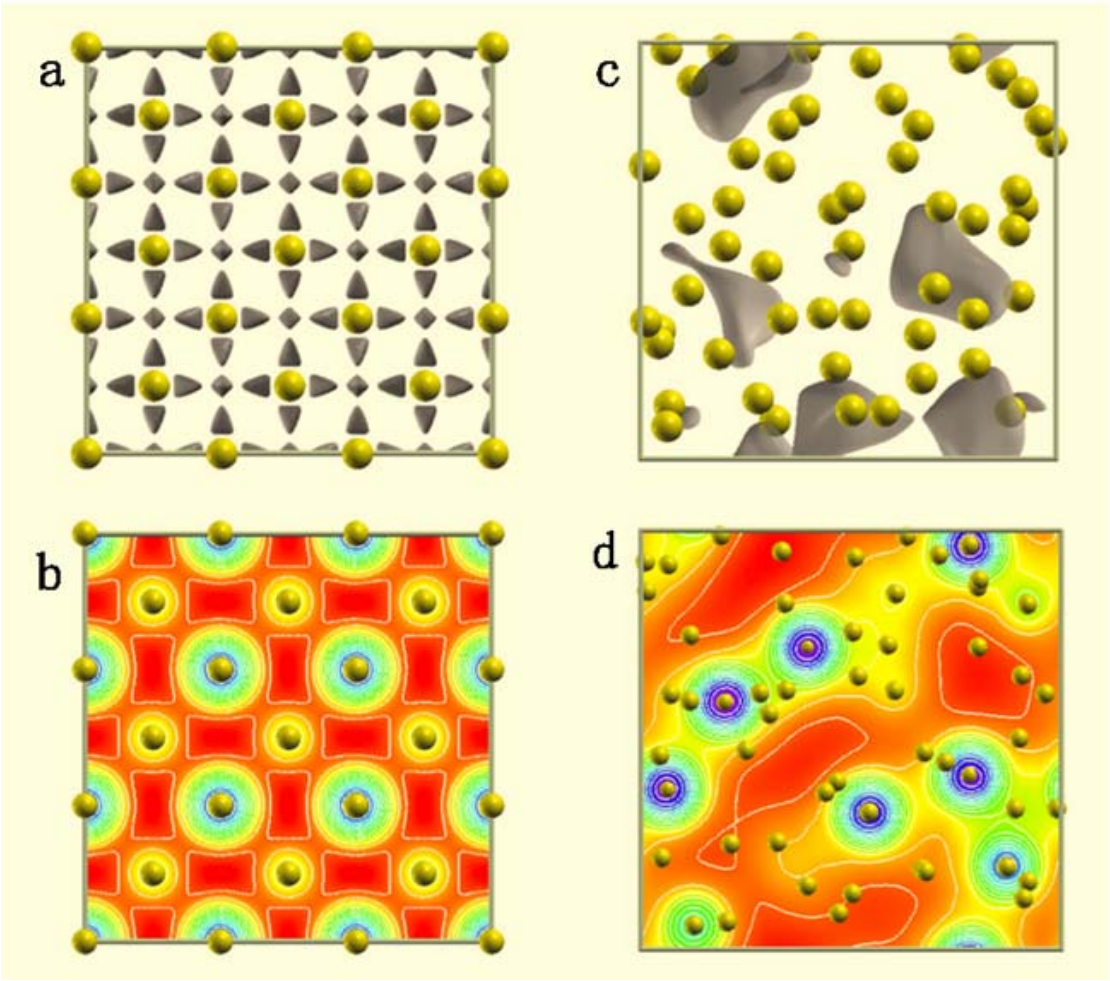
Electronic structures of Iron along the Hugoniot



Electronic structures transition from cold condensed matter to ideal ionized gas plasma

Phys. Rev. Lett. 104: 245001 (2010)

Electronic structures of Iron along the Hugoniot



Hugoniot for Iron: the present calculation

- **Rankine–Hugoniot relations:**

$$(U - U_0) - (P + P_0)(V_0 - V)/2 = 0$$

U: Internal Energy (U_0 is important)

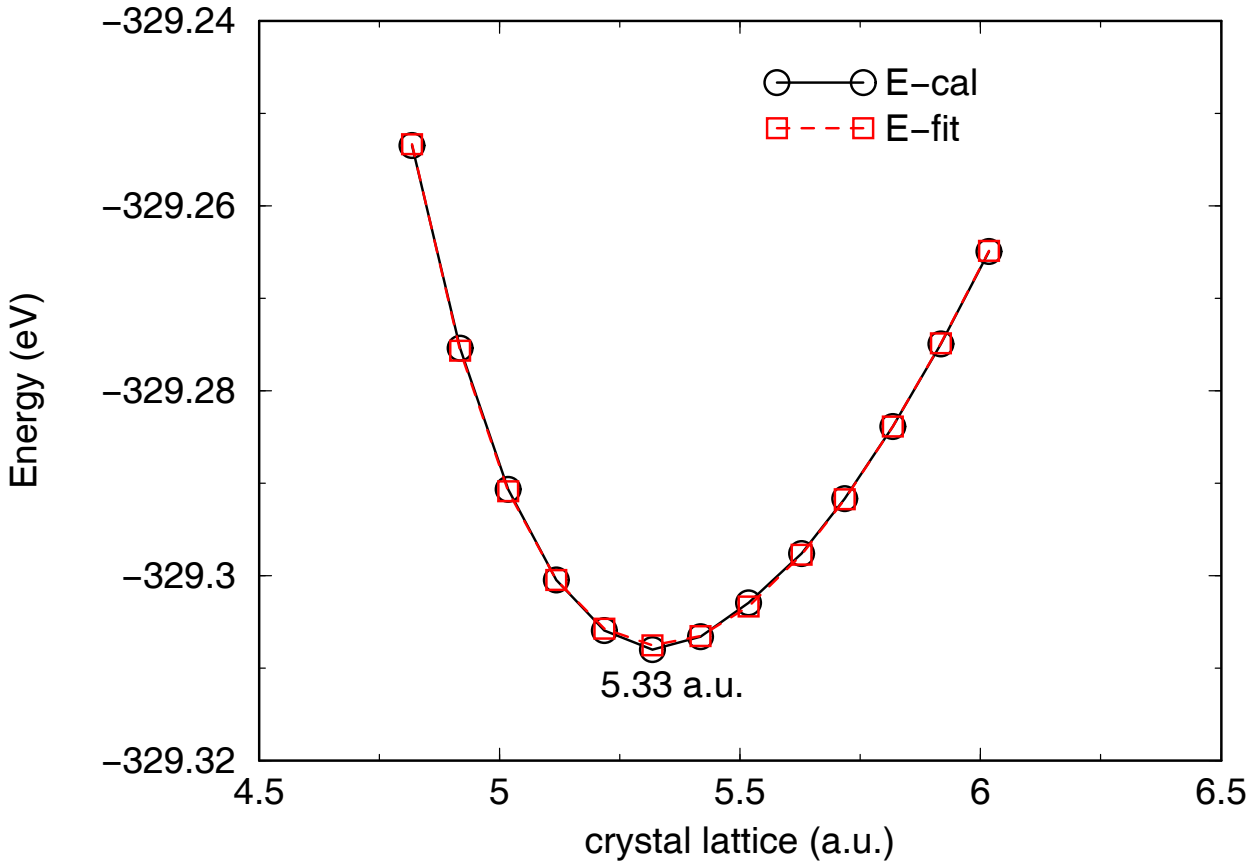
P: Pressure

V: Volume (V_0 is very important)

Comparison of QLMD results with PIMC results (PRE,79: 155105 (2009) **).** He: 5.35g/cm3，Internal Energy of Militzer (E_M)， Pressure of Militzer (P_M), Internal Energy of QLMD (E_{QLMD}), Pressure of QLMD (P_{QLMD}), Pressure of AA (P_{AA})。Ne is the number of electrons。

T (K)	E_M /Ne (hartree)	E_{QLMD}/Ne (hartree)	P_M (GPa)	P_{QLMD} (GPa)	P_{AA} (GPa)
5000	-1.29739[a]	-1.2956	1560.1[a]	1554.6	3342.7
10000	-1.27401[a]	-1.2689	1681.8[a]	1667.7	3389.8
20000	-1.2313[a]	-1.2278	1878.6[a]	1868.6	3519.6
40000	-1.1449[a]	-1.0876	2217.0[a]	2165.4	3816.2
62500	-1.0456[a]	-1.0209	2608.7[a]	2593.9	4206.8
80000	-0.9554[a]	-0.9467	2941[a]	2968.2	4548.9
125000	-0.7276[a]	-0.7356	3890[a]	3800.2	5552.9
250000	-0.0380[b]	-0.0360	6640[b]	6809.9	8885.0
333333	0.4717[b]	0.4598	8780[b]	8941.8	11311.1
500000	1.6229[b]	1.6095	13687[b]	14213.6	16348.6
571428	2.1410[b]	2.1329	15920[b]	16422.3	18560.8
666667	2.8429[b]	2.8319	18969[b]	19591.3	21549.9
800000	3.8485[b]	3.8528	23334[b]	23589.5	25790.1
1×10^6	5.3367[b]	5.2599	29972[b]	30749.1	32228.0
2×10^6	12.775[b]	12.812	63676[b]	63375.4	64941.0
4×10^6	27.326[b]	27.356	130941[b]	131413.1	131123.9
8×10^6	56.052[b]	55.878	264847[b]	261539.5	265089.8

Test for the Pseudopotential



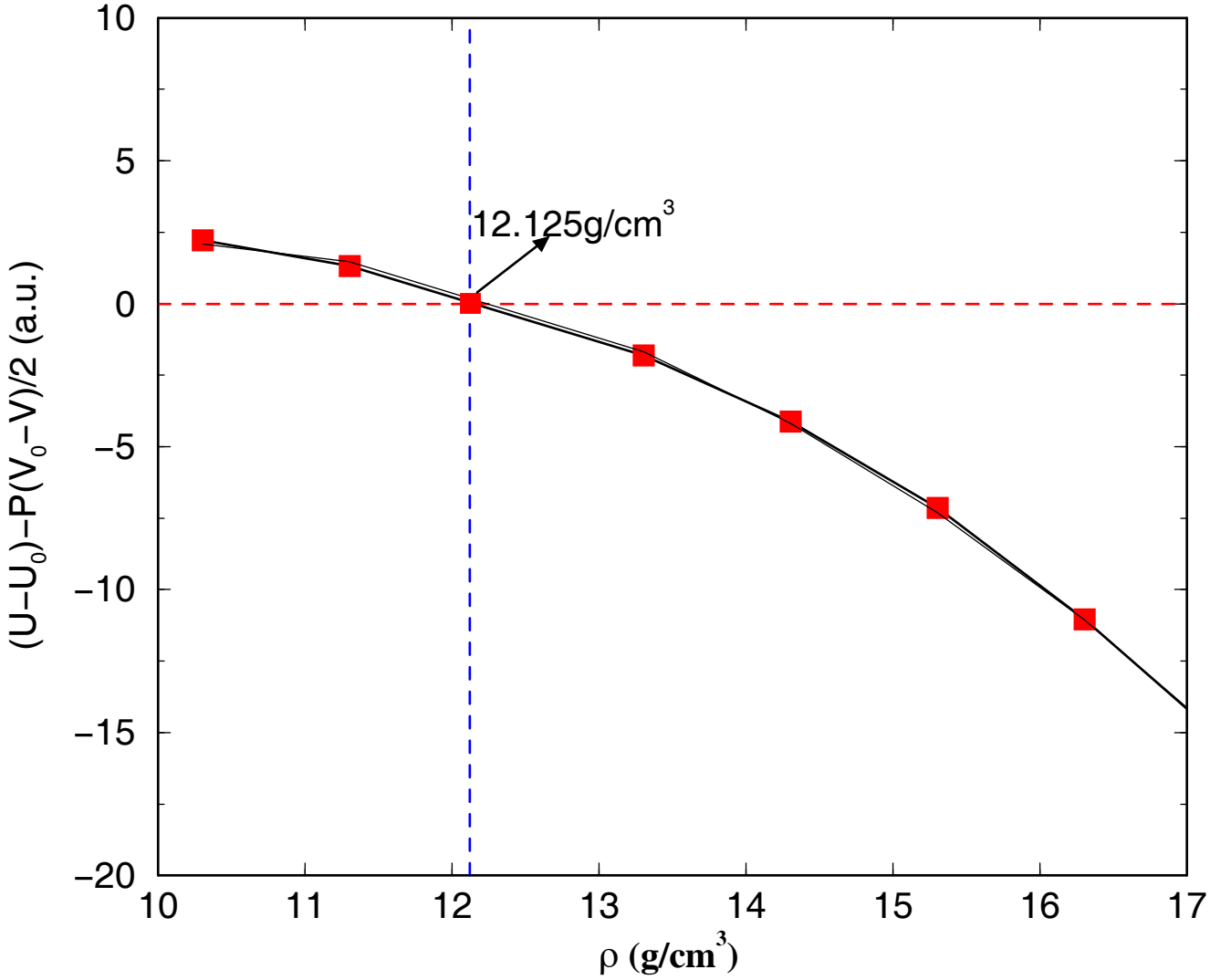
Bulk modulus:

B=170 GPa

FLAPW: 5.268-5.342 (PRB, 82, 132409 (2010))

Bulk modulus: 169-200 GPa

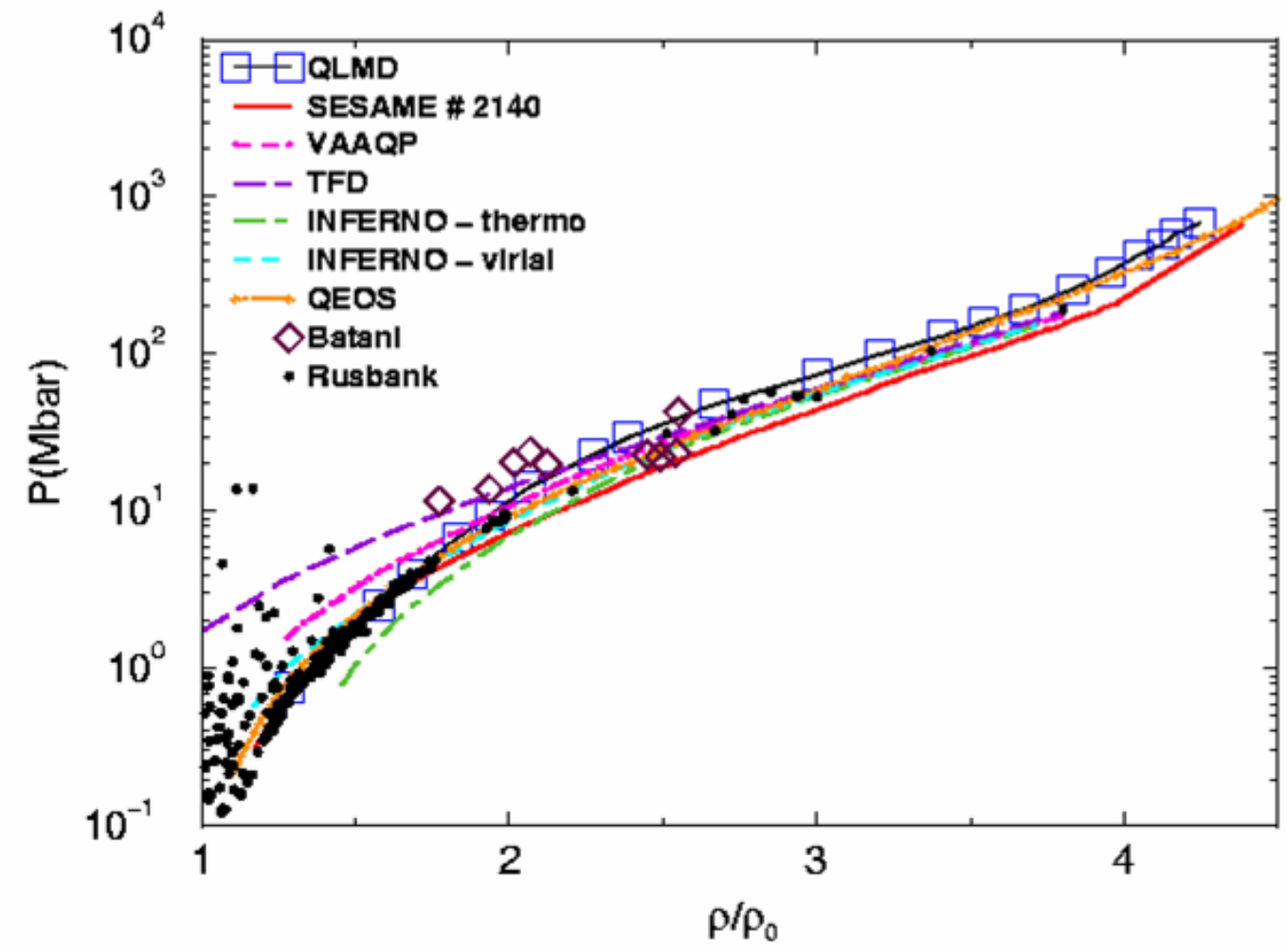
Hugoniot point example at 0.5 eV



Hugoniot: Comparison with SESAME

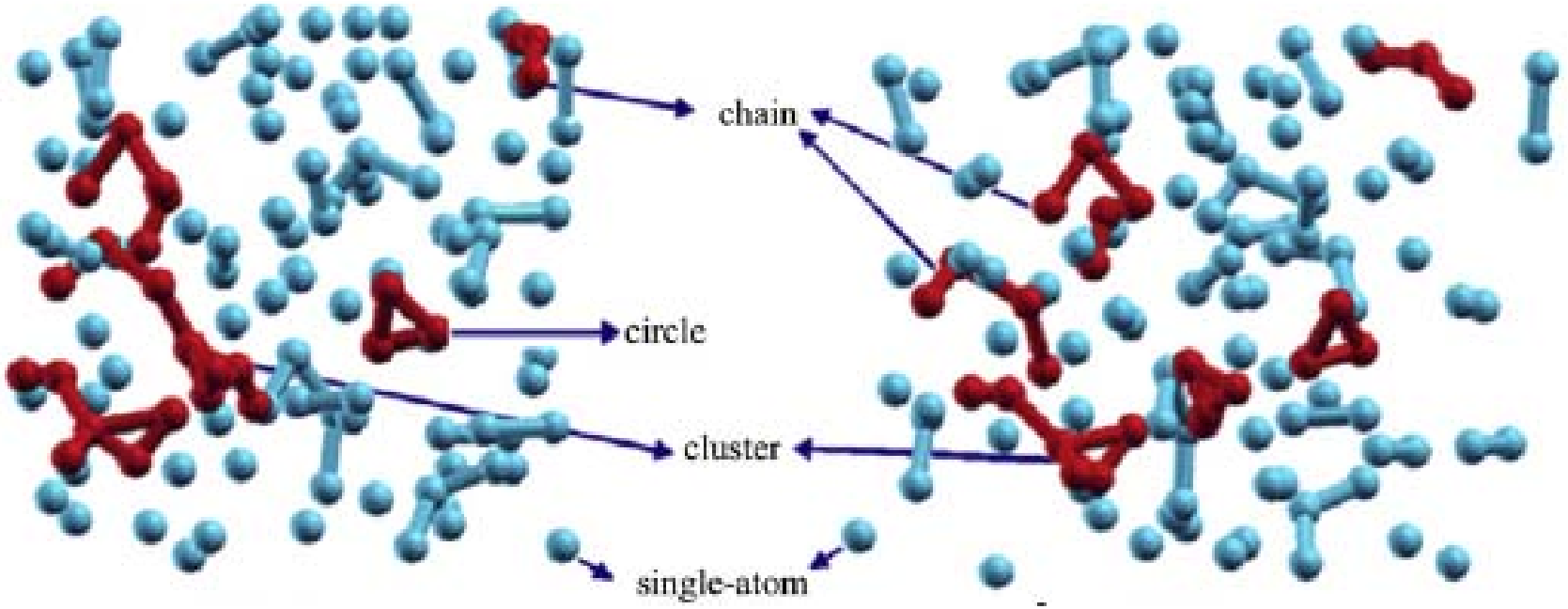
Temperature (eV)	ρ_S (g/cm^3)	ρ_Q (g/cm^3)	P_S (Mbar)	P_Q (Mbar)
0.1	10	10.1	0.625	0.76
1	13.26	13.20	3.568	3.842
5	18.71	17.5	15.28	16.9
10	22.5	20.5	33.08	33.58
100	34.5	33.8	659.9	666.7

Hugoniot of Iron: Density-Pressure



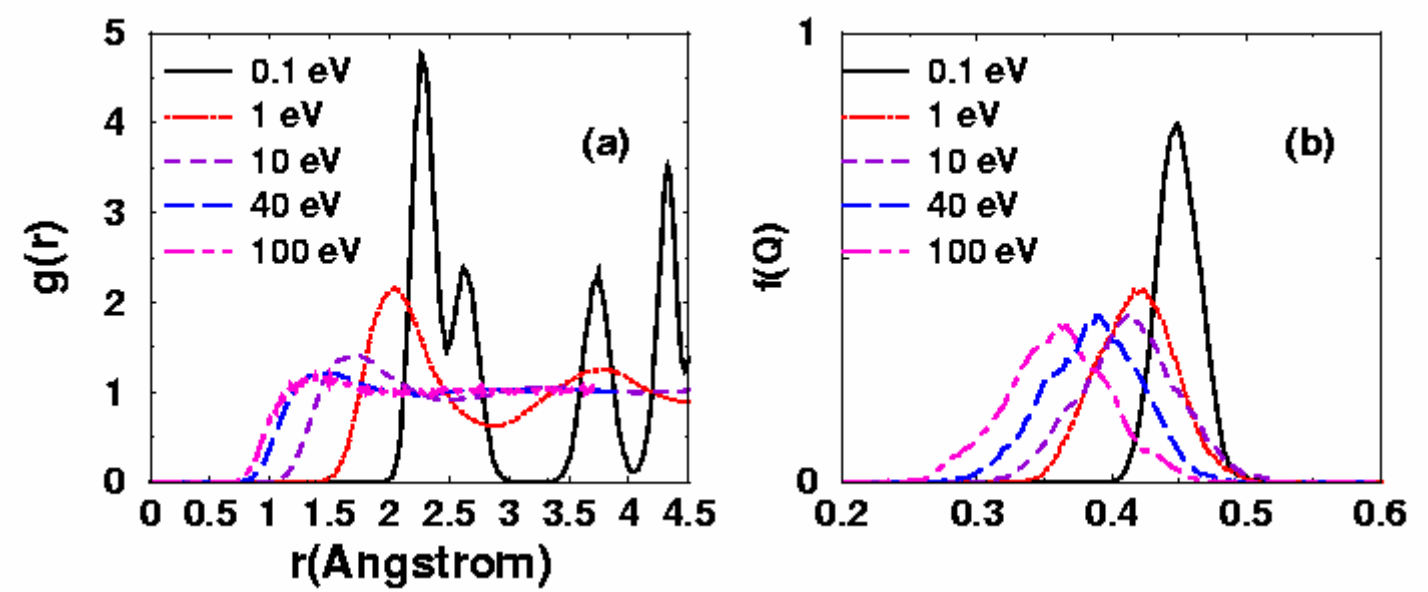
Hugoniot: Ab initio benchmark from the cold normal, across the warm dense, to the hot dense states

Ionic short ordered structures



There are medium or short ordered structures in hot dense matter

Along Hugoniot – ionic structures



Radial distribution and the orientation order number

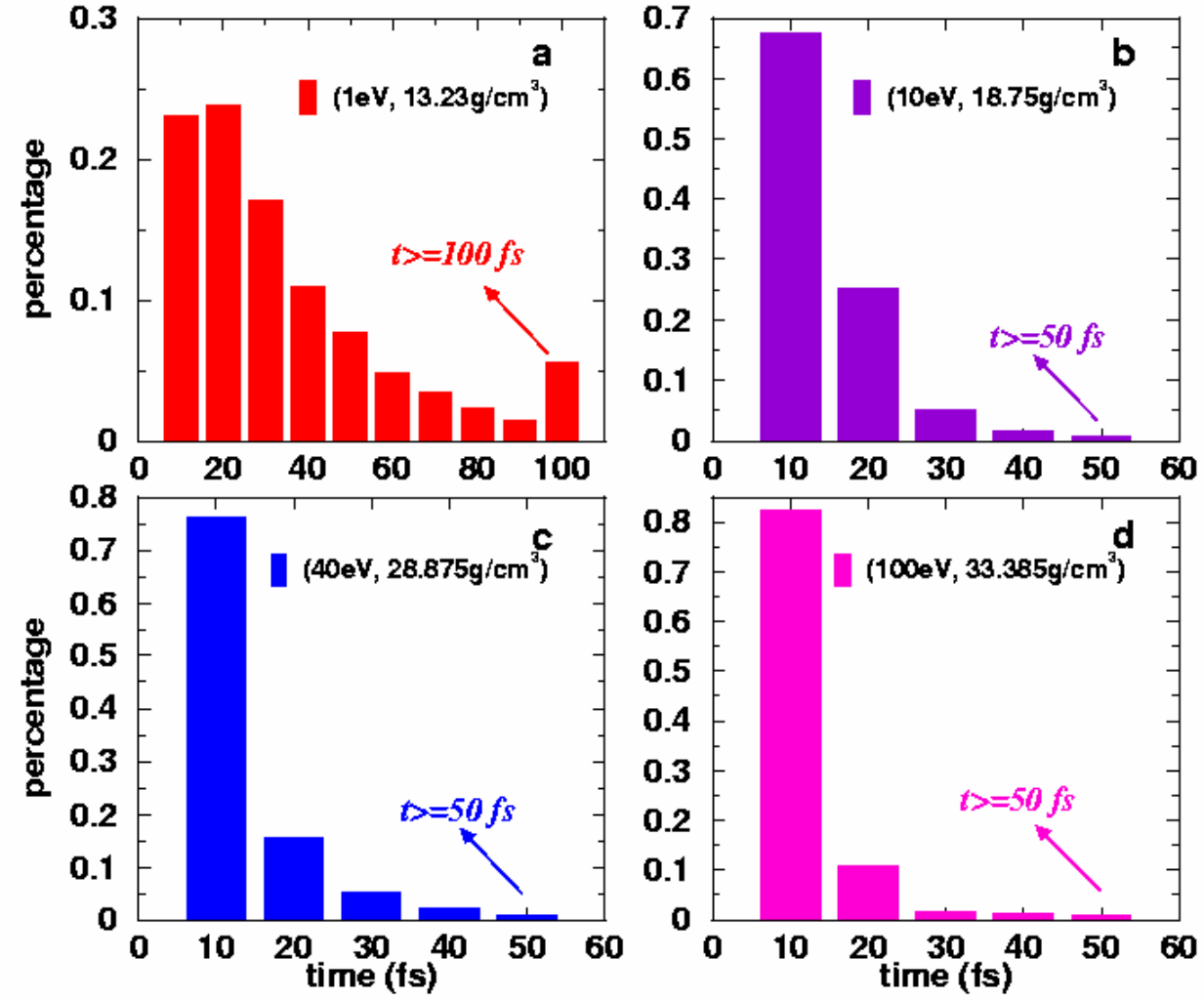
Along Hugoniot – ionic structures

Effective coordination numbers (ECN)

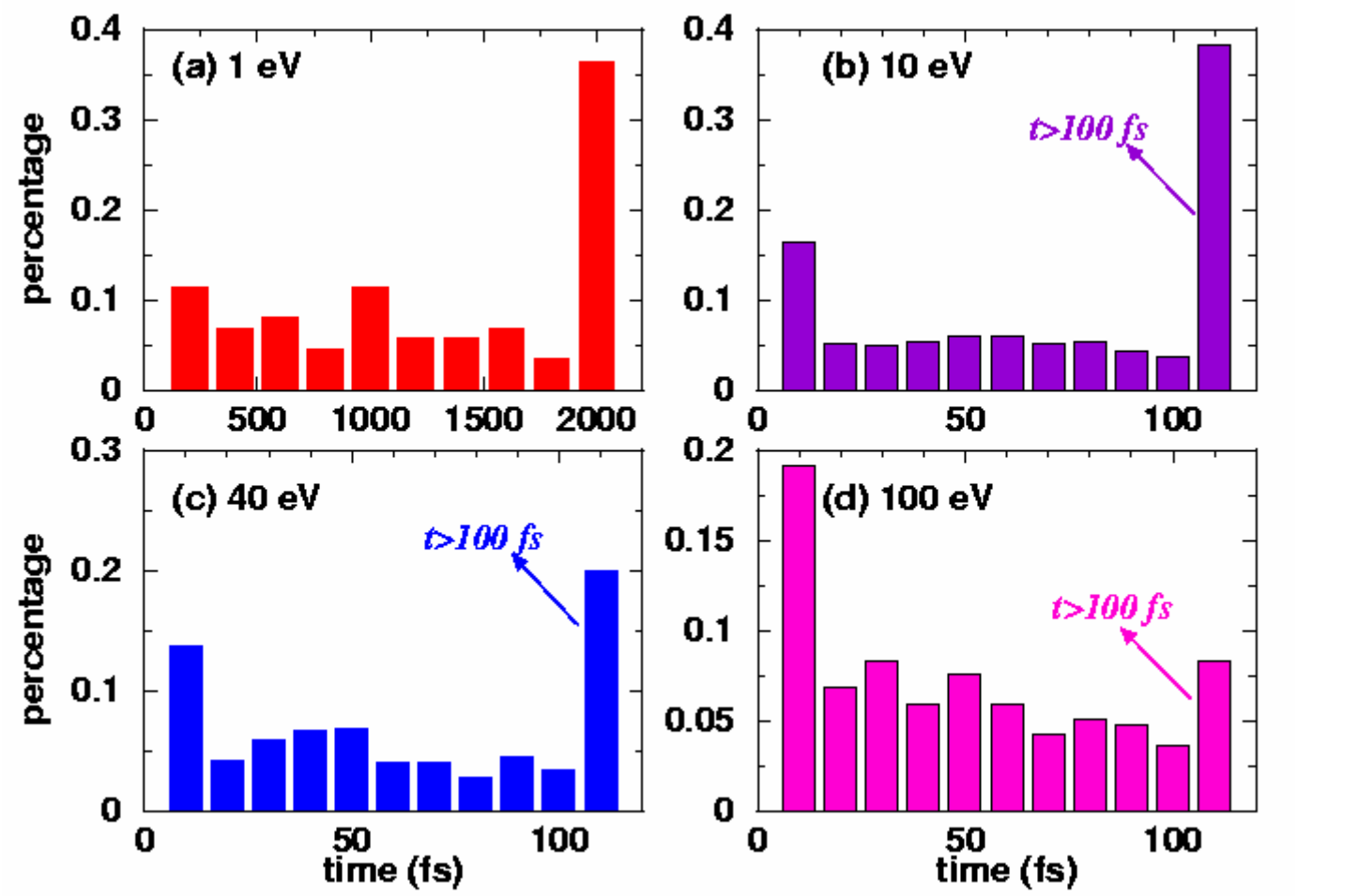
$$ECN = \frac{1}{N}\sum_{i=1}^{N} ECN_i = \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i} \exp\left[1-\left(\frac{d_{ij}}{d_{av}^{i}}\right)^{6}\right]$$

$$d_{av}^{i} = \frac{\sum_{j} d_{ij} \exp\left[1-\left(\frac{d_{ij}}{d_{av}^{i}}\right)^{6}\right]}{\sum_{j} \exp\left[1-\left(\frac{d_{ij}}{d_{av}^{i}}\right)^{6}\right]}, d_{av} = \frac{1}{N}\sum_{i=1}^{N} d_{av}^{i}$$

Along Hugoniot – ionic structures



Along Hugoniot – ionic structures



Self diffusion coefficient - ionic transport properties

Tempature (eV)	ρ_S (g/cm^3)	D_{OFMD} (cm^2/s)	D_{OCP} (cm^2/s)	ρ_Q (g/cm^3)	D_{QLMD} (cm^2/s)
0.1	10	--	--	10.1	3.0×10^{-6}
1	13.26	--	--	13.20	7.5×10^{-5}
5	18.71	4.2×10^{-4}	4.9×10^{-4}	17.5	2.3×10^{-4}
10	22.5	1.1×10^{-4}	1.0×10^{-4}	20.5	3.5×10^{-4}
100	34.5	7.0×10^{-3}	6.4×10^{-3}	33.8	7.0×10^{-3}

F. Lambert et al., Europhys. Lett. 75, 681 (2006).

Conductivity

Kubo-Greenwood formula:

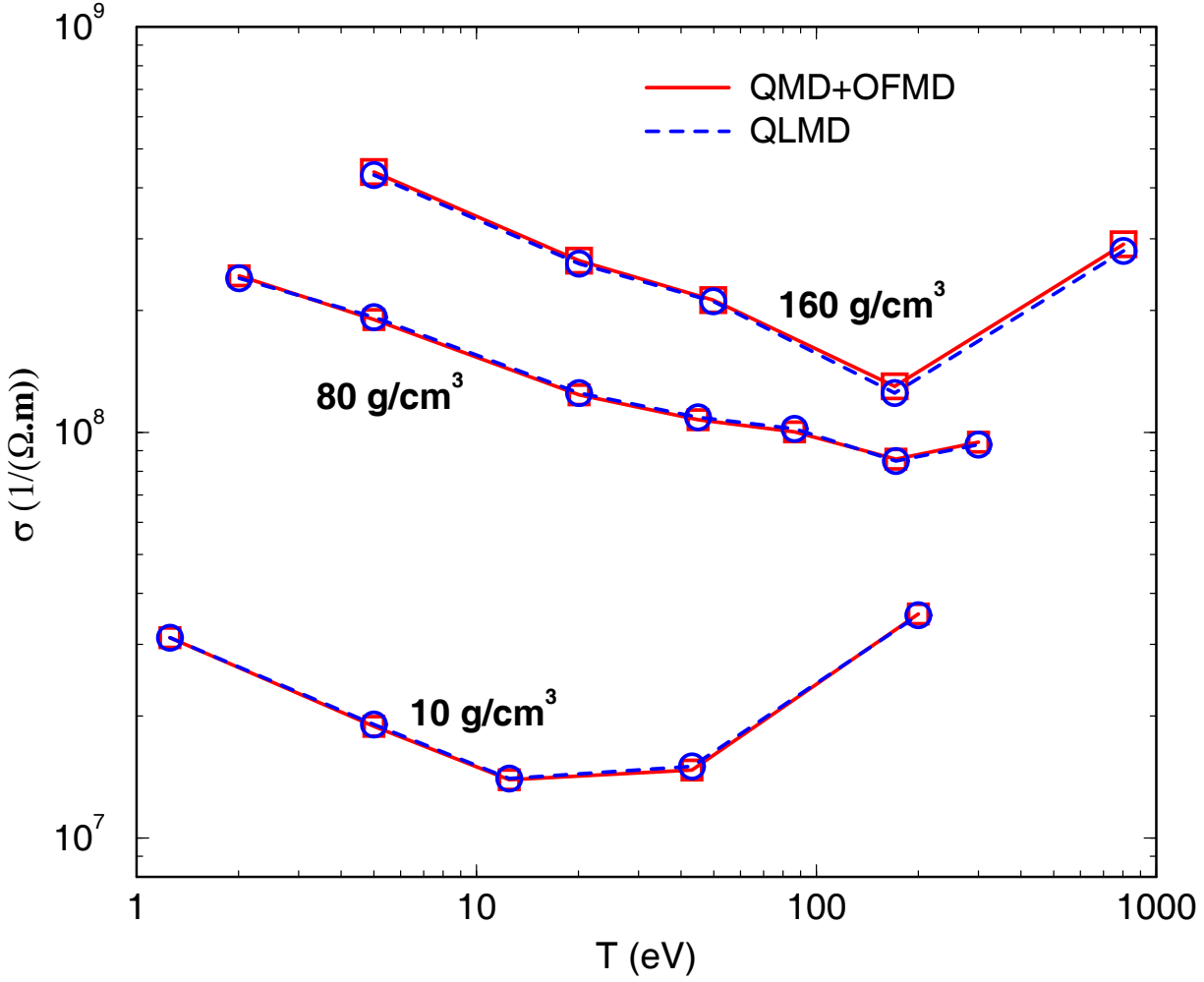
$$\sigma(\omega) = \frac{2\pi e^2}{3\omega} \int d\vec{k} \sum_{n,m} (f_n - f_m)$$

$$\times \left| \left\langle \psi_n \left| \hat{\mathbf{v}} \right| \psi_m \right\rangle \right|^2 \delta(E_m - E_n - \hbar\omega)$$

R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).

D.A. Greenwood, Proc. Phys. Soc. London **715**, 585 (1958).

Conductivity of Hydrogen

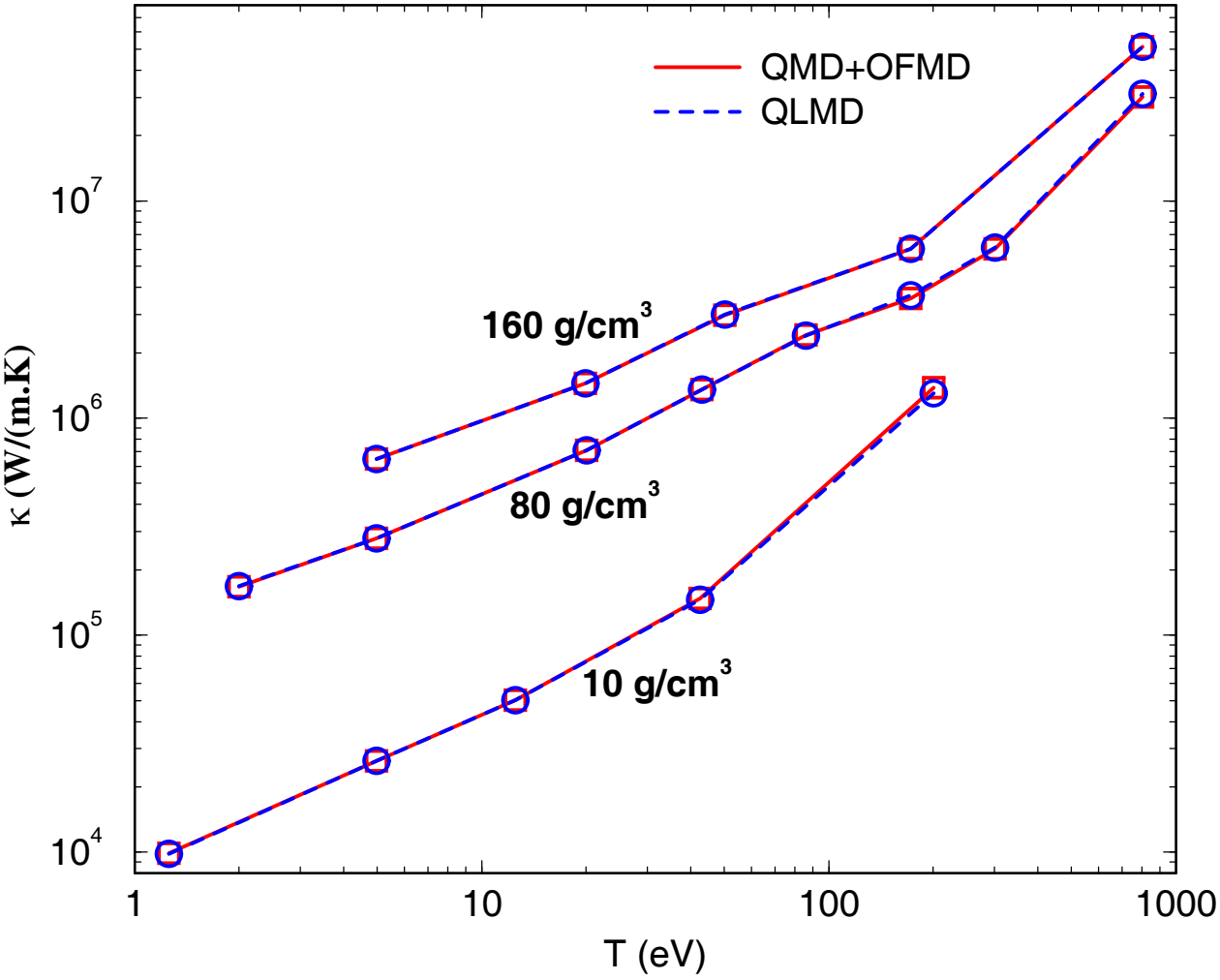


电导率

Electrical Conductivity

Lambert et al. POP, 18, 056306 (2011)

Conductivity of Hydrogen

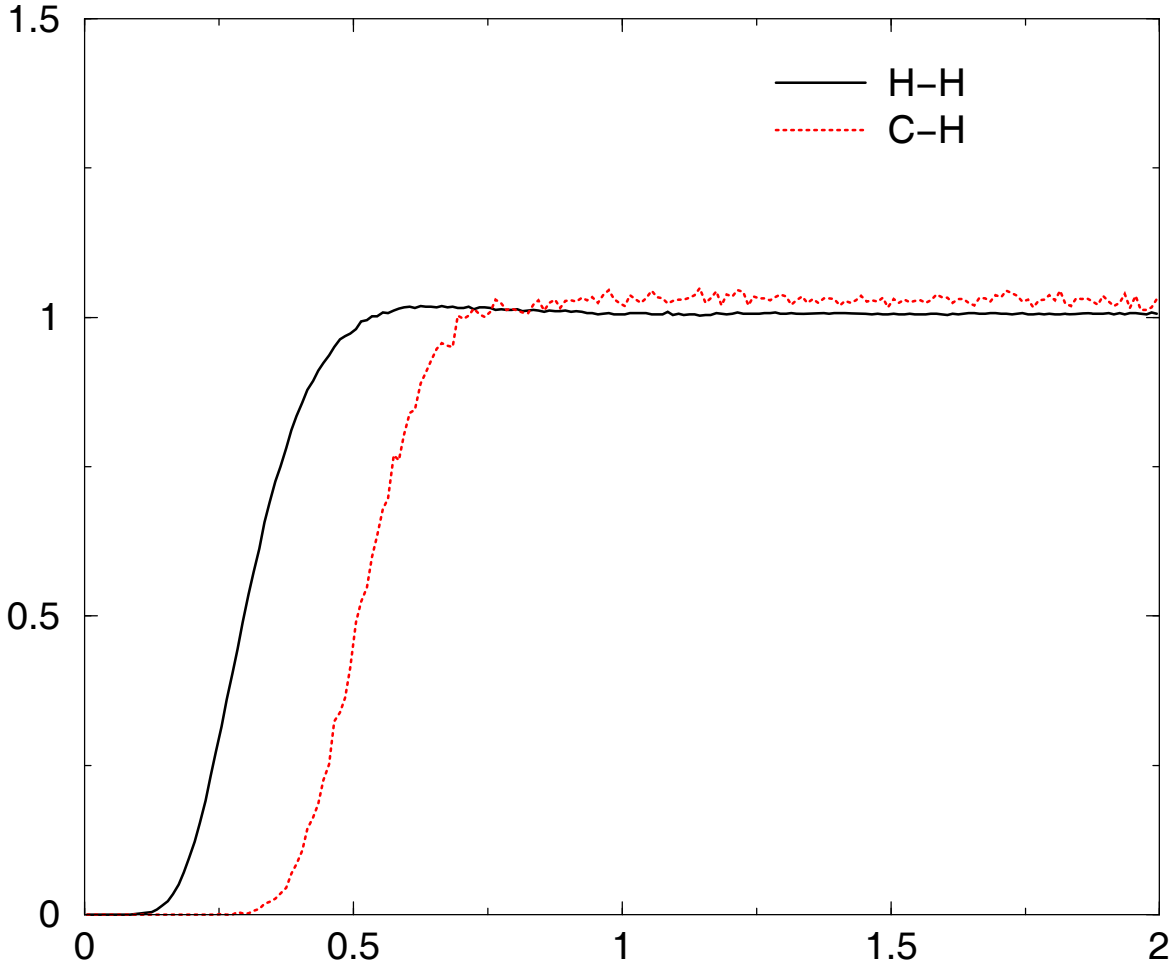


热导率

Thermal Conductivity

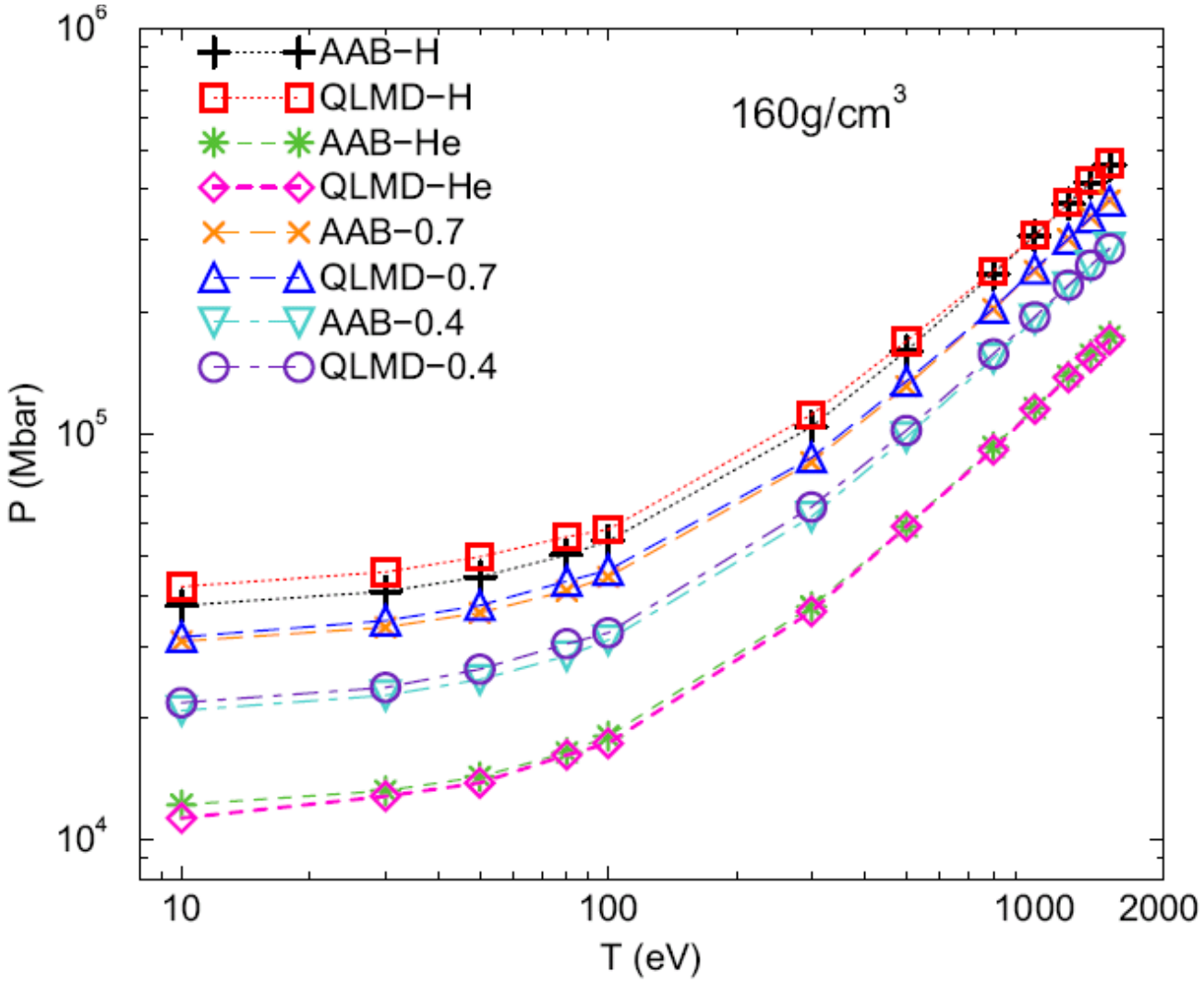
Lambert et al. POP, 18, 056306 (2011)

Carbon in Dense Hydrogen (10g/cm^3,10eV)



The size of the Coulomb hole depends on the ionic charge

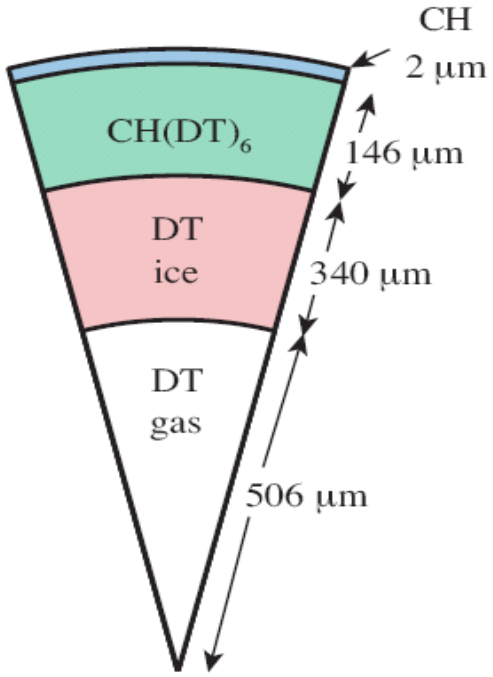
Application: EOS for solar-interior



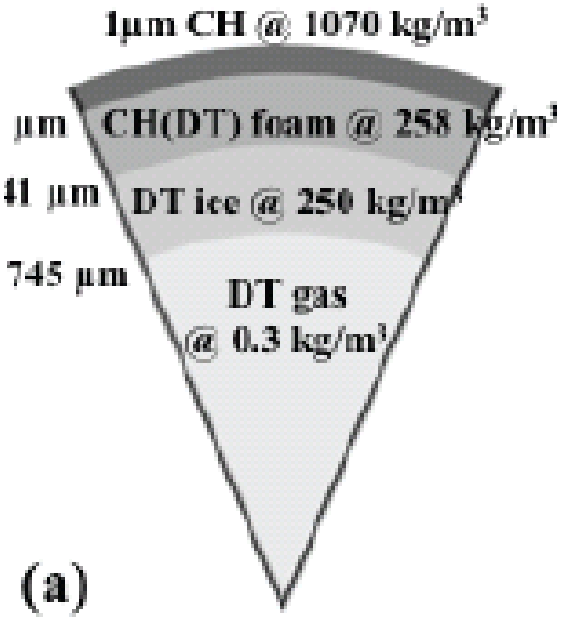
ApJ. 721: 1158 (2010)

Application: ICF target

High demand for the uniformities



OMEGA



LMJ

NJP, 12 (2010) 043037

- How to diagnose the state and the electronic, ionic structures in the process of laser-target interactions.
- How the carbon atoms affect the states (may induce instability)?
- What's the influence of local structures on physical properties?

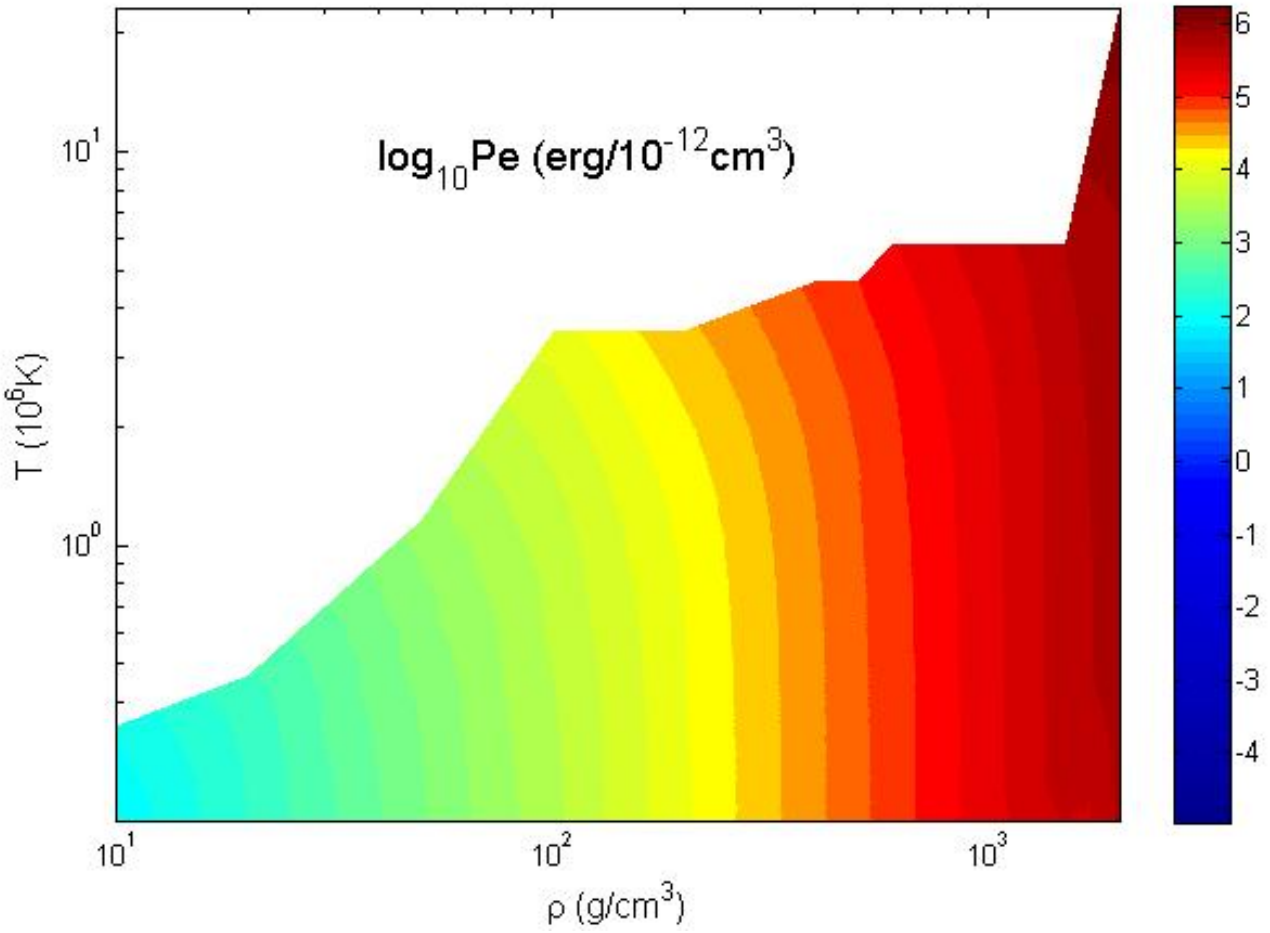
Application: EOS table for ICF Capsule

- Wide temperature and wide density

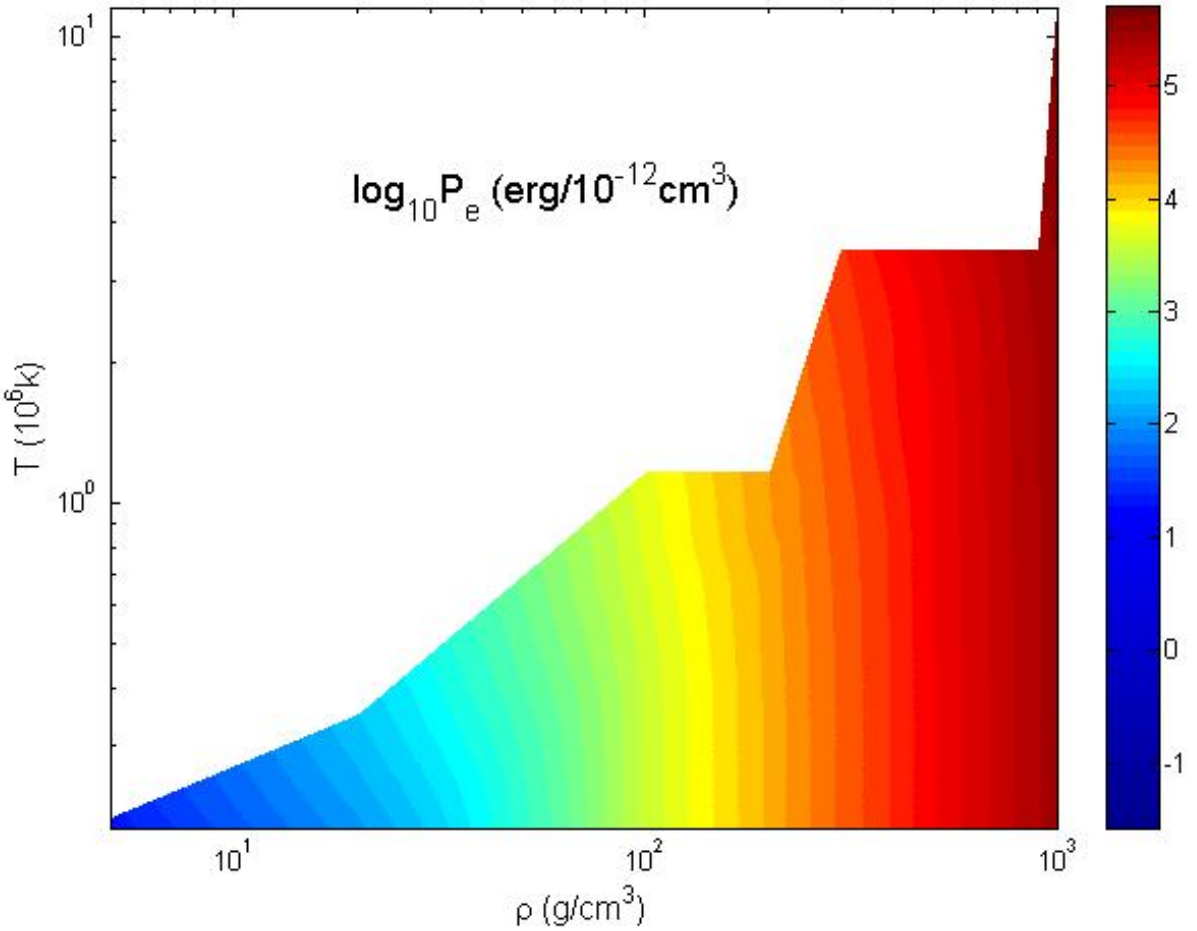
- Important for the simulation of hydrodynamics

- Dominant Ingredients:
  - D-T (gas, ice, solid, warm dense, and hot dense)
  - Plastic (outside face)

EOS table for Deuterium-Tritium mixture



EOS table for Plastic (C_8H_8)



Conclusions

- QLMD can do simulations from warm dense matter to hot dense plasmas.
- EOS, transport properties can be shown within the framework of QLMD.
- Principal Hugoniot of Iron is calculated from first principles up to 100 eV. The results are in agreement with SESAME table and most experiments, and more consistent with experiments than SESAME at high temperature.
- The basic idea of Langevin equation provide the flexibility of cutting the system (or degree of freedom) from the environment and reduce the complexity to be manageable.
- Reliability of the results depends on a adequate fluctuation-dissipation model.

Acknowledgements:

Colleagues:

Jiayu Dai, Yong Hou, Dongdong Kang

Zengxiu Zhao, Jiaolong Zeng

Supported by:

National Natural Science Foundation of China

Thanks for your attention!