РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

7-th School-Conference on

Atomistic Simulation of Functional Materials

(ASFM-2018 Fall) Moscow, September 12–13, 2018

Ab initio simulation of formation of the conducting solid hydrogen at high pressures

G.E. Norman, I.M. Saitov

ОБЪЕДИНЕННЫЙ ИВТАН

ВЫСШАЯ ШКОЛА ЭКОНОМИКИ

МФТИ

Outline

1. Metallic hydrogen. Introduction.
2. Calculation method.
3. Validation.
4. Molecular phase at high pressure.
5. Conducting phase.
6. Conclusions.

§ 2. V.L. Ginzburg's list of
'Especially Important and Interesting Problems'

1. Controlled thermonuclear fusion
2. High and room-temperature superconductivity
3. Metallic hydrogen.

4.
5.

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totally 30 problems in
macrophysics, microphysics and astrophysics

Wigner, E.; Huntington, H.B.

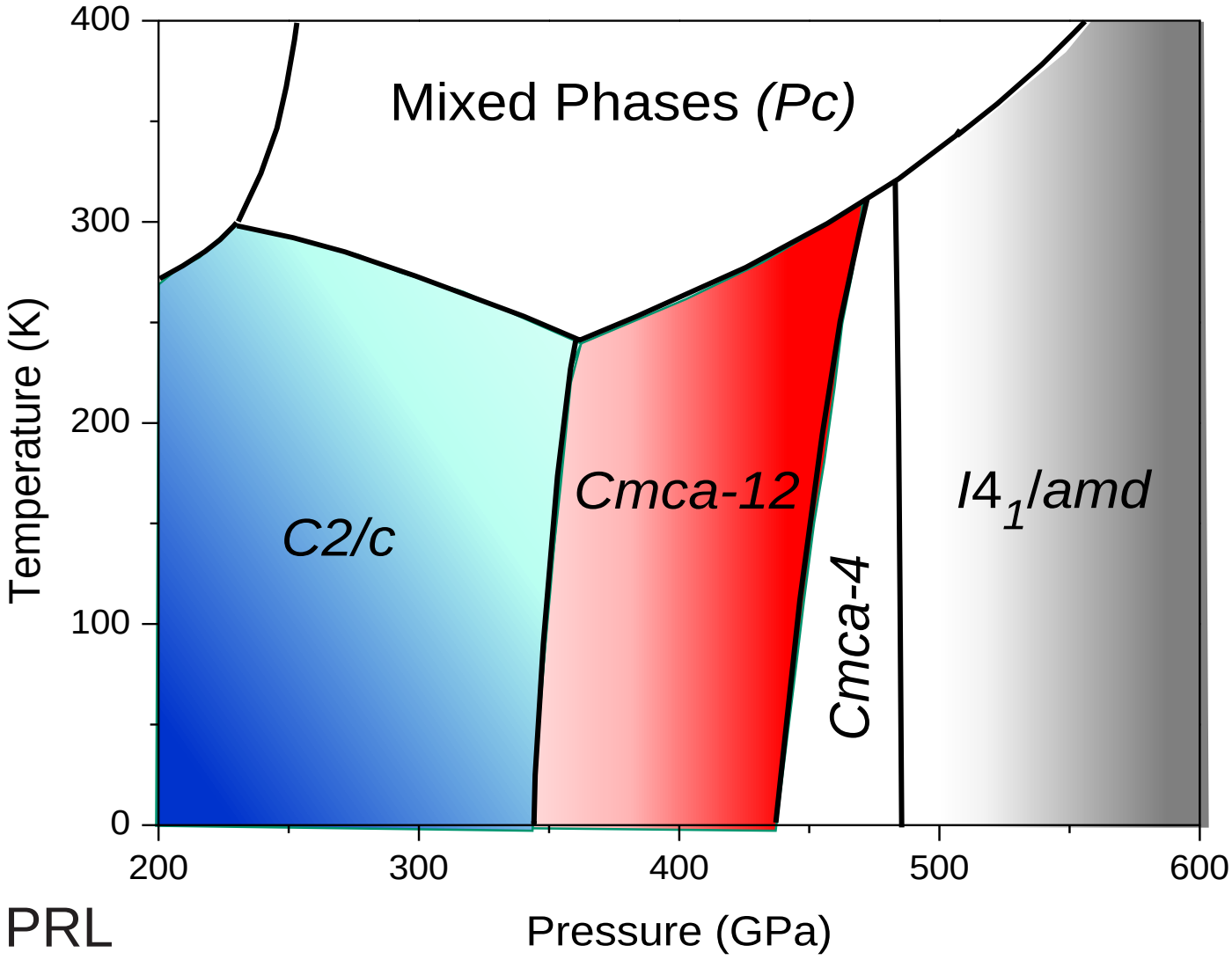
On the possibility of a metallic modification of hydrogen

Journal of Chemical Physics. 3, no. 12. 764 (1935)

0.25 Mbar

T = 0 K

Theoretical phase diagram of solid hydrogen



S. Azadi PRL 112, 165501 (2014)

High temperature superconductor

N. W. Ashcroft, Metallic Hydrogen: A High Temperature Superconductor? Phys. Rev. Lett. 21, 1748–1749 (1968).

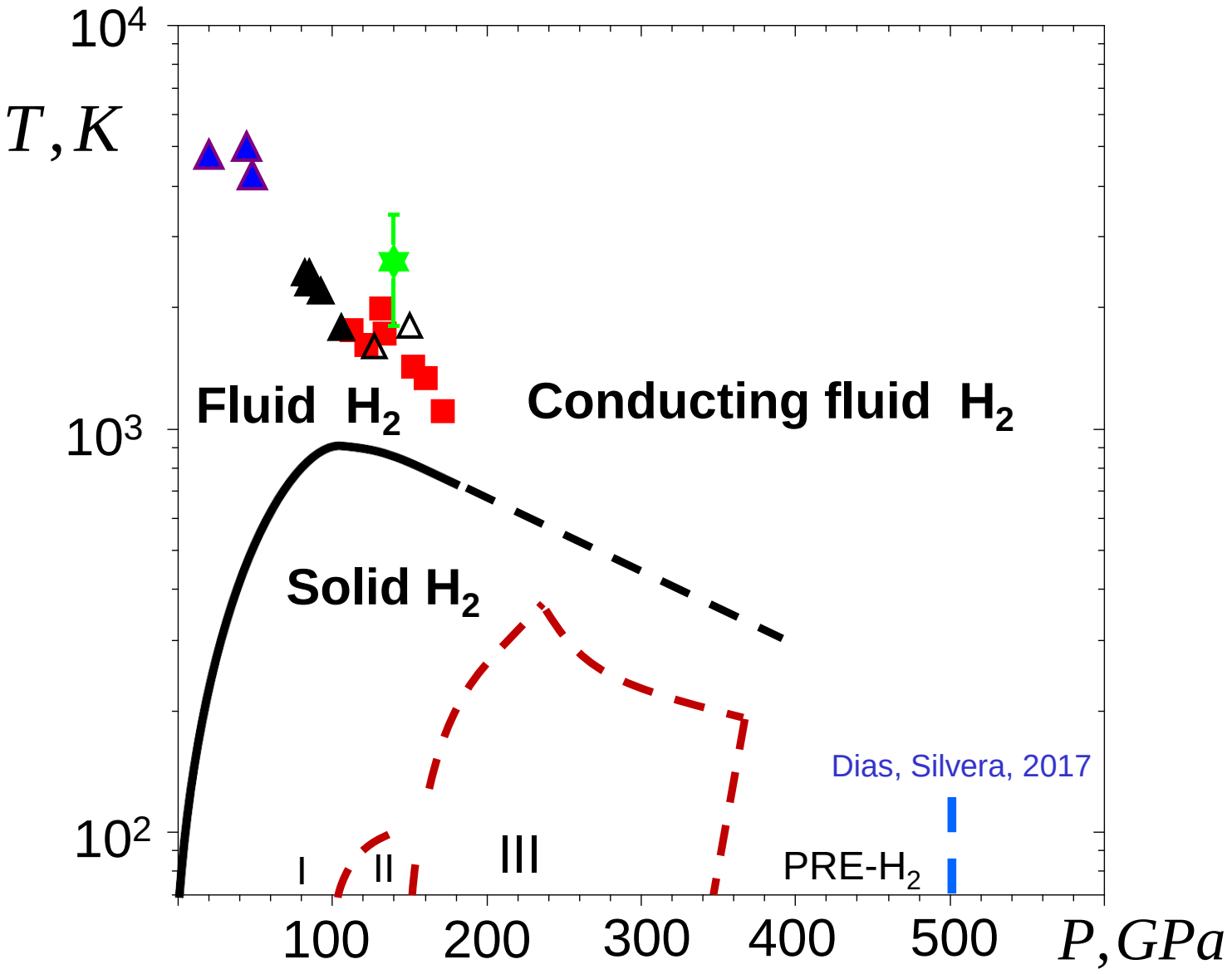
J. M. McMahon, D. M. Ceperley, High-temperature superconductivity in atomic metallic hydrogen. Phys. Rev. B 84, 144515 (2011).

M. Borinaga, I. Errea, M. Calandra, F. Mauri, A. Bergara, Anharmonic effects in atomic hydrogen: Superconductivity and lattice dynamical stability. Phys. Rev. B 93, 174308 (2016).

Metastability at normal pressure

E. G. Brovman, Y. Kagan, A. Kholas, Structure of Metallic Hydrogen at Zero Pressure. *Sov. Phys. JETP* 34, 1300–1315 (1972).

Dense H_2 phase diagram



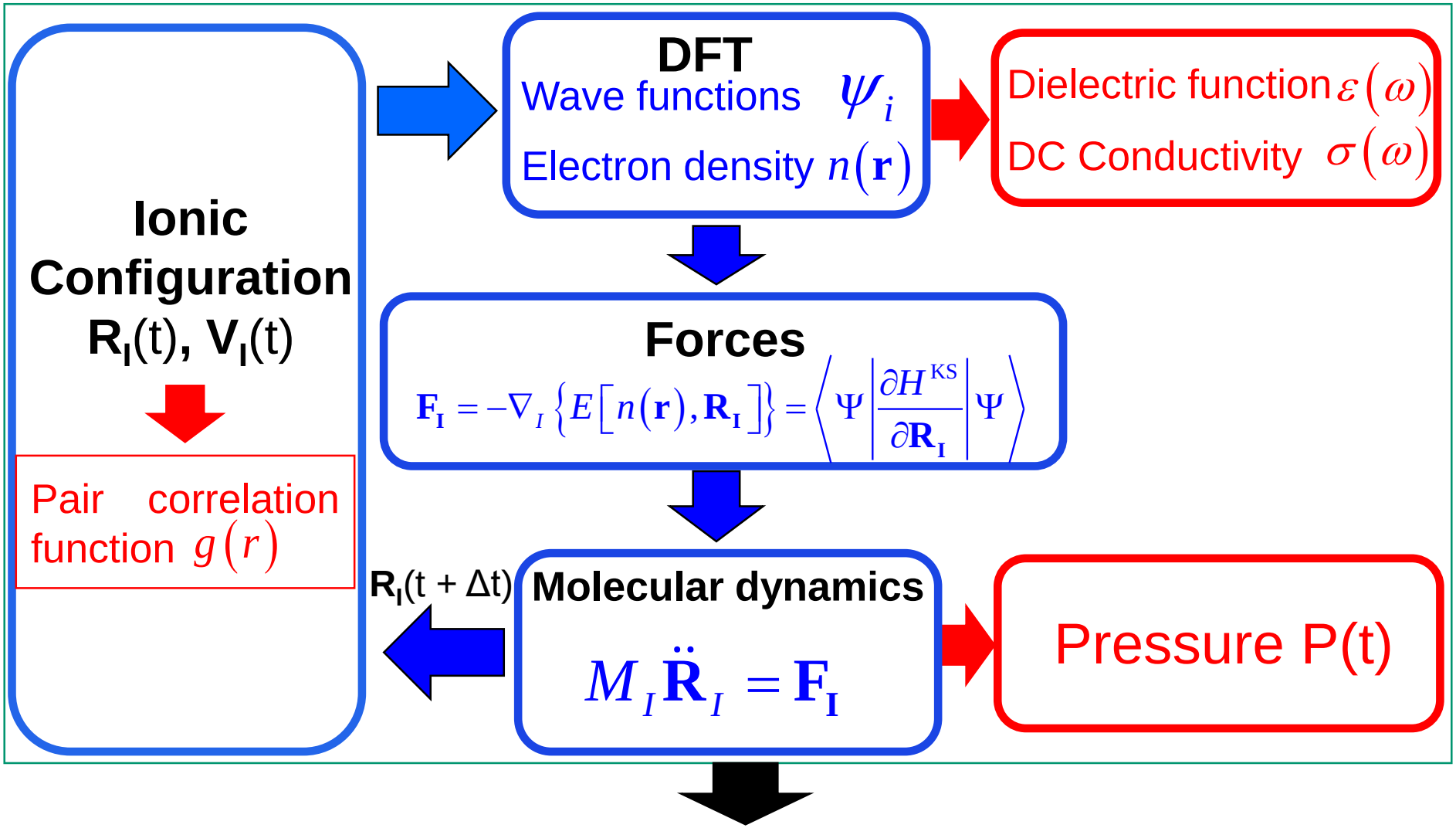
2. Calculation method.

METHOD

1. Calculation of the ions trajectories
determined by the solution of
the Newton's equations of motion
with forces obtained within the DFT

2. Equilibration of the system

3. Calculation of parameters of the system:
Proton-proton pair correlation function g(r)
Pressure
Conductivity



Averaging over configurations

Pair correlation function, pressure, DC conductivity

Finite temperature Density Functional Theory

$$\Omega\left[n(\mathbf{r})\right] = \sum_i f_i \int \psi_i^* \left(-\frac{\hbar^2}{2m}\Delta \right) \psi_i d\mathbf{r} + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} +$$

$$+ \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{xc}\left[n(\mathbf{r})\right] - TS\left[n(\mathbf{r})\right]$$

$$n(\mathbf{r}) = \sum_i f_i(E_i, T) |\psi_i(\mathbf{r})|^2 \qquad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$$\left(-\frac{\hbar^2}{2m}\Delta + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r})$$

$$V_H = \frac{e^2}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \qquad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}\left[n(\mathbf{r})\right]}{\delta n(\mathbf{r})}$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}}^{\mathbf{G}_{\max}} C_{\mathbf{k}n\mathbf{G}} \cdot e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \qquad E_{cut} = \frac{\hbar^2 G_{\max}^2}{2m}$$

Dielectric function

$$\varepsilon = \varepsilon^{(1)} + i \cdot \varepsilon^{(2)}$$

Longitudinal expression for the imaginary part of dielectric function:

$$\varepsilon^{(2)}(\omega) = \frac{1}{3} \cdot \frac{4\pi^2 e^2}{\Omega} \lim_{|\mathbf{q}|\to 0} \frac{1}{|\mathbf{q}|^2} \sum_{i,j,\alpha,\mathbf{k}} 2w_{\mathbf{k}} \cdot \left[f\left(\mathrm{E}_{i,\mathbf{k}+\mathbf{q}}\right) - f\left(\mathrm{E}_{j,\mathbf{k}}\right) \right] \times$$

$$\times \left| \left\langle \Psi_{i,\mathbf{k}+\mathbf{e}_\alpha q} \middle| \Psi_{j,\mathbf{k}} \right\rangle \right|^2 \cdot \delta\left(\mathrm{E}_{i,\mathbf{k}+\mathbf{q}} - \mathrm{E}_{j,\mathbf{k}} - \hbar\omega\right)$$

$$\delta(x) \to \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

Kramers-Kronig transformation

for the imaginary part of the dielectric function:

$$\varepsilon^{(1)}(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\varepsilon^{(2)}(\omega')\omega'}{\omega'^2 - (\omega + i\eta)^2} d\omega'$$

$$\sigma^{(1)}(\omega) = \varepsilon_0 \omega \varepsilon^{(2)}(\omega)$$

effective collisional frequency η = 0.01 eV

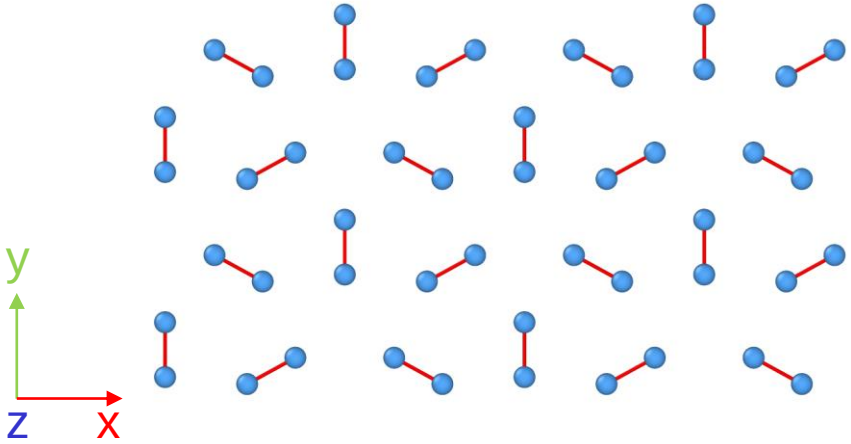
3. Validation.

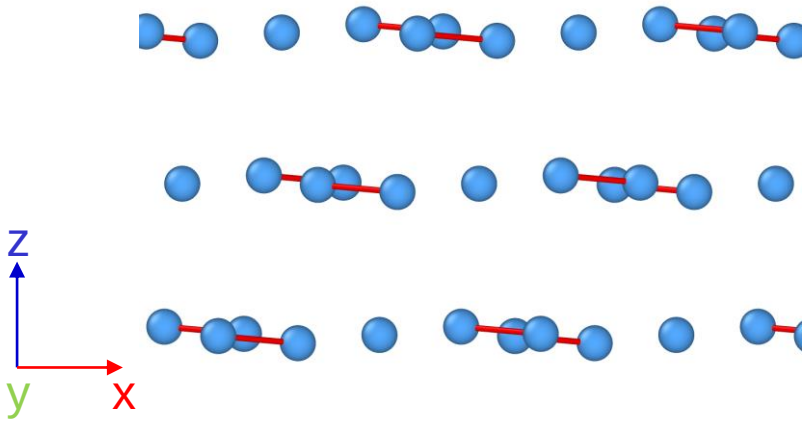
Initial configuration

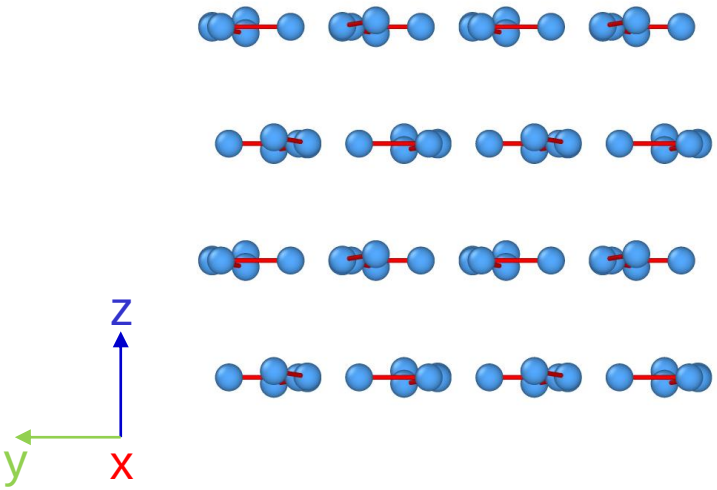
Monocline structure
with **C2/c** space group
24 atoms in the unit cell

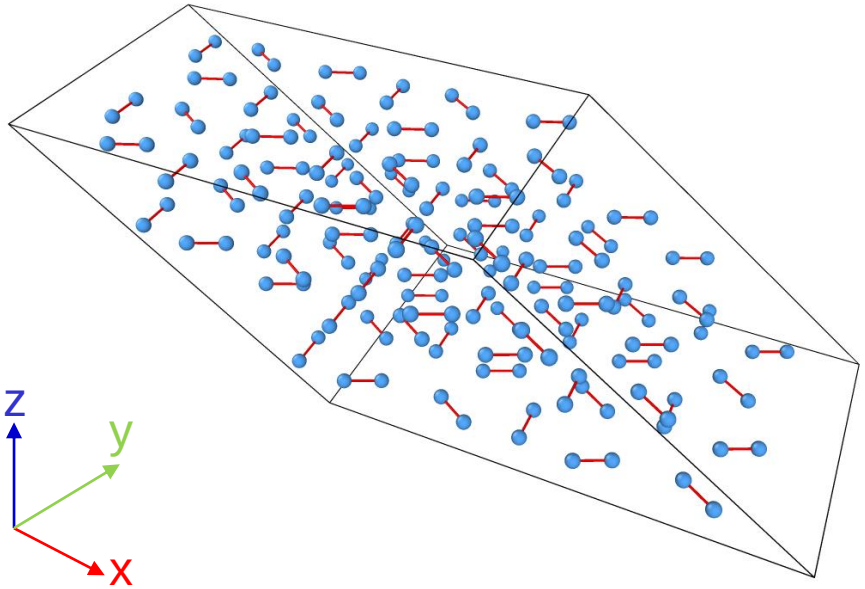
Density: 1.14 g/cm^3
Pressure: 302 GPa
Number of particles: 192

C.J. Pickard, R.J. Needs // Nature Phys. **3,** 473 (2007)

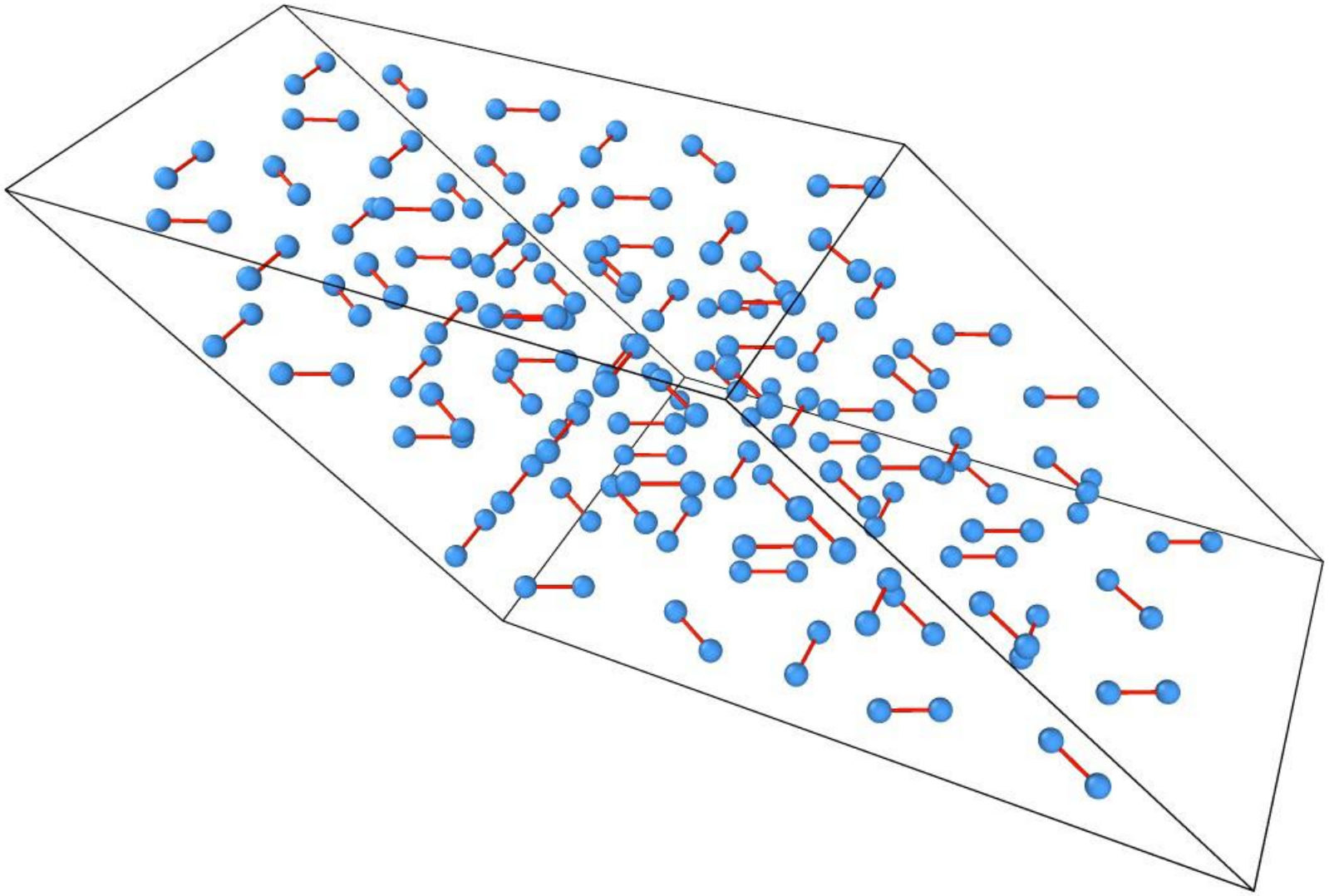






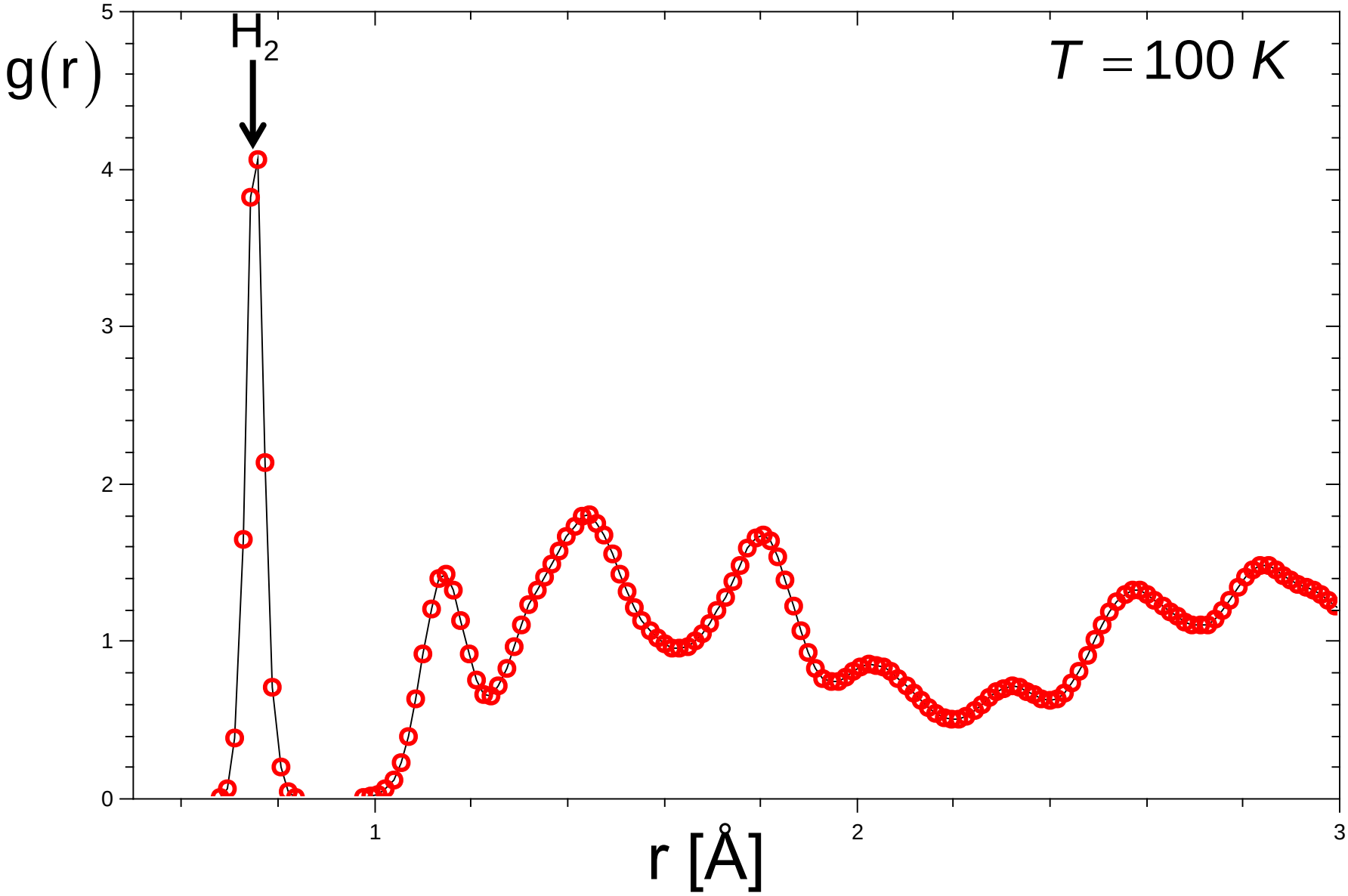


MD at initial density



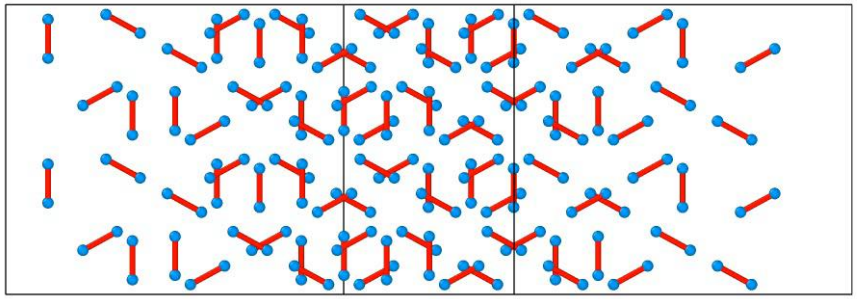
Conductivity: 0.58 $(Ohm \cdot cm)^{-1}$

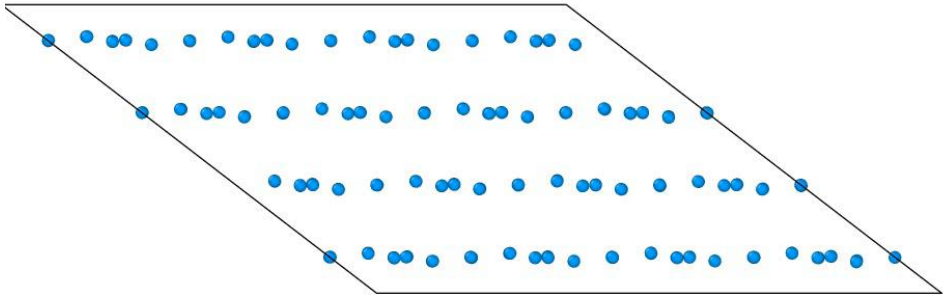
Pair correlation function at pressure 302 GPa

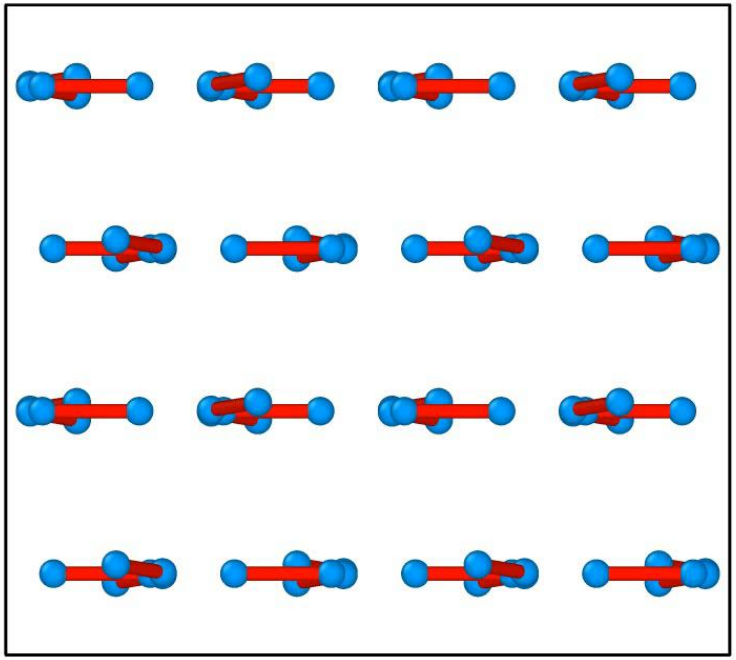


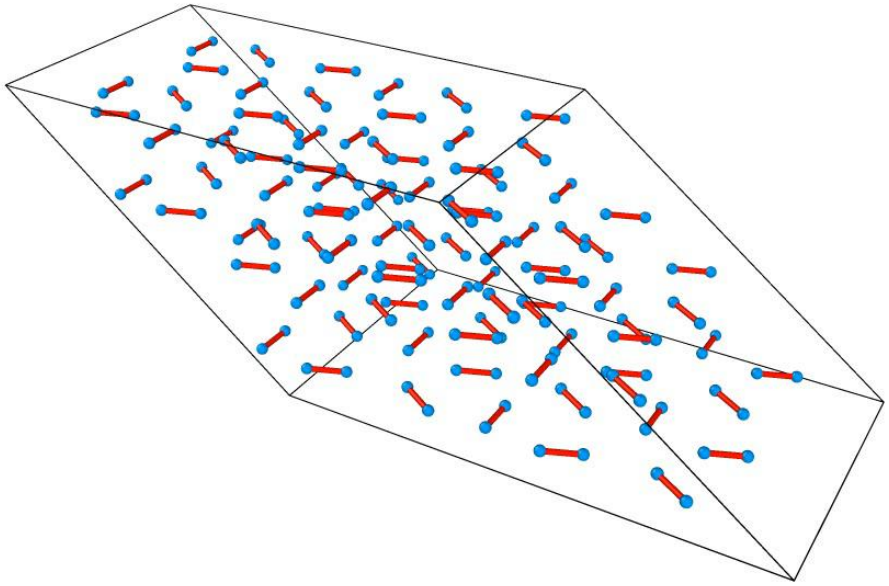
4. Molecular phase at high pressure

MD at density 1.55 g/cm^3

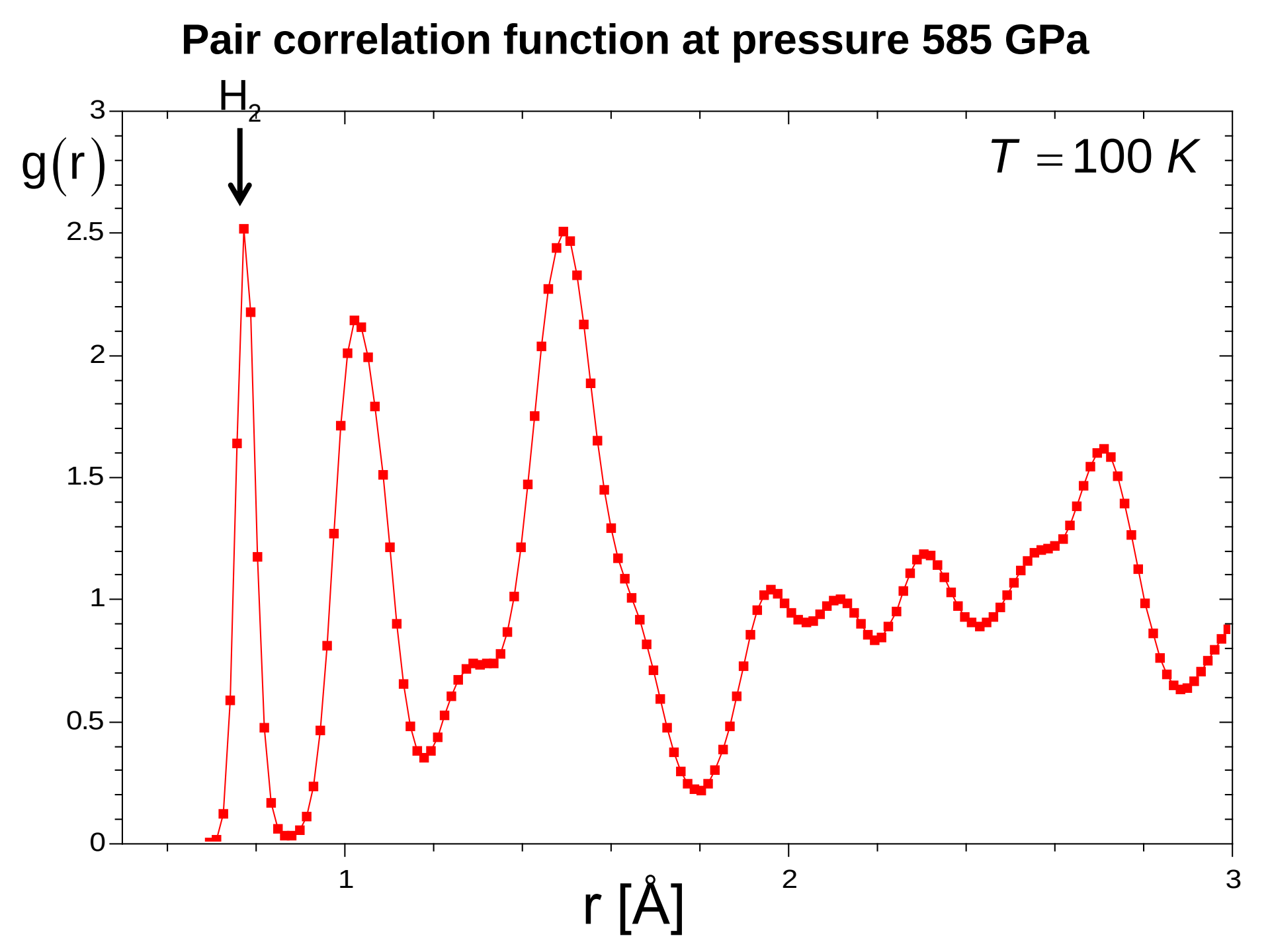








Conductivity at density 1.55 g/cm^3: 5.32 (Ohm·cm)$^{-1}$


Pair correlation function at pressure 585 GPa
H2
g(r)
T = 100 K
3
2.5
2
1.5
1
0.5
0
1
2
3
r [Å]

Space group: *Cmca*

a=1.450	b=2.567	c=2.482	H1	0.0000	0.1132	0.1262
α=90.00	β=90.00	γ=90.00				

C.J. Pickard, R.J. Needs // Nature Phys. 3, 473 (2007)

Comments

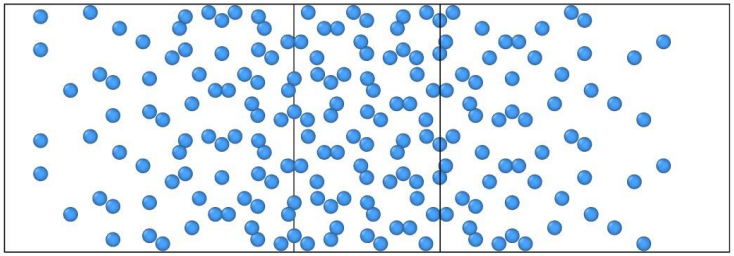
We do nothing to create structures.

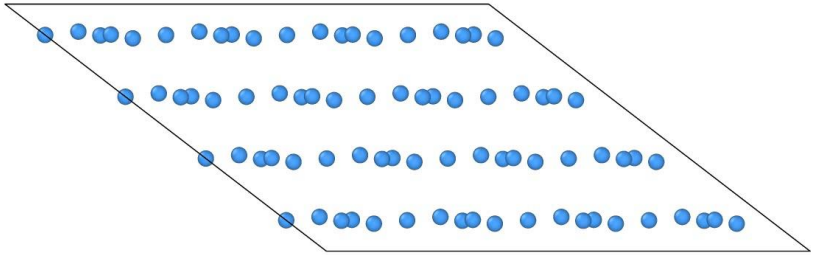
We use the structure with C2/c space group as are initial conditions in each case.

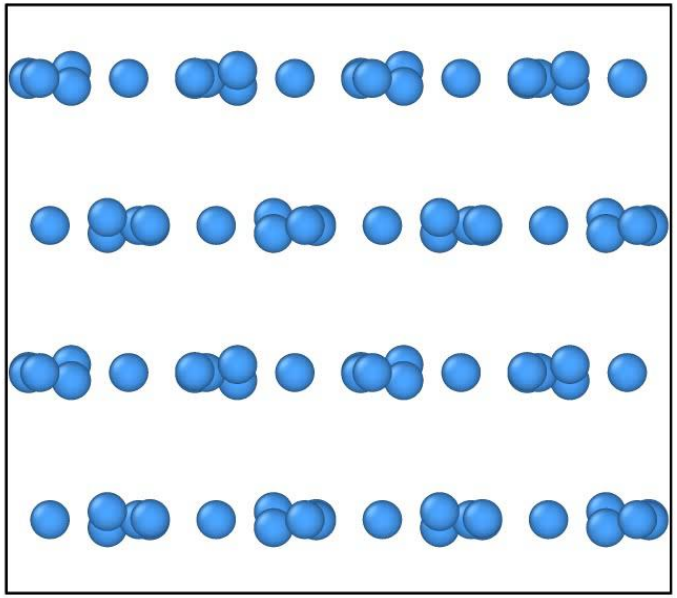
Formation of one or another molecular structure is a result of equilibration at the quantum molecular dynamics simulation

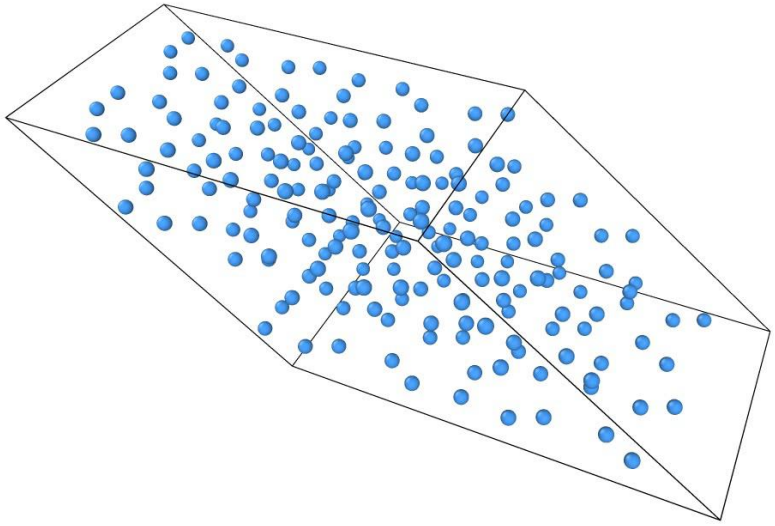
5. Conducting phase

MD at density 1.563 g/cm^3



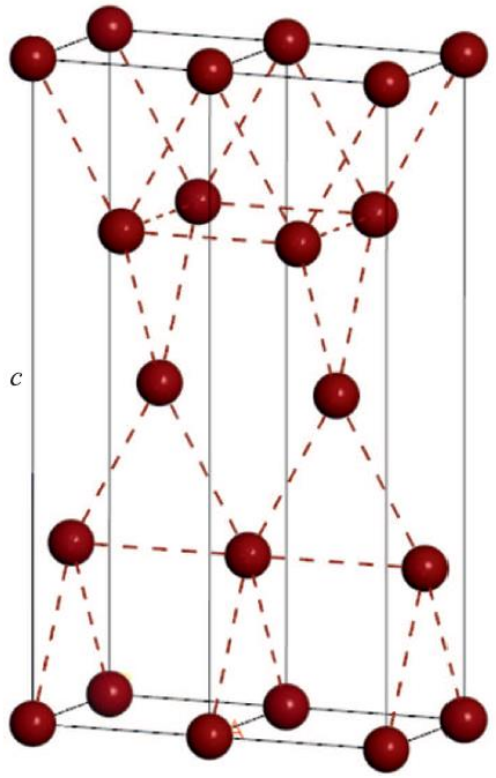






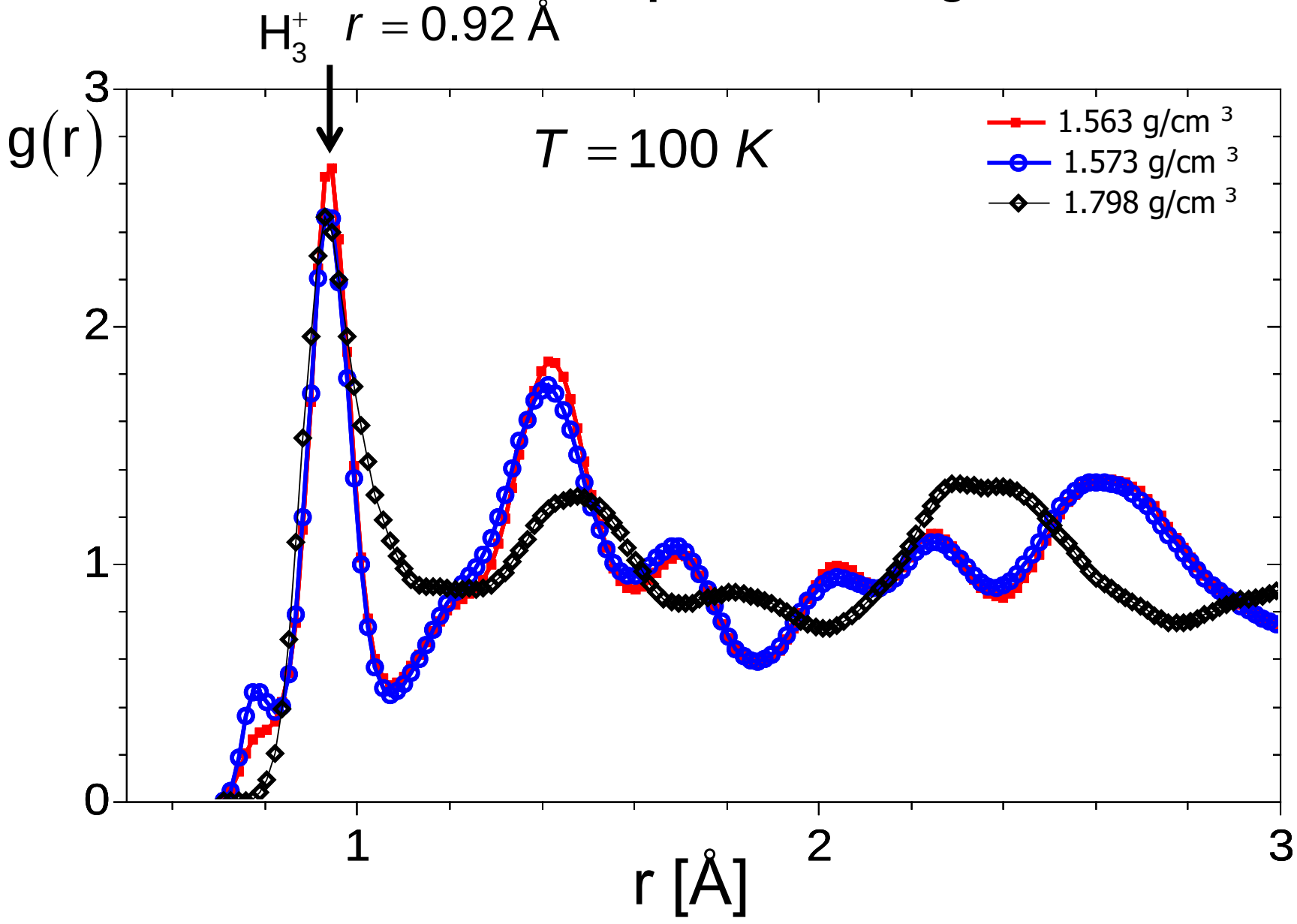
Conductivity at density 1.563 g/cm^3: 85300 (Ohm·cm)$^{-1}$

Space group: $I4_1/amd$



Н.Н. Дегтяренко, Е.А. Мазур. Устойчивая структура металлического водорода при давлении 500 ГПа // Письма в ЖЭТФ, **104**, №5, с. 329 – 333 (2016)

Pair correlation functions at pressure range 607 - 836 GPa



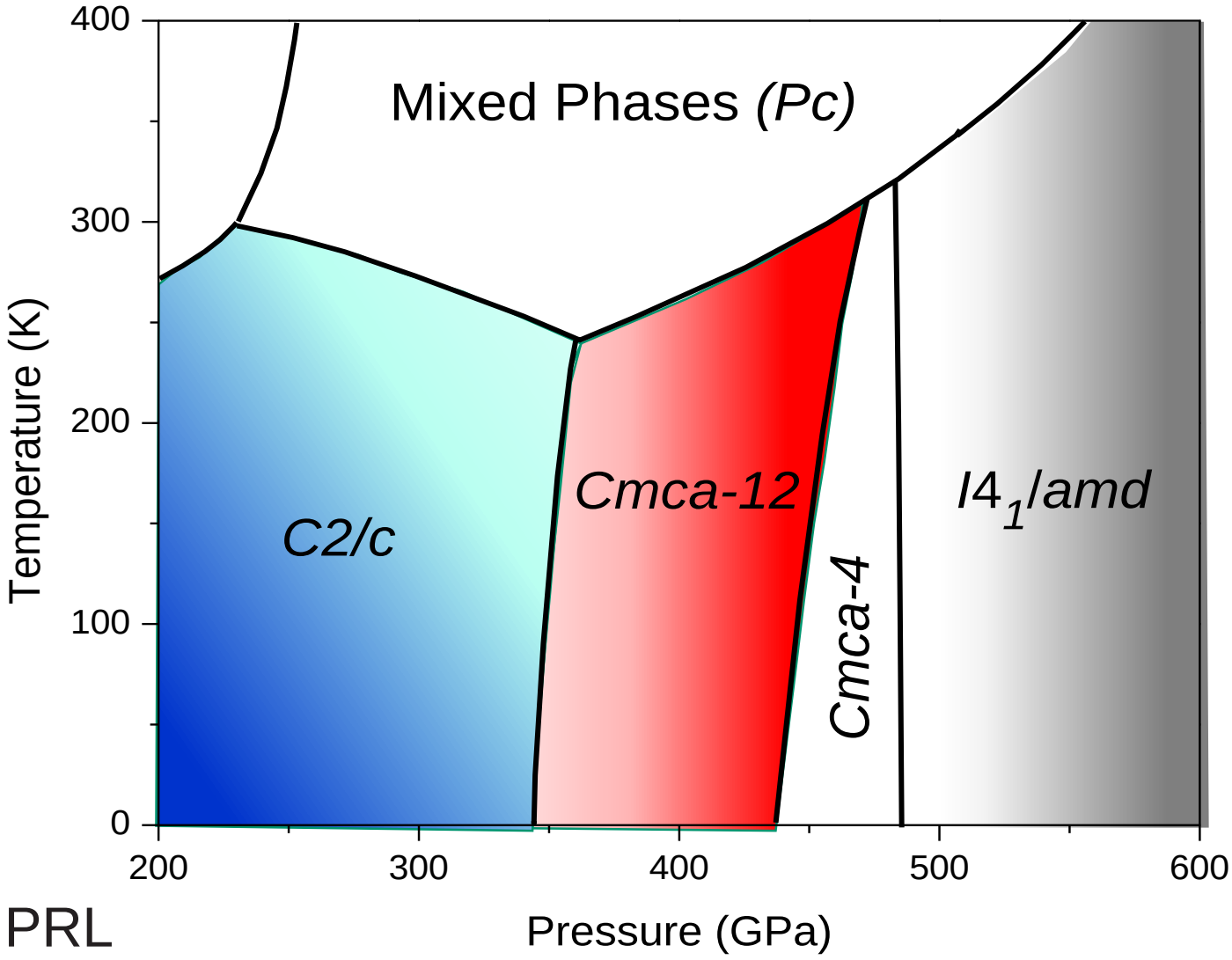
Comments

We do nothing to create
a new conducting structure.

We use the structure with C2/c space group as
the initial condition in each case.

Formation of the conducting structure
is a result of equilibration
at the quantum molecular dynamics simulation

Theoretical phase diagram of solid hydrogen



S. Azadi PRL 112, 165501 (2014)

6. Conclusions

Formation of the intermediate dielectric molecular phase and the final conducting phase is observed during one and the same molecular dynamic trajectory

The PCF peak arises at a distance 0.92 Å at a density of 1.563 g/cm^3 and a pressure of 607 GPa, and it remans at the same distance up to the 836 GPa. The distance 0.92 Å corresponds to the interatomic separation in H_3^+

Wigner and Huntington and all subsequent authors considered only the proton lattice formation at the transition to the conducting state.

Mechanism of the phase transition

1. Ionization

$$H_2 + Q_1 \rightarrow H_2^+ + e$$

2. Subsequent equilibration

$$H_2 + H_2^+ \rightarrow H_3^+ + H + Q_2$$