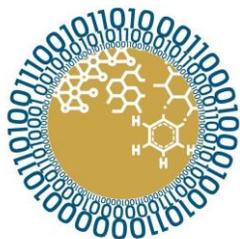




Динамические свойства флюида водорода при высоких давлениях

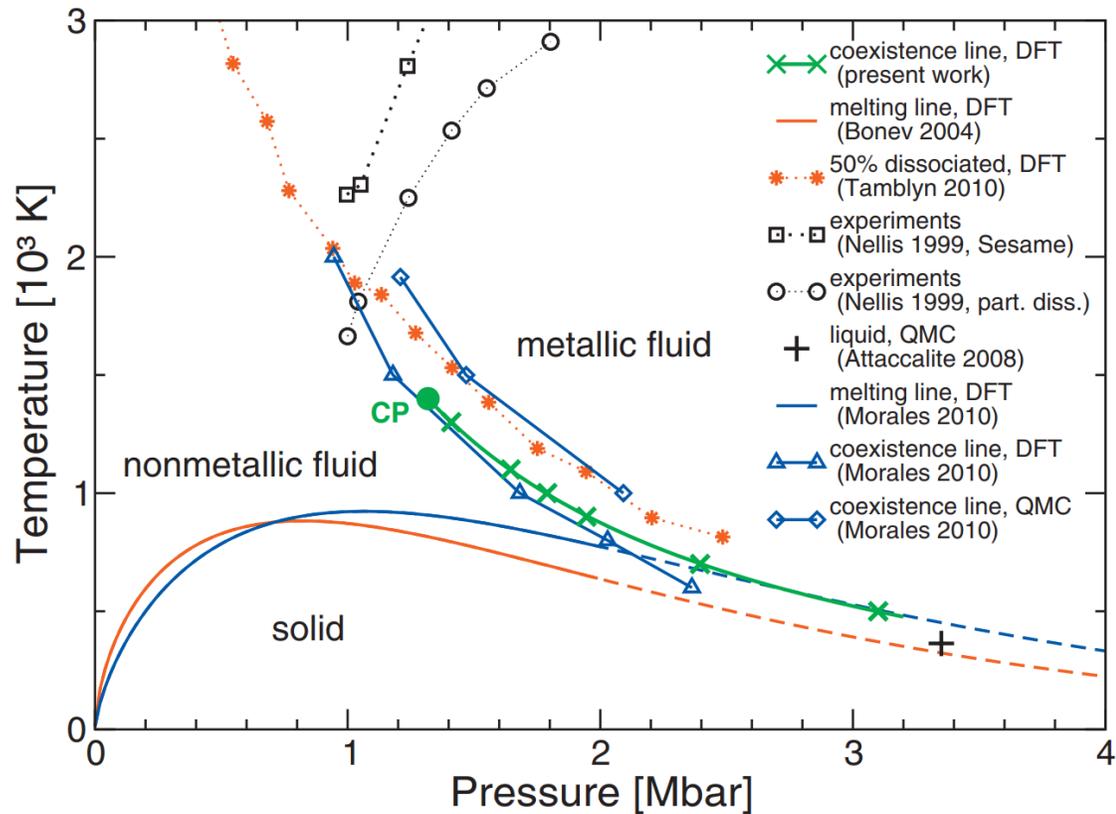
В.Г. Лукьянчук, Г. А. Гляудялис, И. М. Саитов, Н. М. Щелкачев, Николай Кондратюк

kondratyuk@phystech.edu



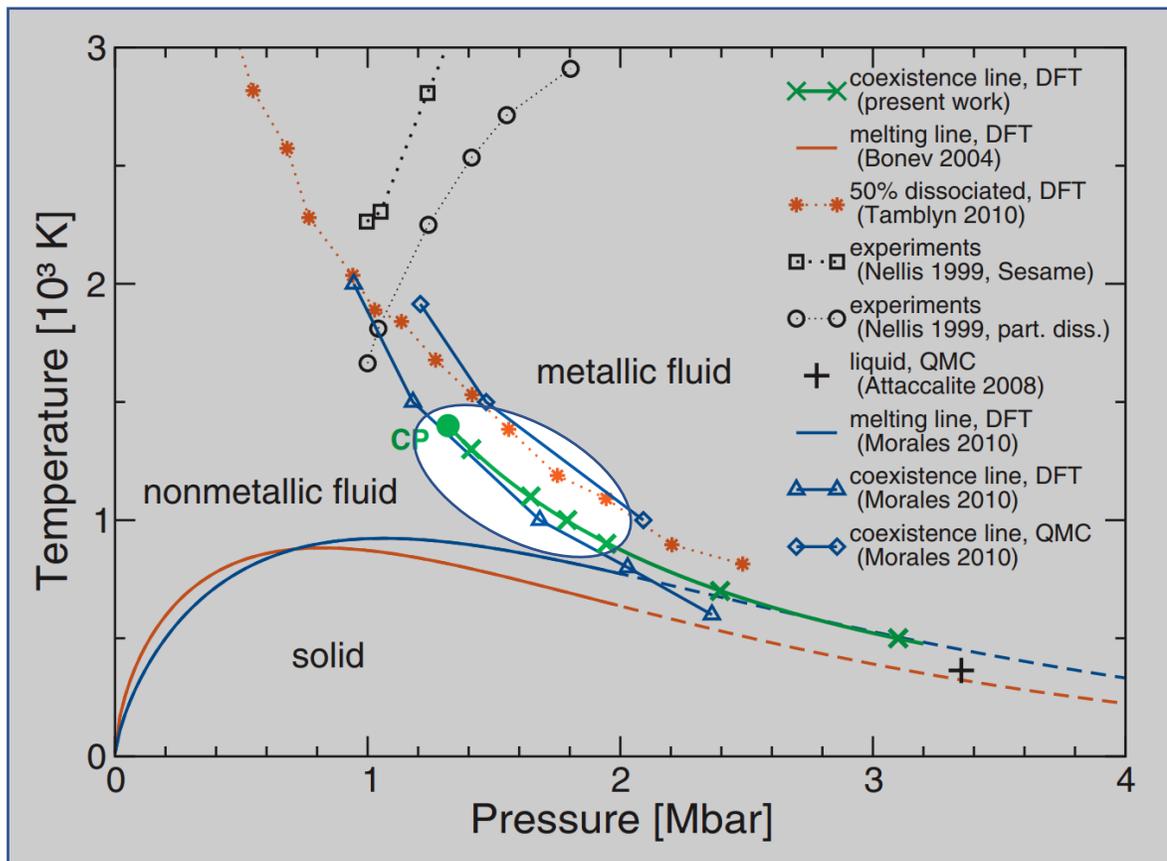
Центр
Вычислительной
Физики
ЛФИ МФТИ

Фазовый переход во флюиде водорода



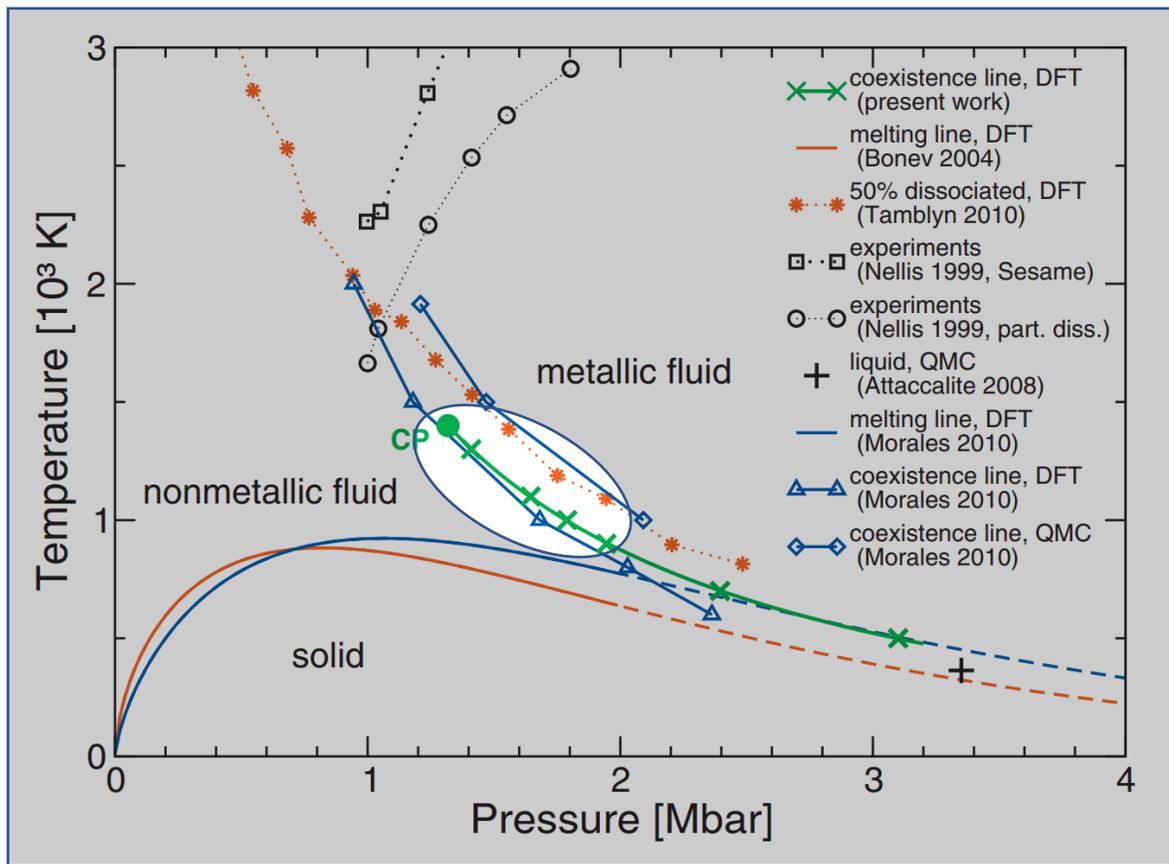
Фазовая диаграмма водорода при высоких давлениях из [1].
Зелёным предсказан фазовый переход жидкость-жидкость

Фазовый переход во флюиде водорода

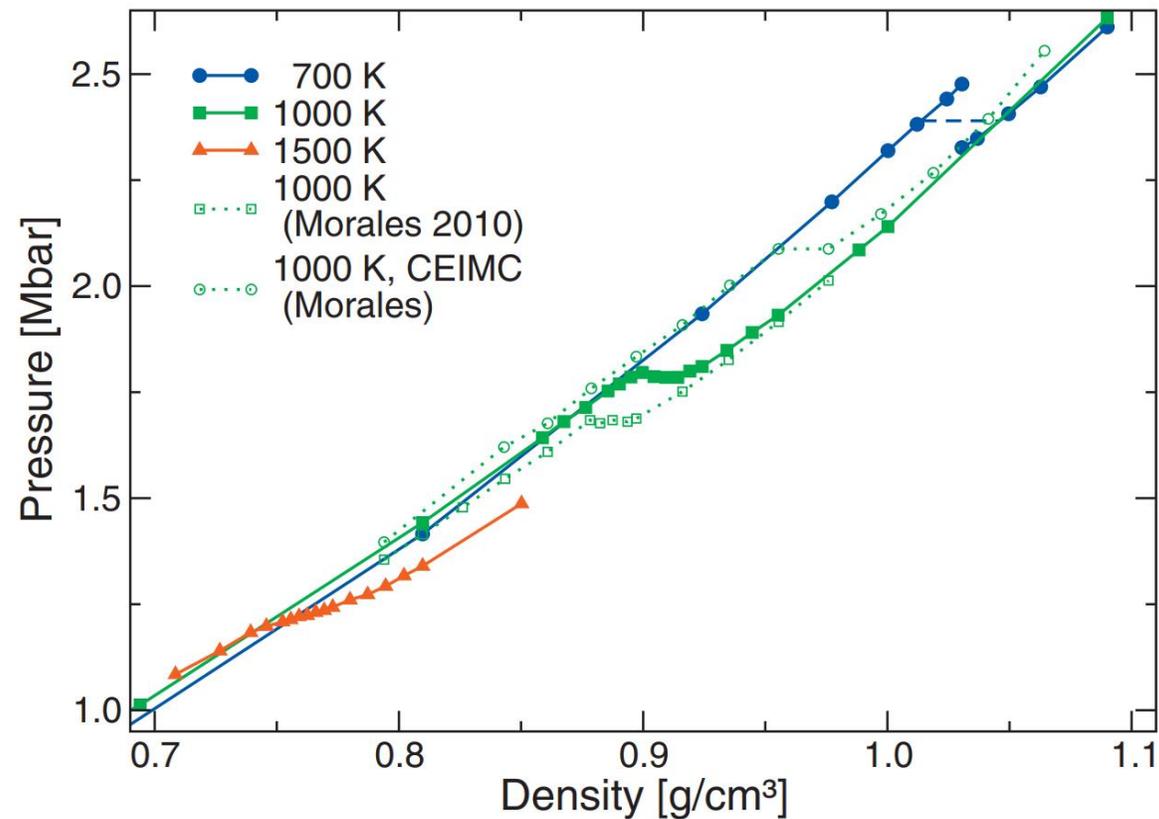


Фазовая диаграмма водорода при высоких давлениях из [1]. Зелёным предсказан фазовый переход жидкость-жидкость

Фазовый переход во флюиде водорода

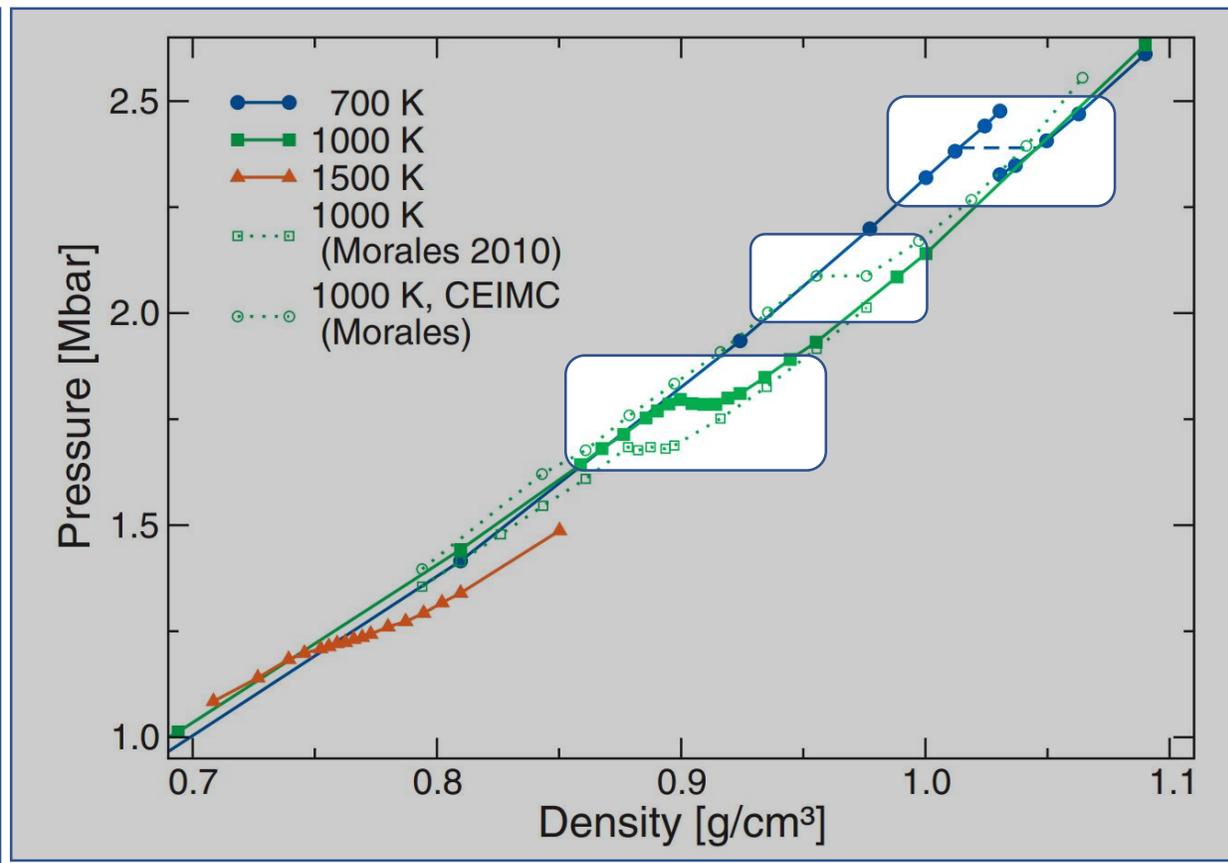
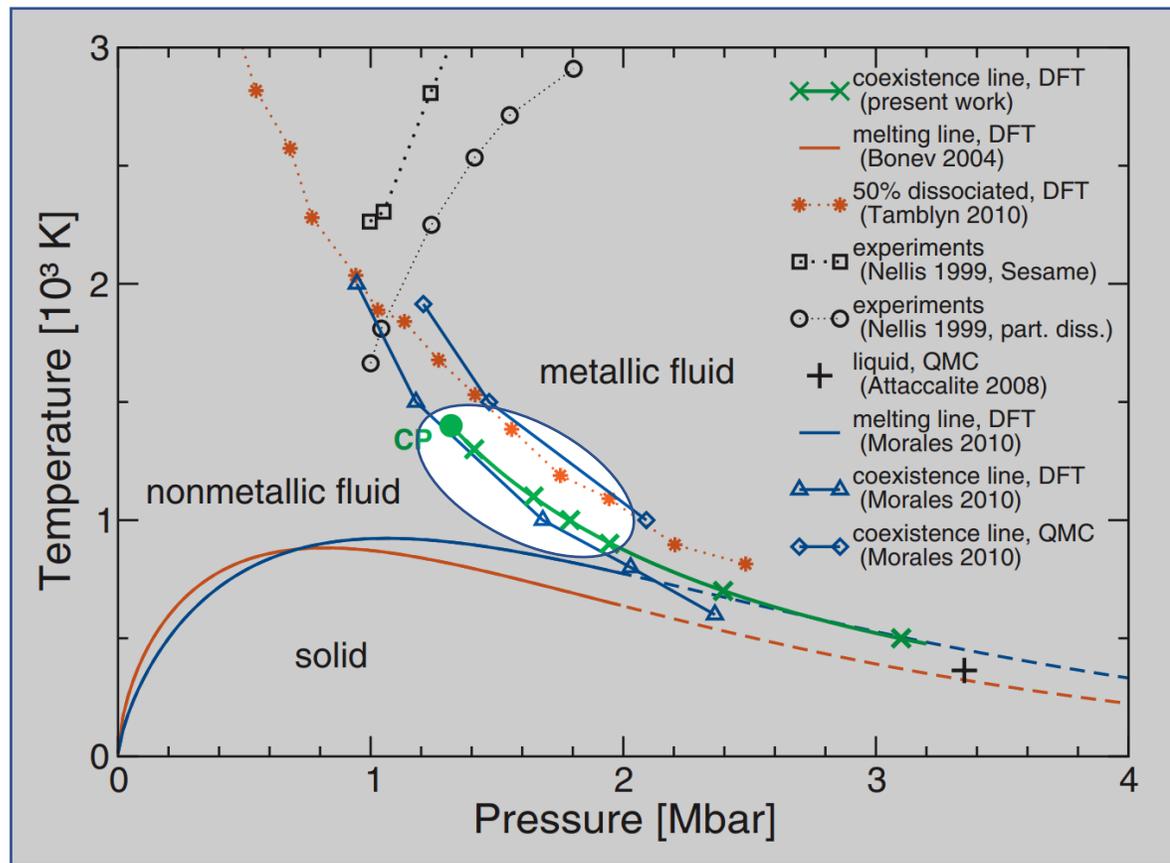


Фазовая диаграмма водорода при высоких давлениях из [1]. Зелёным предсказан фазовый переход жидкость-жидкость



Изотермы жидкого водорода при из [1]. Плато сигнализирует о наличии фазового перехода.

Фазовый переход во флюиде водорода



Фазовая диаграмма водорода при высоких давлениях из [1]. Зелёным предсказан фазовый переход жидкость-жидкость

Изотермы жидкого водорода при из [1]. Плато сигнализирует о наличии фазового перехода.

Article

Evidence for supercritical behaviour of high-pressure liquid hydrogen

<https://doi.org/10.1038/s41586-020-2677-y>

Bingqing Cheng^{1,2,3}, Guglielmo Mazzola⁴, Chris J. Pickard^{5,6} & Michele Ceriotti^{7,8}

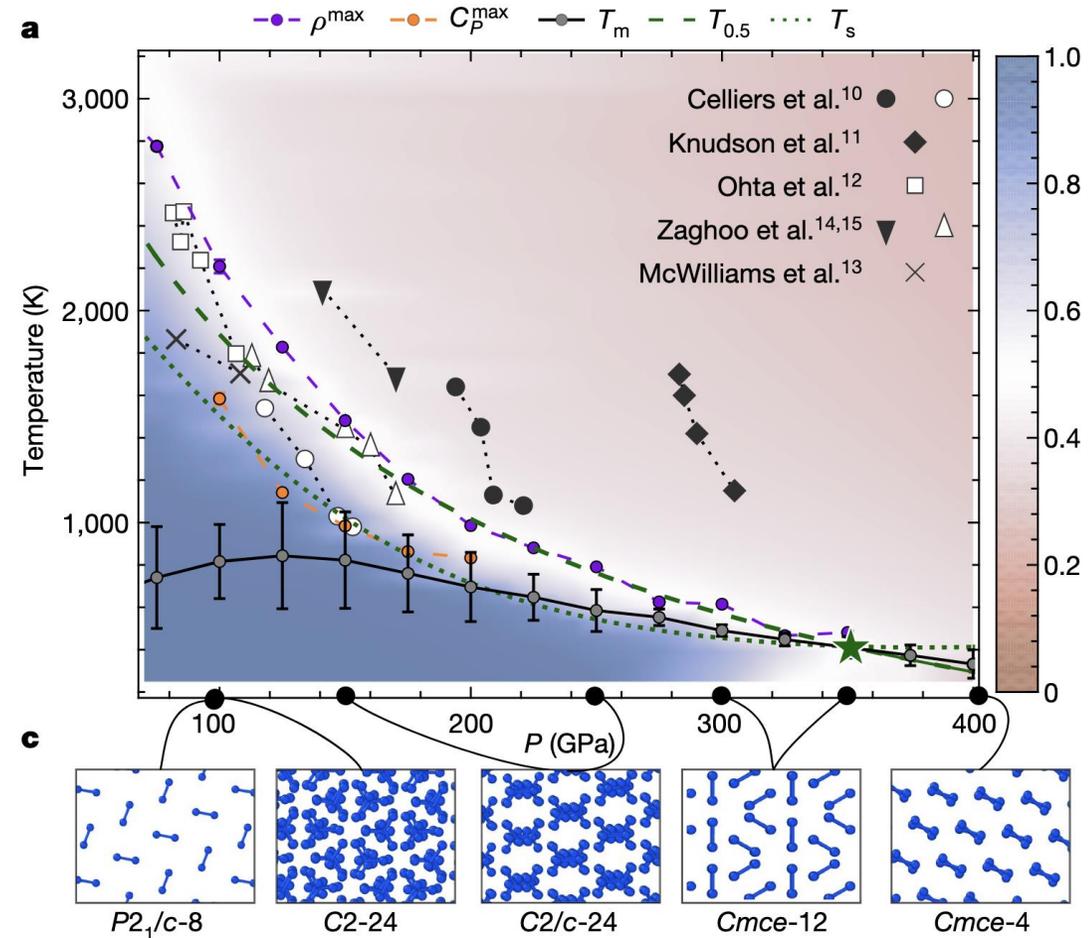
Received: 28 June 2019

Accepted: 10 July 2020

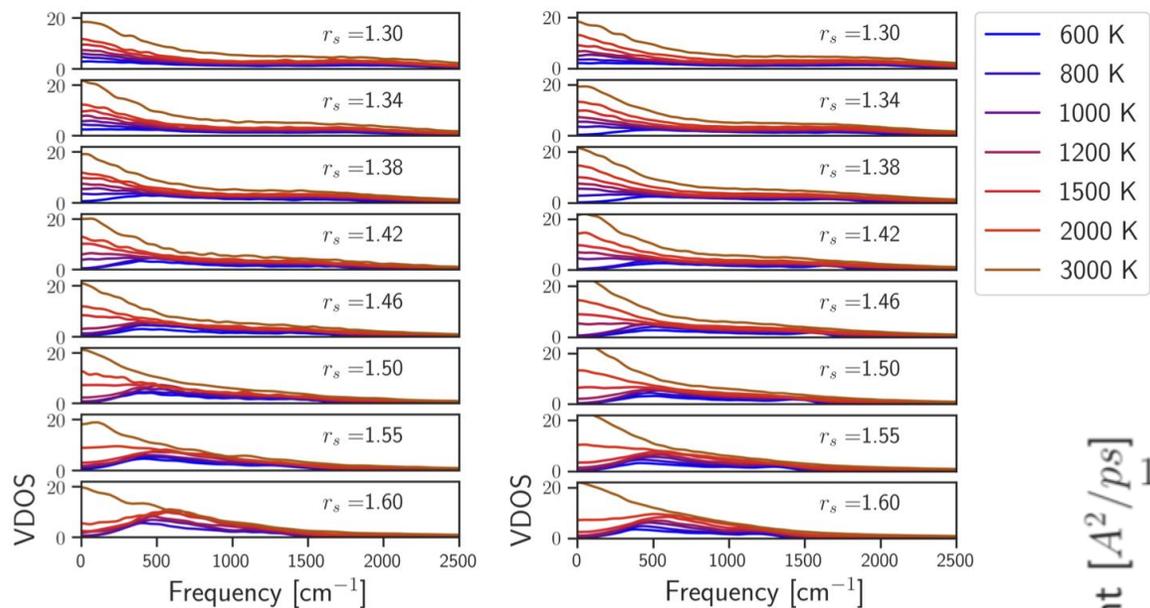
Published online: 9 September 2020

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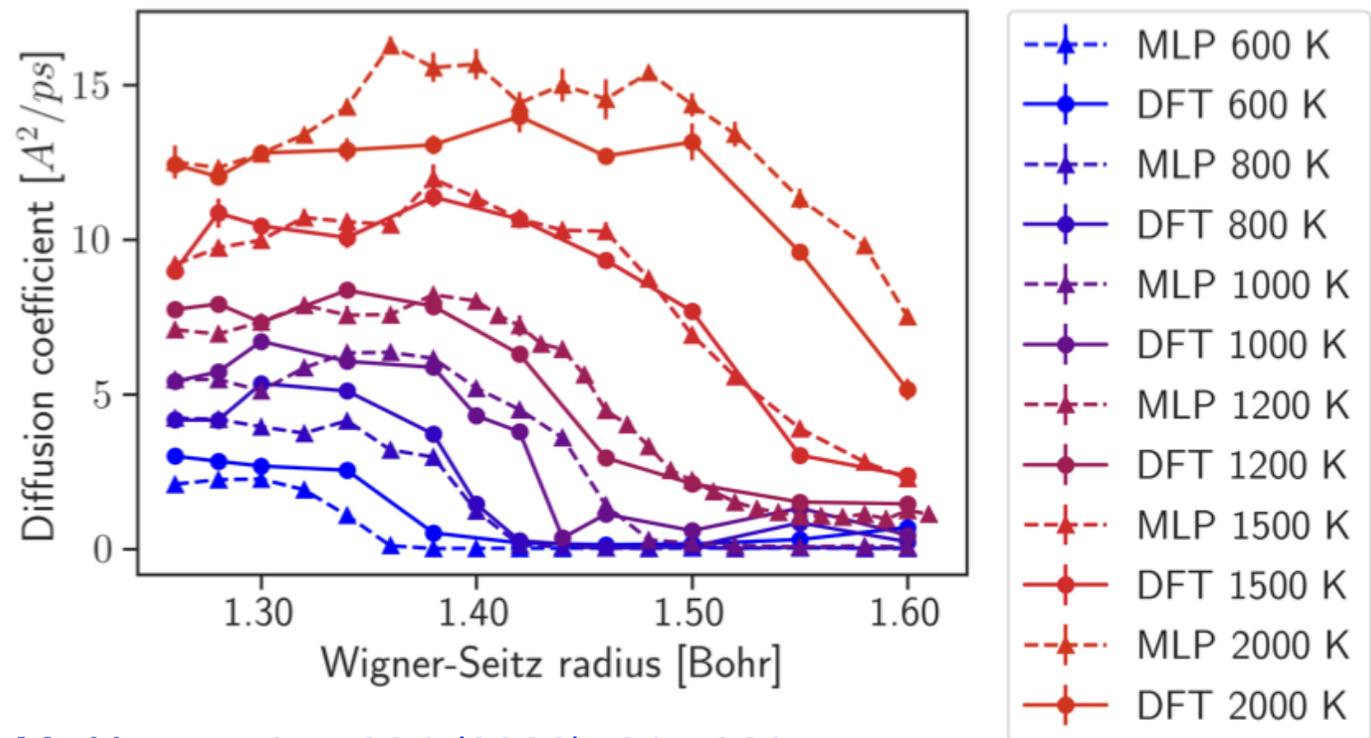
Hydrogen, the simplest and most abundant element in the Universe, develops a remarkably complex behaviour upon compression¹. Since Wigner predicted the dissociation and metallization of solid hydrogen at megabar pressures almost a century ago², several efforts have been made to explain the many unusual properties of dense hydrogen, including a rich and poorly understood solid polymorphism^{1,3–5}, an anomalous melting line⁶ and the possible transition to a superconducting state⁷. Experiments at such extreme conditions are challenging and often lead to hard-to-interpret and controversial observations, whereas theoretical investigations are constrained by the huge computational cost of sufficiently accurate quantum mechanical calculations. Here we present a theoretical study of the phase diagram of dense hydrogen that uses machine learning to ‘learn’ potential-energy surfaces and interatomic forces from reference calculations and then predict them at low computational cost, overcoming length- and timescale limitations. We reproduce both the re-entrant melting behaviour and the polymorphism of the solid phase. Simulations using our machine-learning-based potentials provide evidence for a continuous molecular-to-atomic transition in the liquid, with no first-order transition observed above the melting line. This suggests a smooth transition between insulating and metallic layers in giant gas planets, and reconciles existing discrepancies between experiments as a manifestation of supercritical behaviour.



Спектры



Скачок диффузии



Isotope Quantum Effects in the Metallization Transition in Liquid Hydrogen

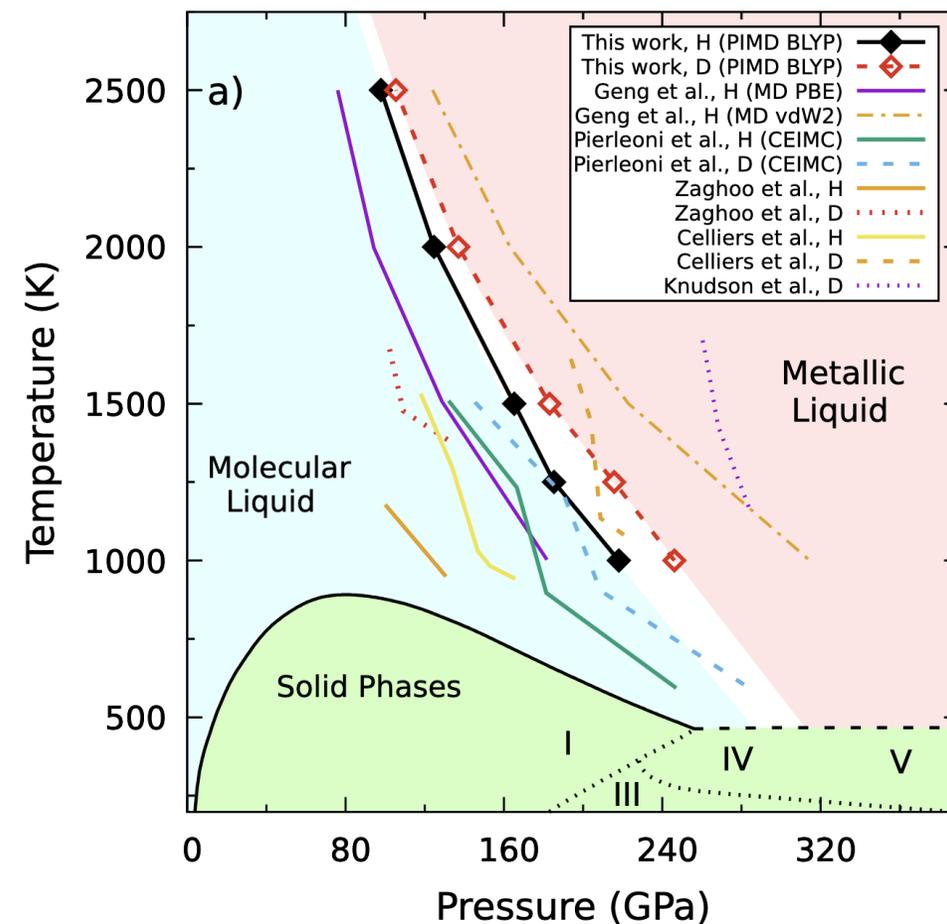
Sebastiaan van de Bund¹, Heather Wiebe¹, and Graeme J. Ackland¹

School of Physics & Astronomy, The University of Edinburgh, Edinburgh EH9 3FD, United Kingdom

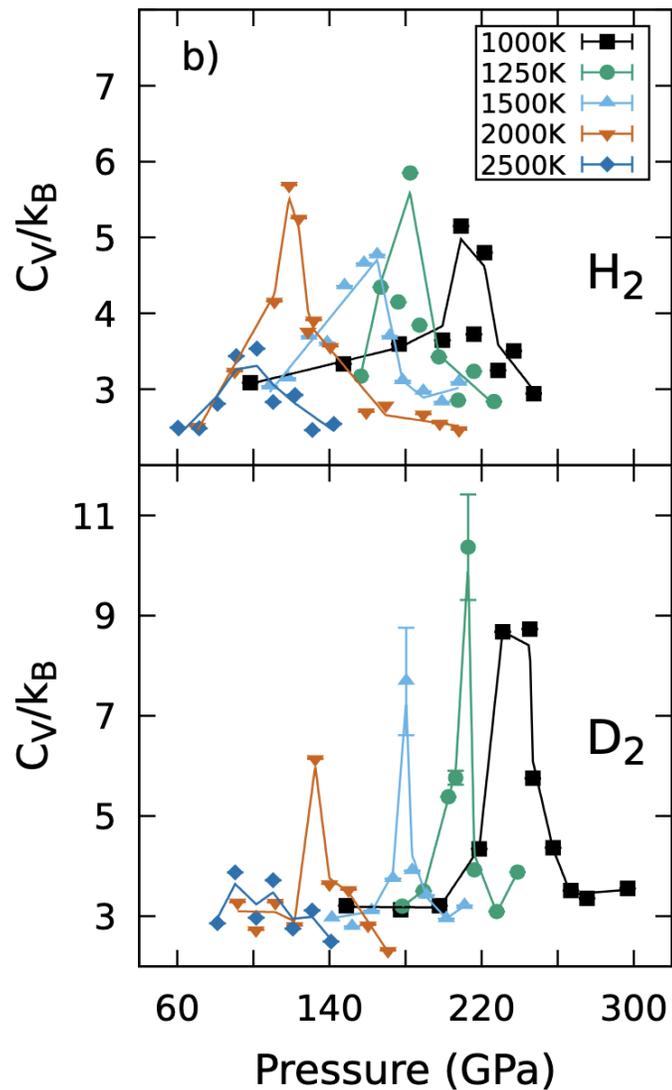
 (Received 13 September 2020; revised 12 November 2020; accepted 21 April 2021; published 2 June 2021)

Quantum effects in condensed matter normally only occur at low temperatures. Here we show a large quantum effect in high-pressure liquid hydrogen at thousands of Kelvins. We show that the metallization transition in hydrogen is subject to a very large isotope effect, occurring hundreds of degrees lower than the equivalent transition in deuterium. We examined this using path integral molecular dynamics simulations which identify a liquid-liquid transition involving atomization, metallization, and changes in viscosity, specific heat, and compressibility. The difference between H_2 and D_2 is a quantum mechanical effect that can be associated with the larger zero-point energy in H_2 weakening the covalent bond. Our results mean that experimental results on deuterium must be corrected before they are relevant to understanding hydrogen at planetary conditions.

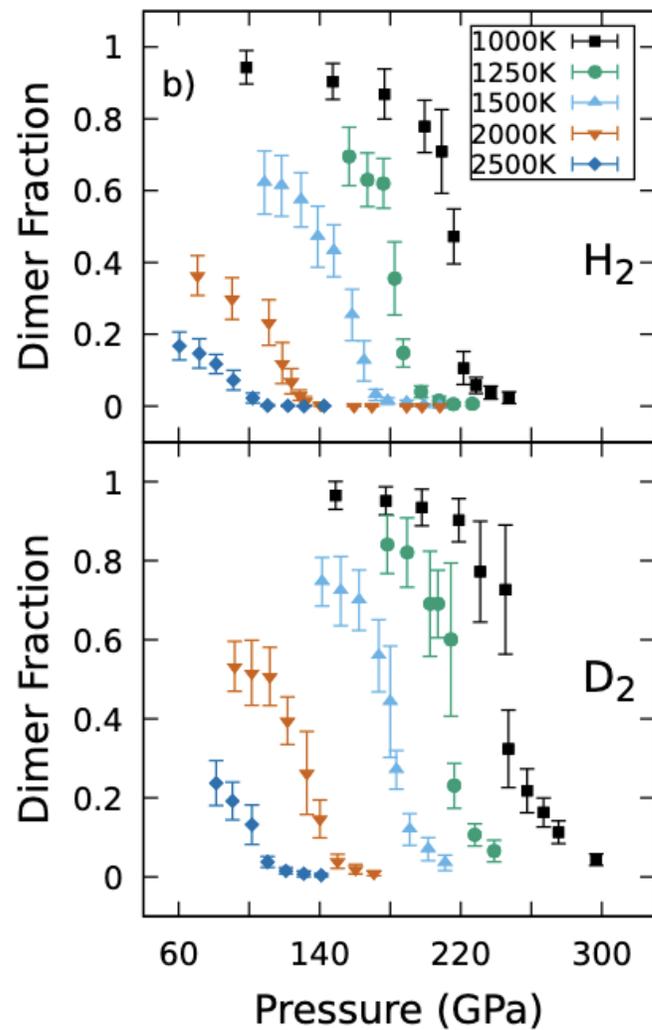
DOI: [10.1103/PhysRevLett.126.225701](https://doi.org/10.1103/PhysRevLett.126.225701)



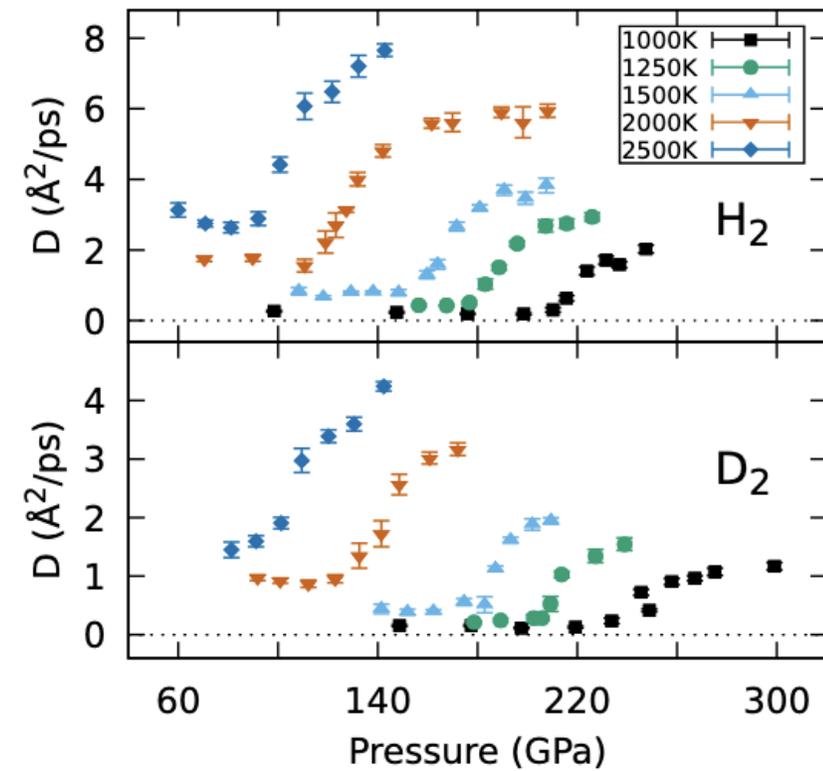
Теплоемкость



Распад молекул



Скачок диффузии



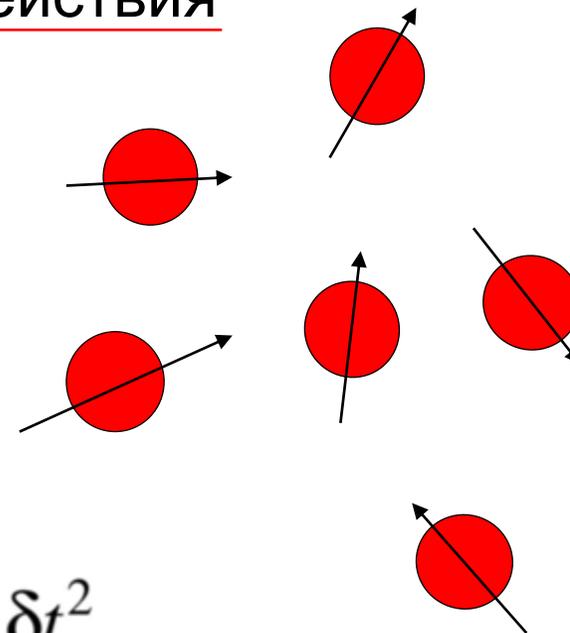
Метод классической МД

Силы между частицами определяются
аналитическим потенциалом взаимодействия

$$\mathbf{F} = -\nabla V(r) \quad \mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}$$

Уравнения движения атомов
решаются численно,

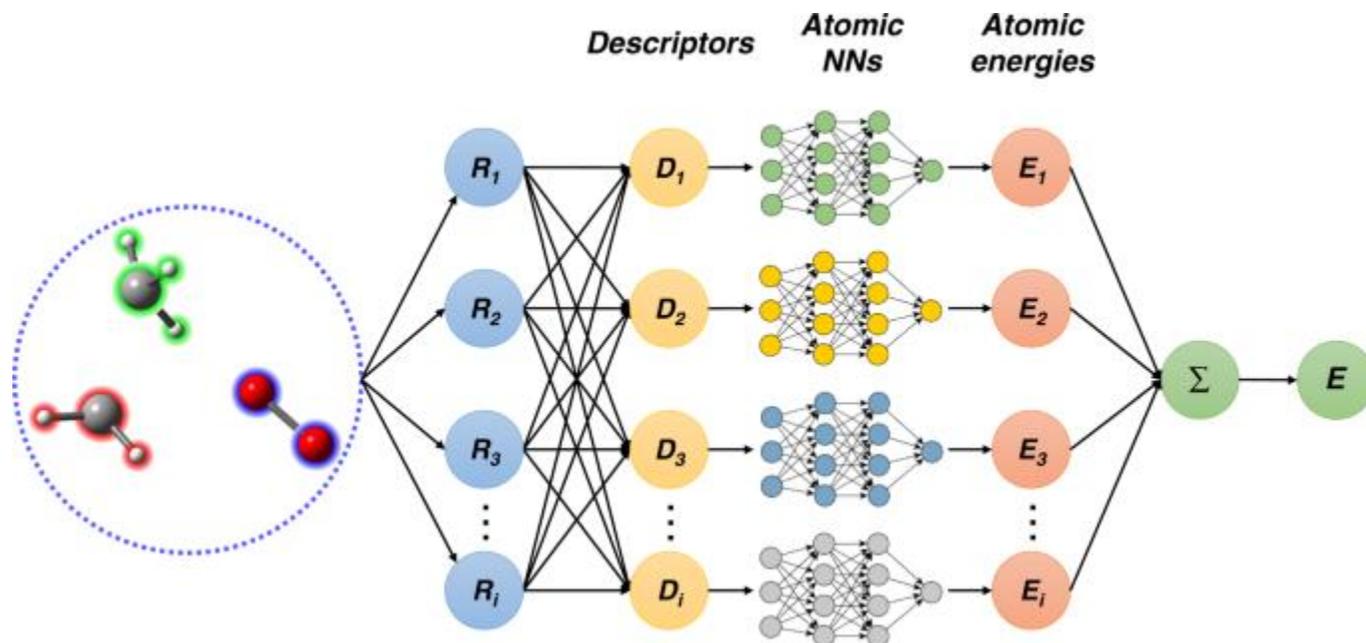
$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t)\delta t + \frac{1}{2}\vec{a}_i(t)\delta t^2$$



Glova, Volgin, Nazarychev, Larin, Lyulin, Gurtovenko // RSC Advances. 9 (66). 38834 (2019)

Bakulin, Kondratyuk, Lankin, Norman // J. Chem. Phys. 155(15). 154501 (2021)

DeepMD

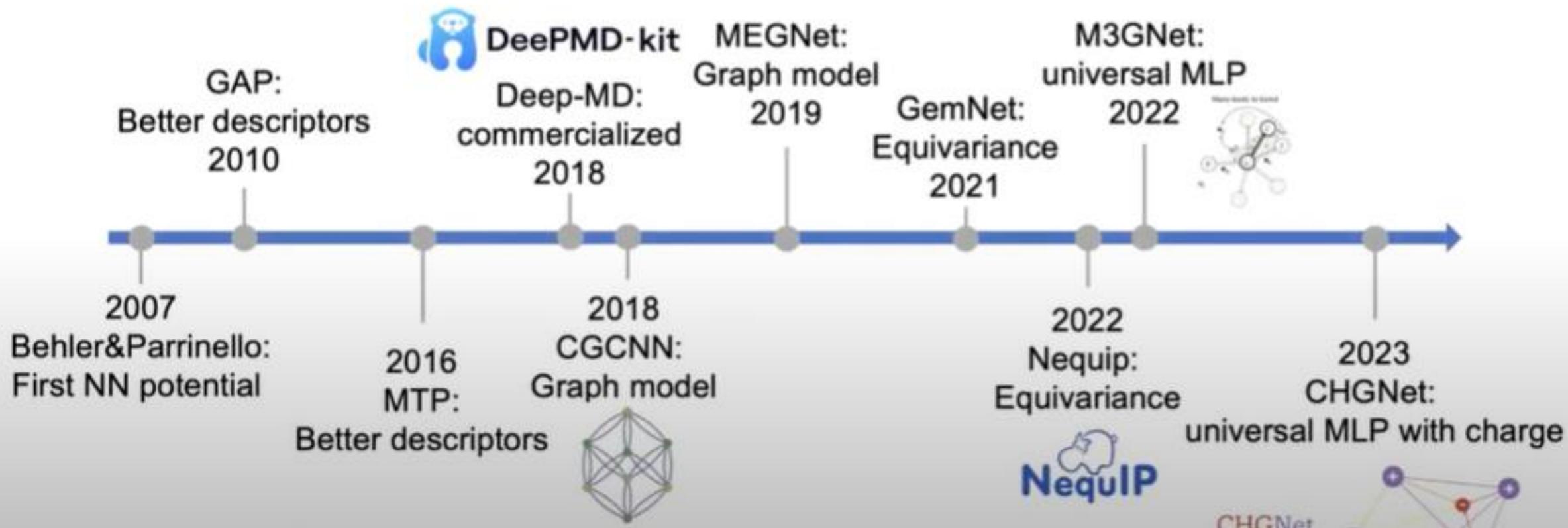


MLIPs are changing the way of atomistic simulations

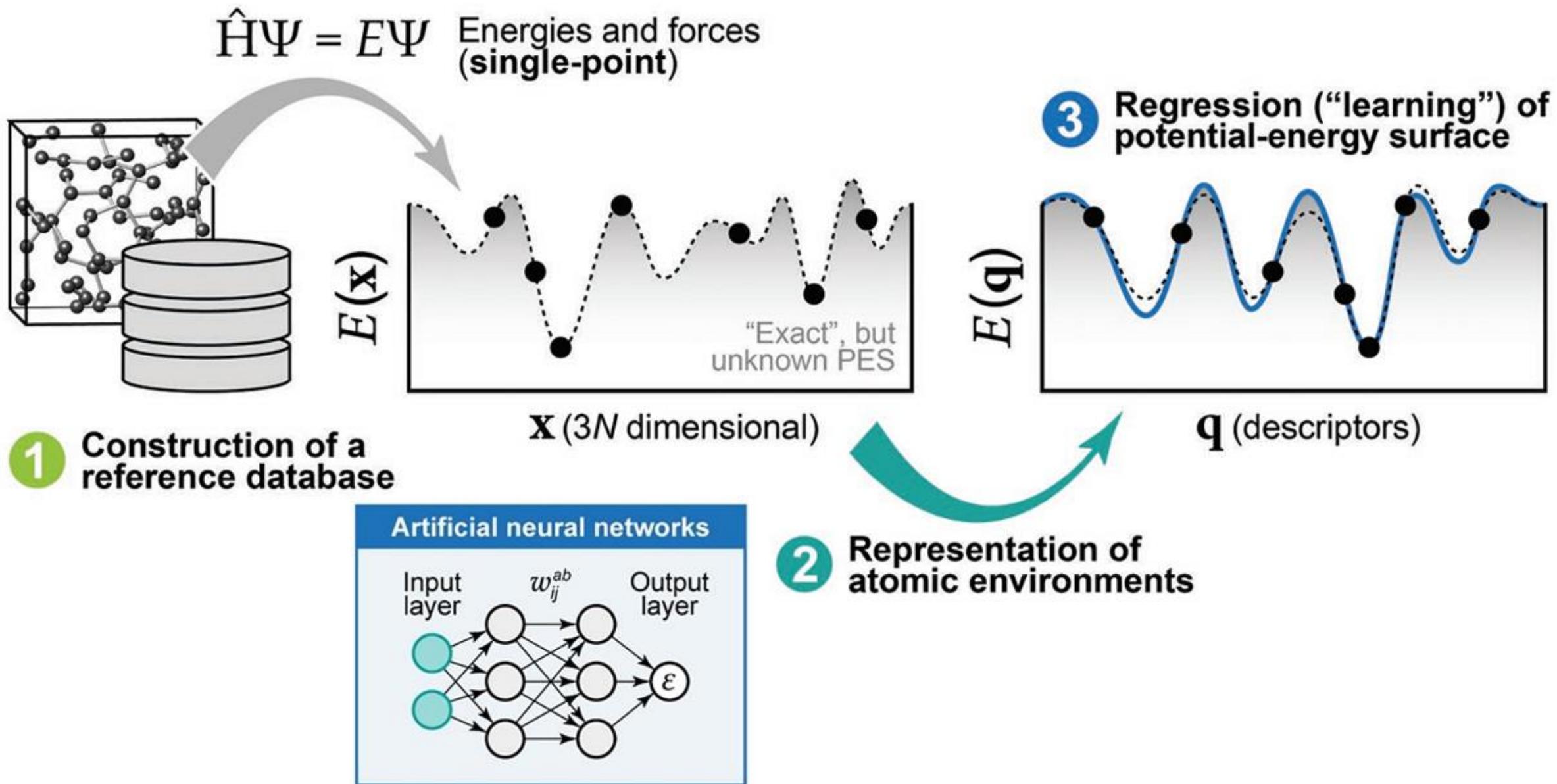


Better descriptors, more physical constraints

Increased data and model size



Deep Neural Network Potential (DNNP) modeling



Standard protocol



DFT calculations

Dataset

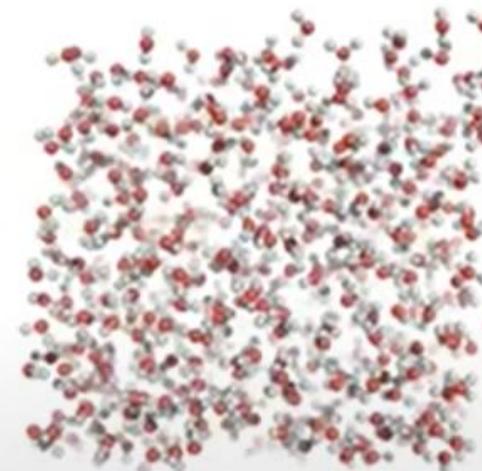
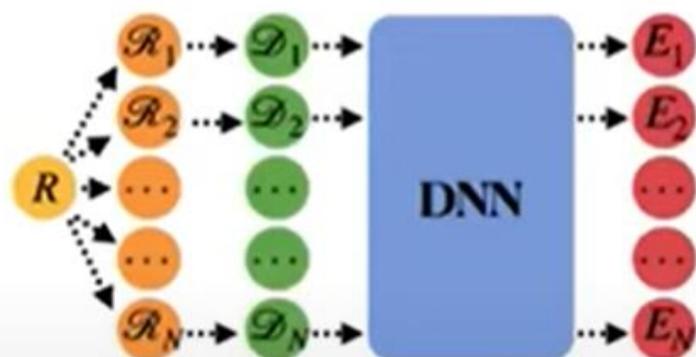


Labeled Dataset



- 1. Atomic species
- 2. Atomic coordinates
- 3. Simulation cell

- 1. Atomic species
- 2. Atomic coordinates
- 3. Simulation cell
- 4. Energy
- 5. Forces
- 6. Virial

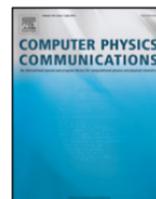




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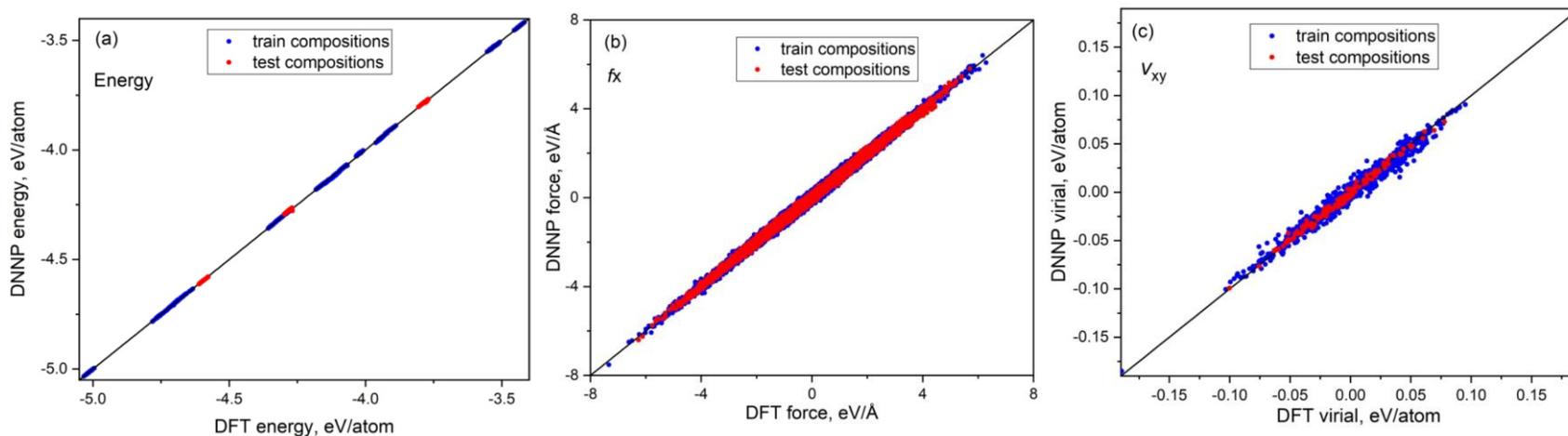
DeePMD-kit: A deep learning package for many-body potential energy representation and molecular dynamics[☆]

 Han Wang^{a,b,*}, Linfeng Zhang^{c,**}, Jiequn Han^c, Weinan E^{c,d,e}
^a Institute of Applied Physics and Computational Mathematics, Fenghao East Road 2, Beijing 100094, PR China

^b CAEP Software Center for High Performance Numerical Simulation, Huayuan Road 6, Beijing 100088, PR China

^c Program in Applied and Computational Mathematics, Princeton University, Princeton, NJ 08544, USA

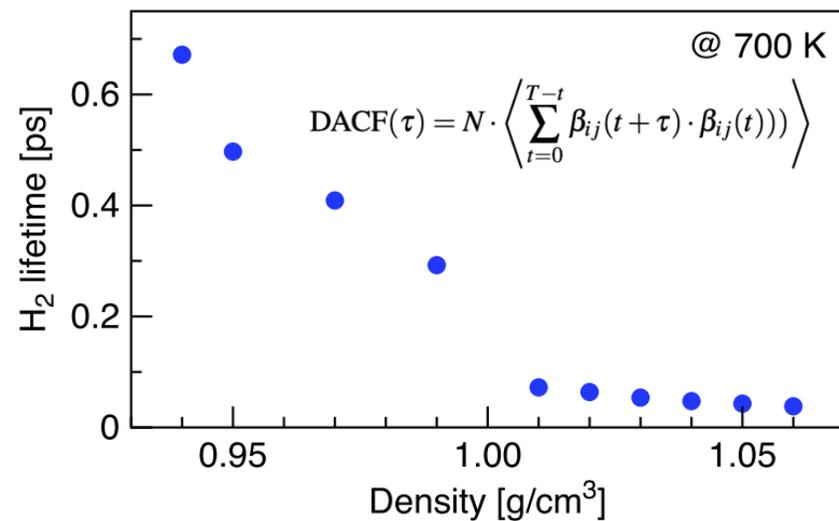
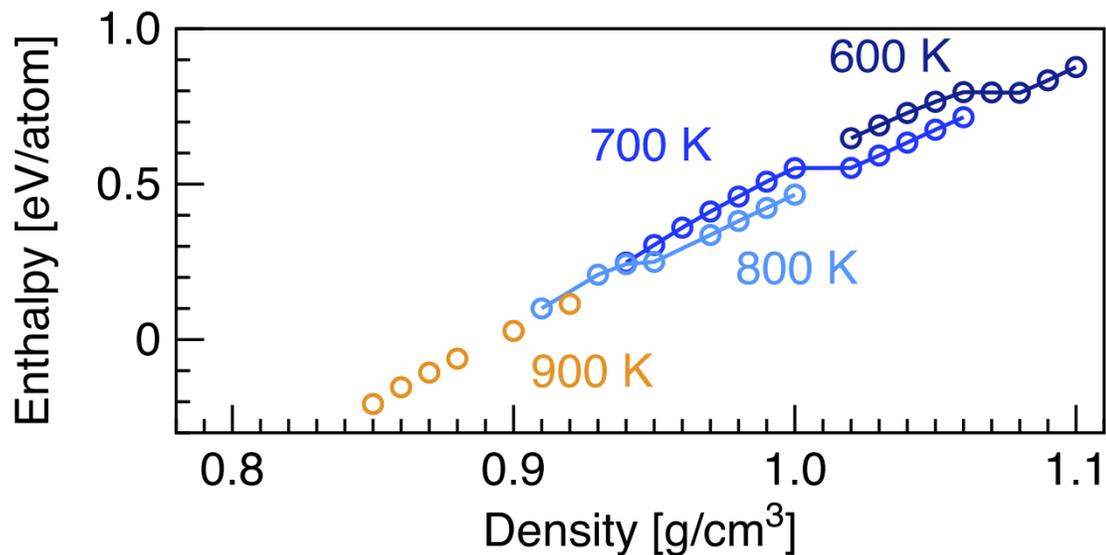
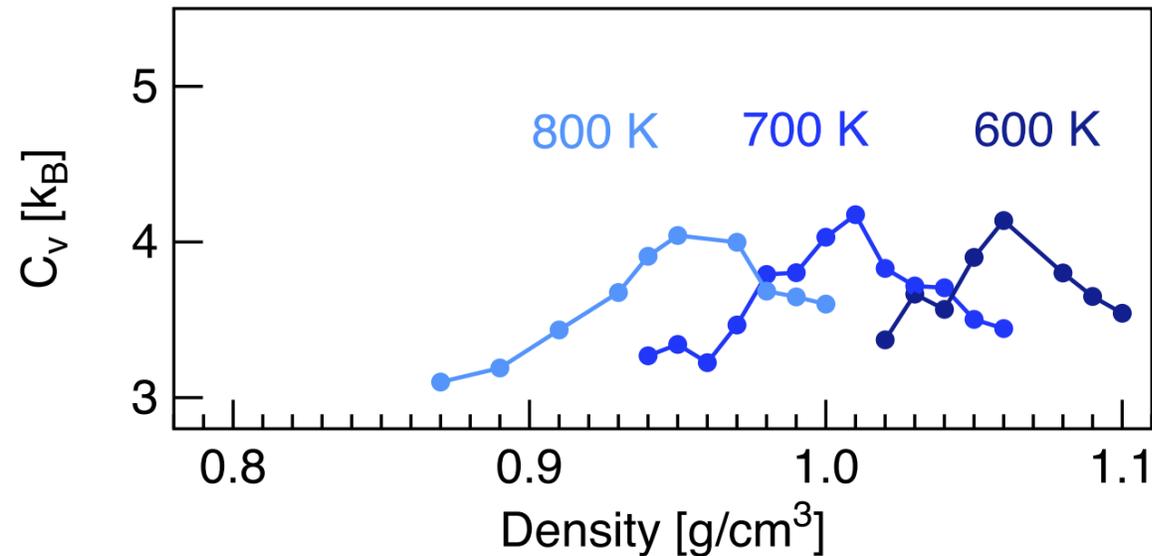
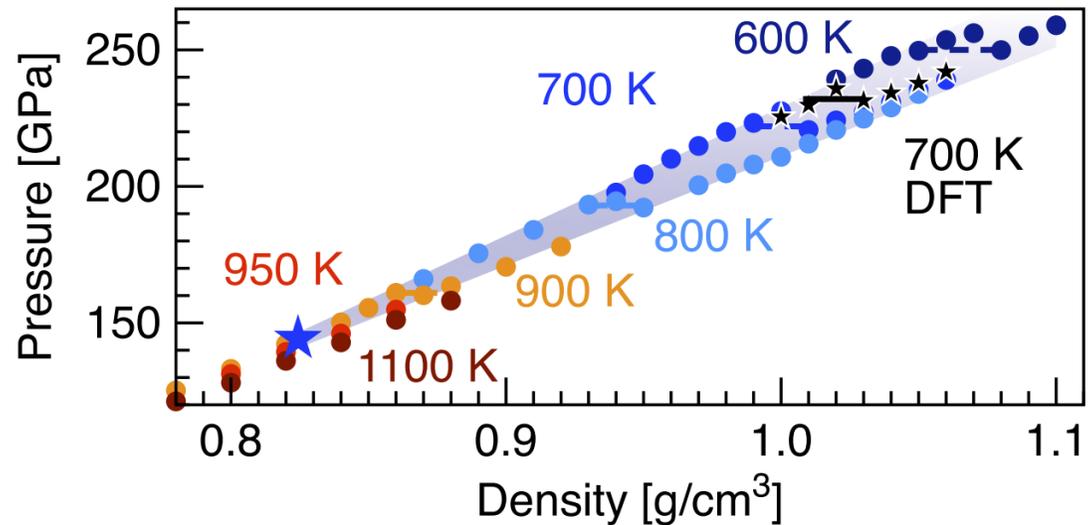
^d Department of Mathematics, Princeton University, Princeton, NJ 08544, USA

^e Beijing Institute of Big Data Research, Beijing, 100871, PR China


Среднеквадратичная ошибка
0.3 эВ/Å для сил и 0.8 мэВ/атом для энергий
по сравнению с DFT.

To describe the interactions in the hydrogen fluid, a temperature dependent^{78,79} DeePMD potential^{80,81} is trained based on the configurations calculated in VASP using the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional^{82–85} in the NVT ensemble at T=100–3000 K for the better sampling. The simulations are carried out using a cut-off kinetic energy limit of 1200 eV for the plane-wave basis set and 1000 *k*-points per reciprocal atom (kAtom)⁸⁶, an electronic convergence criterion of 10^{−6} eV is used together to Fermi smearing with the width following the ionic temperature in MD. The formation of the starting training dataset is based on the VASP quantum Molecular Dynamics (QMD). Then in the active learning approach (dpgen package⁸⁷), configurations for which the greatest uncertainty in the potential prediction is observed are selected from the classical MD trajectories with the pre-trained potential. For these configurations, an *ab initio* calculation of energies and forces is performed, they are added to the training set, and the potential is retrained. The DeepMD potential is prepared using “se-a” descriptors with “rcut-smth”=1.0 and “rcut”=4.0 (Å), and with 20 angle neurons; the embedding net and the fitting net have [32, 64, 128] and [240, 240, 240] neurons in the hidden layers correspondingly. The root-mean-square error of predicting the energy and forces by the created potential is 0.8 meV/atom and 0.3 eV/Å, respectively.

Термодинамика перехода в DeepMD



АКФС и спектры

1. Для равновесной траектории атомов рассчитать автокорреляционную функцию скорости

$$C_v(t) = \langle \vec{v}(0) \vec{v}(t) \rangle$$

Первый этап усреднения по атомам:

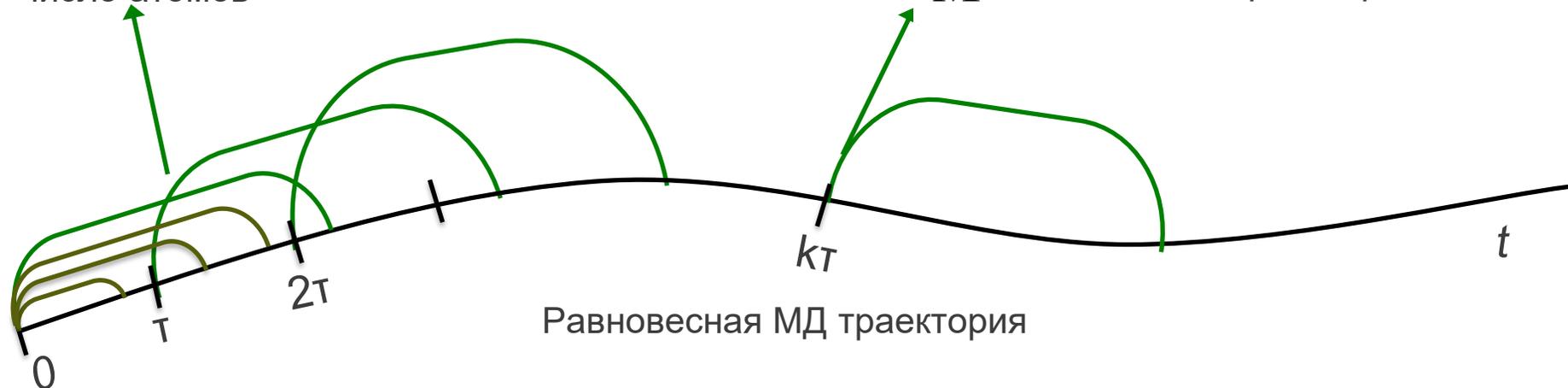
$$C_v(t) = \sum_N \vec{v}_i(0) \vec{v}_i(t) / N$$

N - число атомов

Второй этап усреднения по времени:

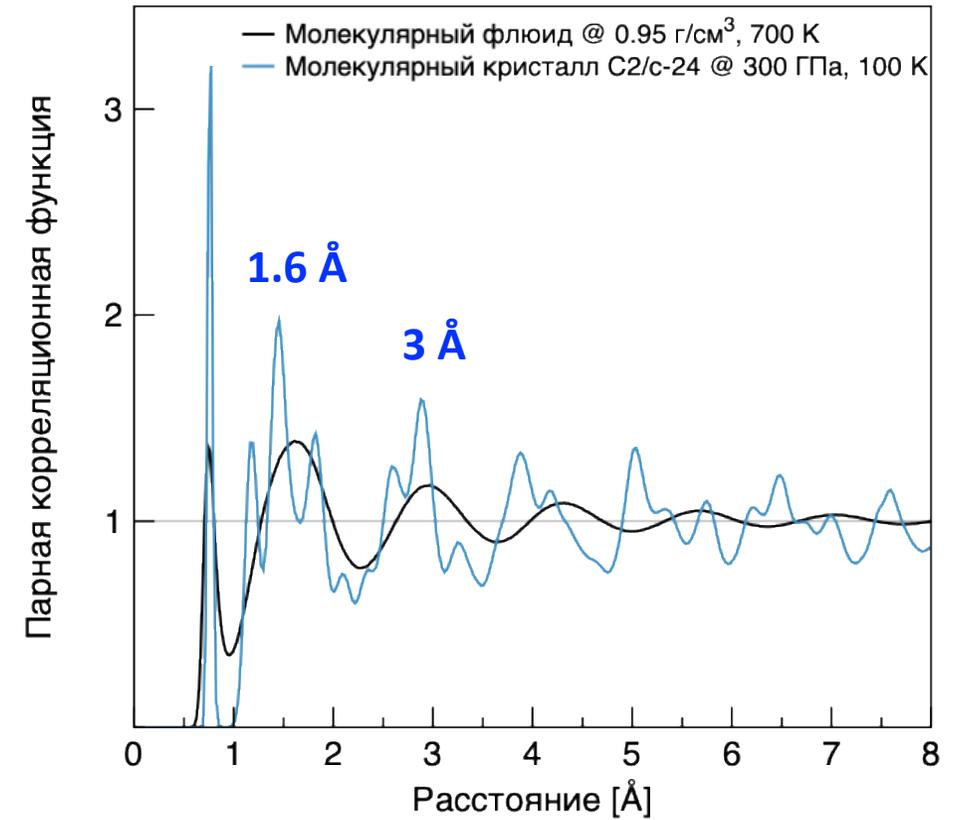
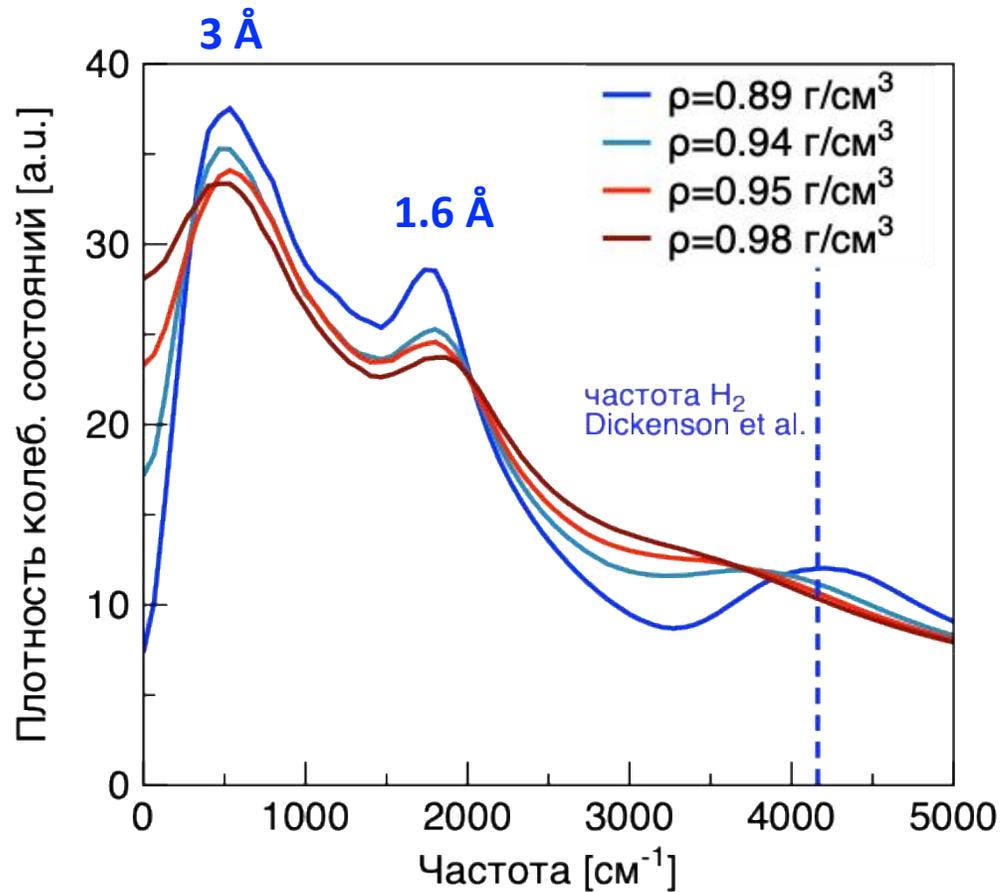
$$C_v(t) = \sum_k^M C_v(t)_{k\tau} / M$$

M - число точек траектории



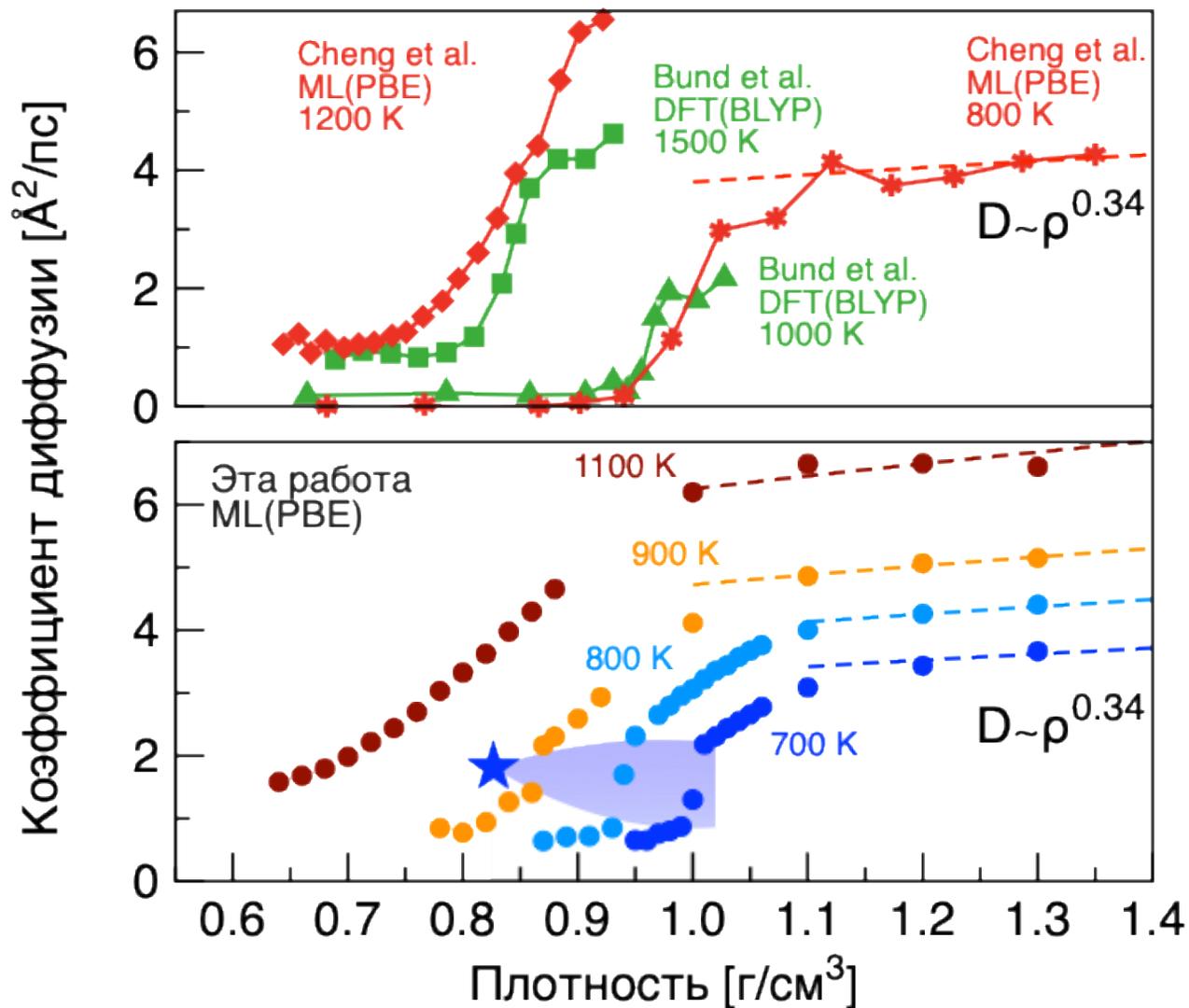
2. Рассчитать преобразование Фурье автокорреляционной функции скорости

АКФС и спектры



Скачок диффузии при соответствующих плотностях

$$\begin{aligned}
 D &= \lim_{t \rightarrow \infty} \frac{1}{2dt} \langle |x(t) - x(0)|^2 \rangle \\
 &= \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |r(t) - r(0)|^2 \rangle \\
 &= \lim_{t \rightarrow \infty} \frac{1}{d} \langle (r(t) - r(0)) \cdot v(t) \rangle \\
 &= \lim_{t \rightarrow \infty} \frac{1}{d} \int_0^t d\tau \langle v(\tau) \cdot v(t) \rangle \\
 &= \lim_{t \rightarrow \infty} \frac{1}{d} \int_0^t d\tau \langle v(0) \cdot v(t - \tau) \rangle \\
 &= \frac{1}{d} \int_0^\infty dt \langle v(0) \cdot v(t) \rangle
 \end{aligned}$$

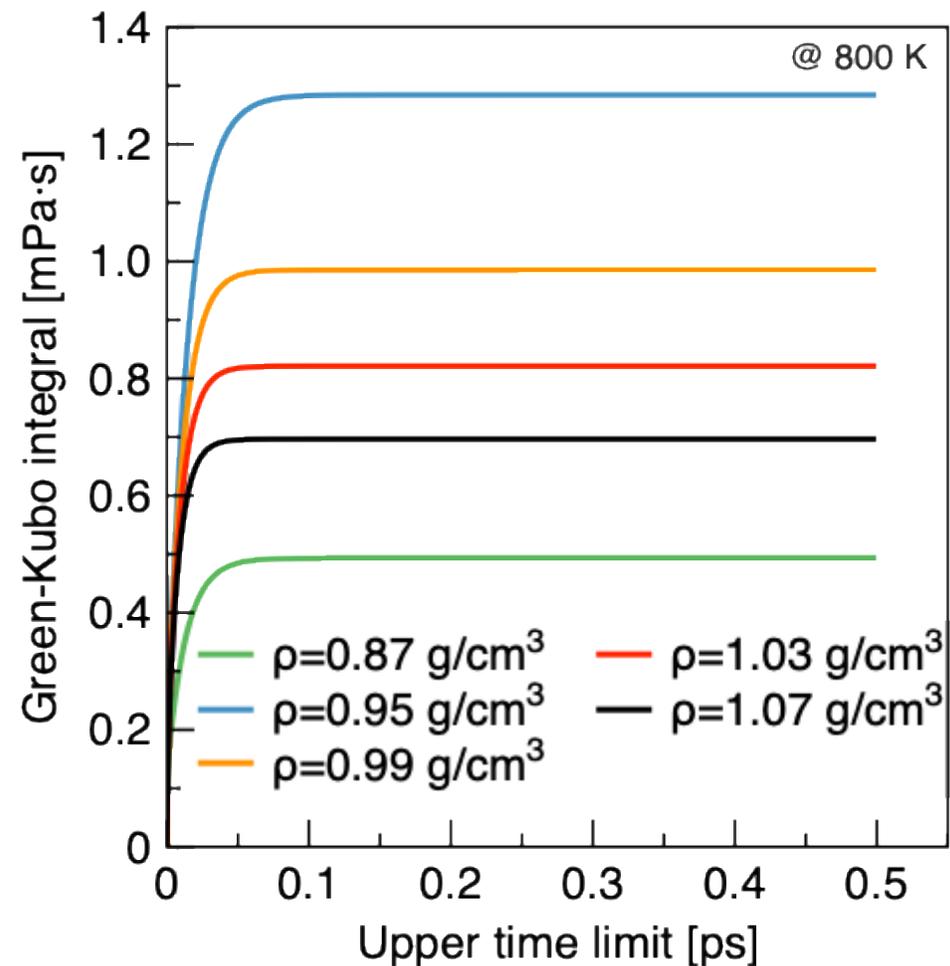


Метод Грина-Кубо для вязкости

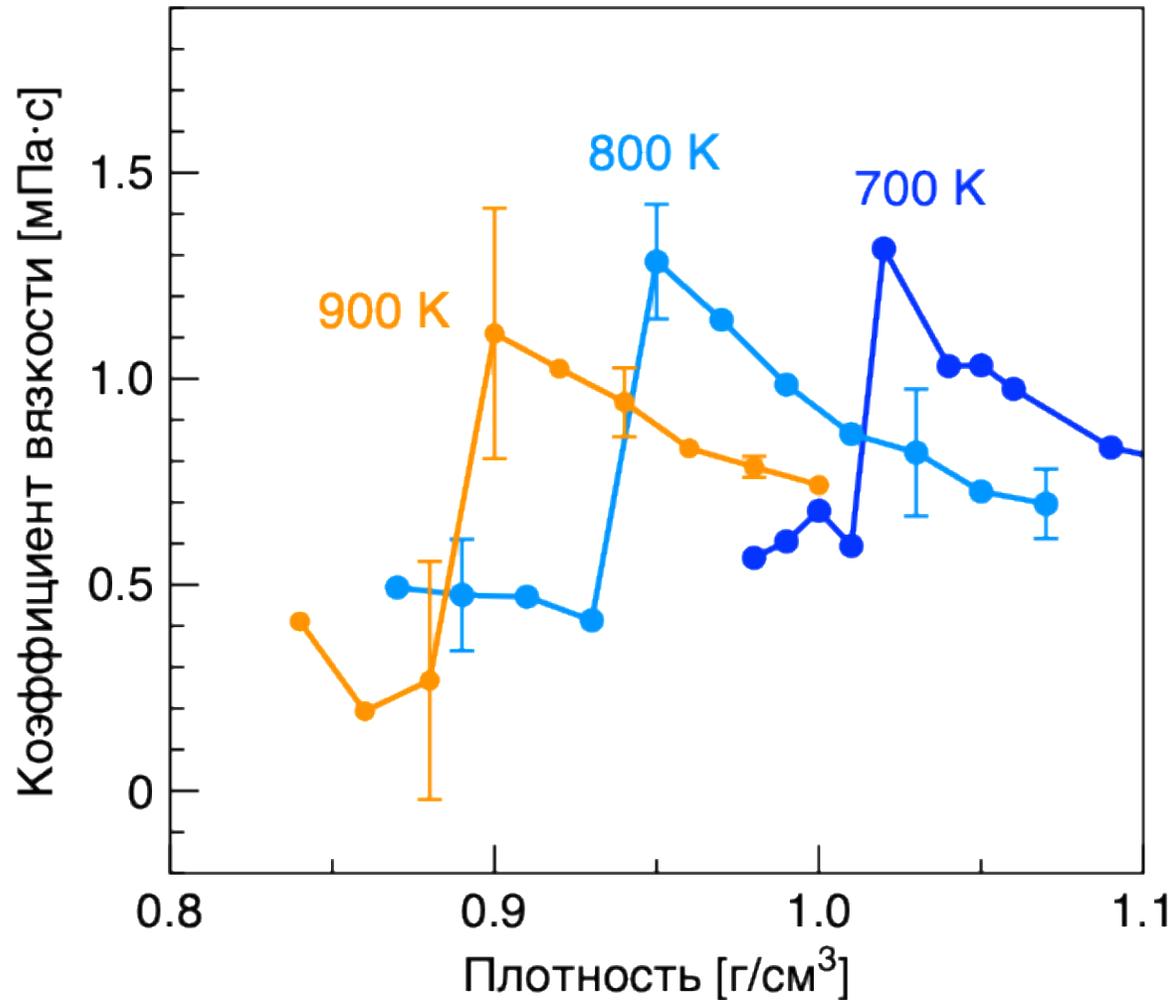
$$\sigma_{\alpha\beta}V = \sum_{i=1}^N m_i v_{i\alpha} v_{i\beta} + \sum_{i=1}^{N'} r_{i\alpha} f_{i\beta}$$

$$C_{\sigma}(t) = \langle \sigma_{\alpha\beta}(0) \sigma_{\alpha\beta}(t) \rangle$$

$$\eta_{\alpha\beta} = \frac{V}{k_B T} \int_0^{\infty} C_{\sigma}(t) dt$$



Скачок вязкости при соответствующих плотностях



Вязкость флюида водорода близка к значениям вязкости жидкого Li (~0.5 мПа с).

Вязкость флюида водорода при высоких давлениях может вести себя так же, как и для расплавов щелочных металлов.

Оценка размерного эффекта

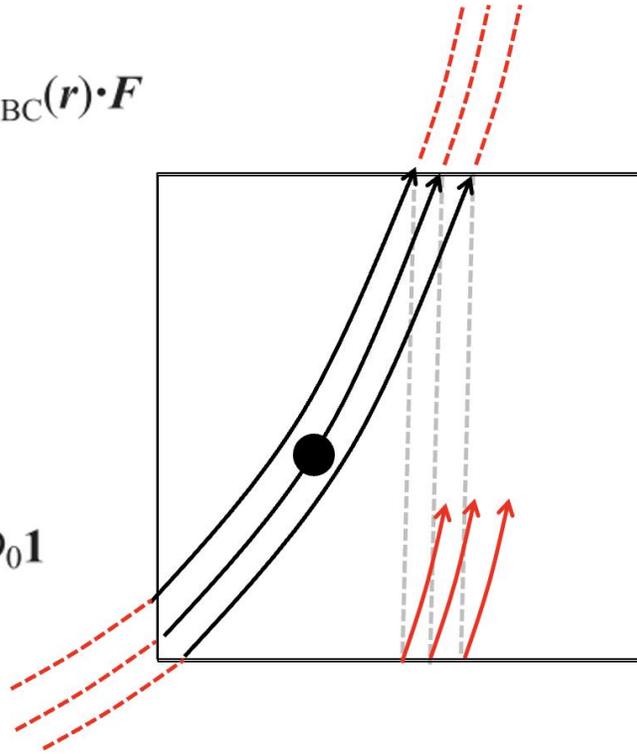
For Periodic Boundary Conditions:

$$T_{\text{PBC}}(\mathbf{r}) = \sum_{\mathbf{k} \neq 0} \frac{\exp(-i\mathbf{k} \cdot \mathbf{r})}{\eta k^2 V} \left(\mathbf{1} - \frac{\mathbf{k}\mathbf{k}}{k^2} \right)$$

For infinite system:

$$T_0(\mathbf{r}) = \frac{1}{8\pi\eta r} \left(\mathbf{1} + \frac{\mathbf{r}\mathbf{r}}{r^2} \right) = (k_B T)^{-1} D_0 \mathbf{1}$$

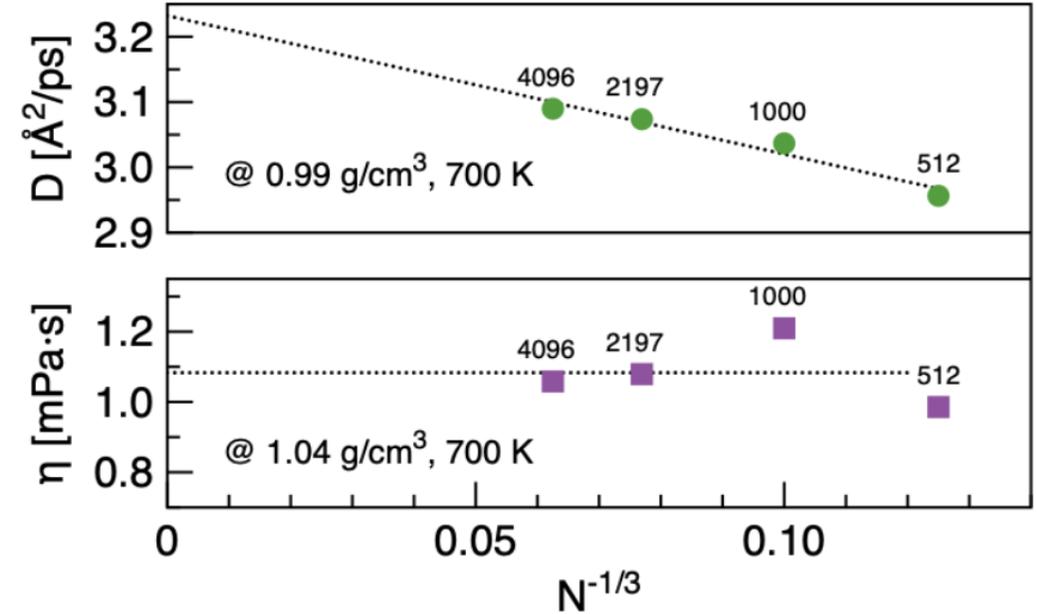
$$\mathbf{v}(\mathbf{r}) = T_{\text{PBC}}(\mathbf{r}) \cdot \mathbf{F}$$



$$D_{\text{PBC}} = D_0 \mathbf{1} + k_B T \lim_{r \rightarrow 0} [T_{\text{PBC}}(\mathbf{r}) - T_0(\mathbf{r})]$$

*I. Yeh and G. Hummer // J. Phys. Chem. B. 2004. V. 108. N. 40. P. 15873

$$D_{\text{PBC}} = D_0 - \frac{k_B T \xi}{6\pi\eta L}$$



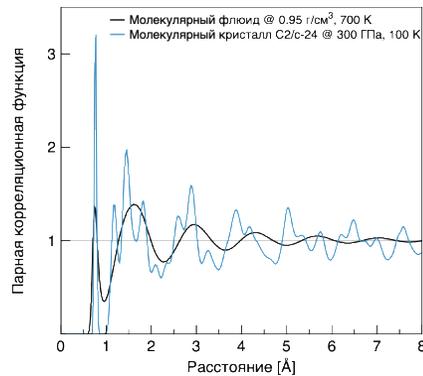
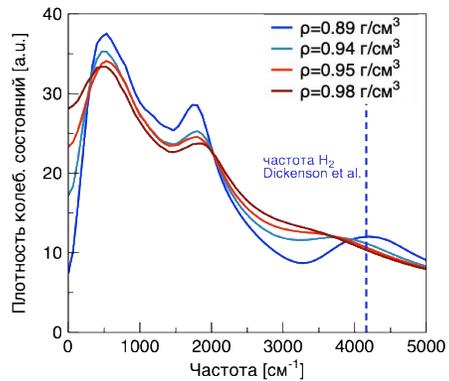
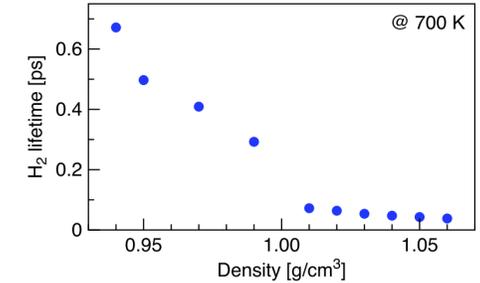
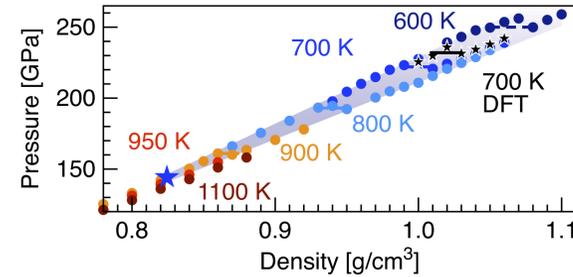
Поправка для диффузии – 10%

Вязкость от размера системы не зависит

Kim, K. S., Han, M. H., Kim, C., Li, Z., Karniadakis, G. E., & Lee, E. K. (2018). J. Chem. Phys. 149(4).

Выводы

Потенциал воспроизводит фазовый переход в флюиде водорода.
 Время жизни молекул H_2 составляет 0.7 пс,
 в проводящем состоянии резко сокращается до 7 фс,
 что подтверждает диссоциацию молекул.



В молекулярной фазе колебательный спектр имеет выраженный пик на 4161 cm^{-1} , соответствующий моде молекулы H_2 . В проводящем состоянии этот пик исчезает из-за диссоциации молекул.

Коэффициент диффузии флюида водорода увеличивается с ростом плотности, испытывает скачок при давлении фазового перехода.
 Вязкость также резко возрастает, ее значения близки к расплаву Li.

