NPP-2010

ДИССОЦИАЦИЯ

И

ДИССОЦИАТИВНЫЙ ФАЗОВЫЙ ПЕРЕХОД

В ПЛОТНОМ ВОДОРОДЕ

Хомкин А.Л., Шумихин А.С.
Объединенный институт высоких температур РАН

VOLUME 89, NUMBER 16 PHYSICAL REVIEW LETTERS 14 OCTOBER 2002

Shock Compression of Deuterium near 100 GPa Pressures

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(Received 19 February 2002; published 26 September 2002)

The shock-compression curve (Hugoniot) of D2 near 100 GPa pressures (1 Mbar) has been controversial because the two published measurements have limiting compressions of fourfold and sixfold. Our purpose is to examine published experimental results to decide which, if either, is probably correct. The published Hugoniot data of low-*Z* diatomic molecules have a universal behavior. The deuterium data of Knudson *et al.* (fourfold limiting compression) have this universal behavior, which suggests that Knudson *et al.* are correct and shows that deuterium behaves as other low-*Z* elements at high temperatures. In D2, H2, N2, CO, and O2, dissociation completes and average kinetic energy dominates average potential energy above 60 GPa. Below 30 GPa, D2, H2, N2, CO, and O2 are diatomic. D2 dissociation is accompanied by a temperature-driven nonmetal-metal transition at 50 GPa.

DOI: 10.1103/PhysRevLett.89.165502 PACS numbers: 62.50.+p, 64.30.+t

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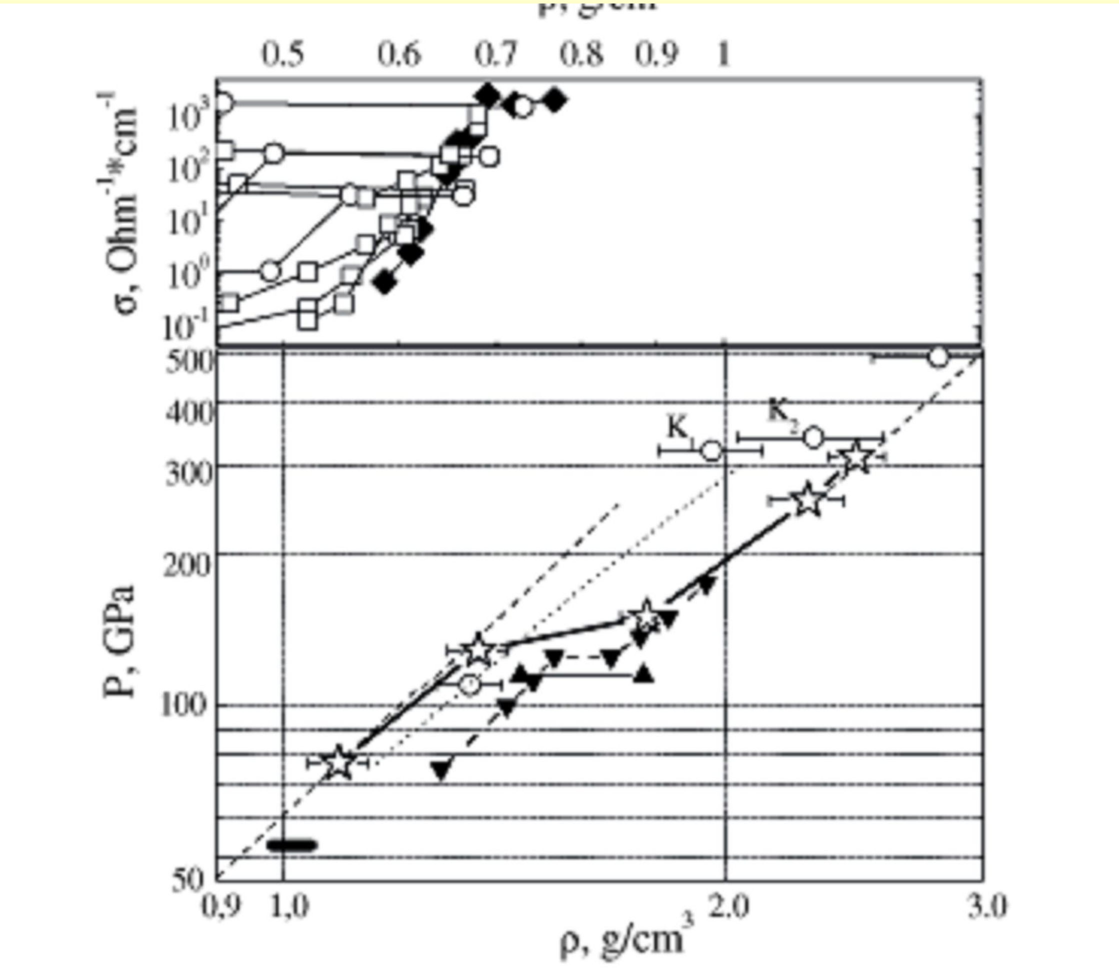

Phase Transition in a Strongly Nonideal Deuterium Plasma Generated by Quasi-Isentropical Compression at Megabar Pressures

V. E. Fortov[1] R. I. Ilkaev[2] V. A. Arinin[2]
V.V. Burtzev[2] V. A. Golubev[2] I. L. Iosilevskiy[4] V.V. Khrustalev[2]
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(Received 14 November 2006; published 29 October 2007)

Филинов и др.

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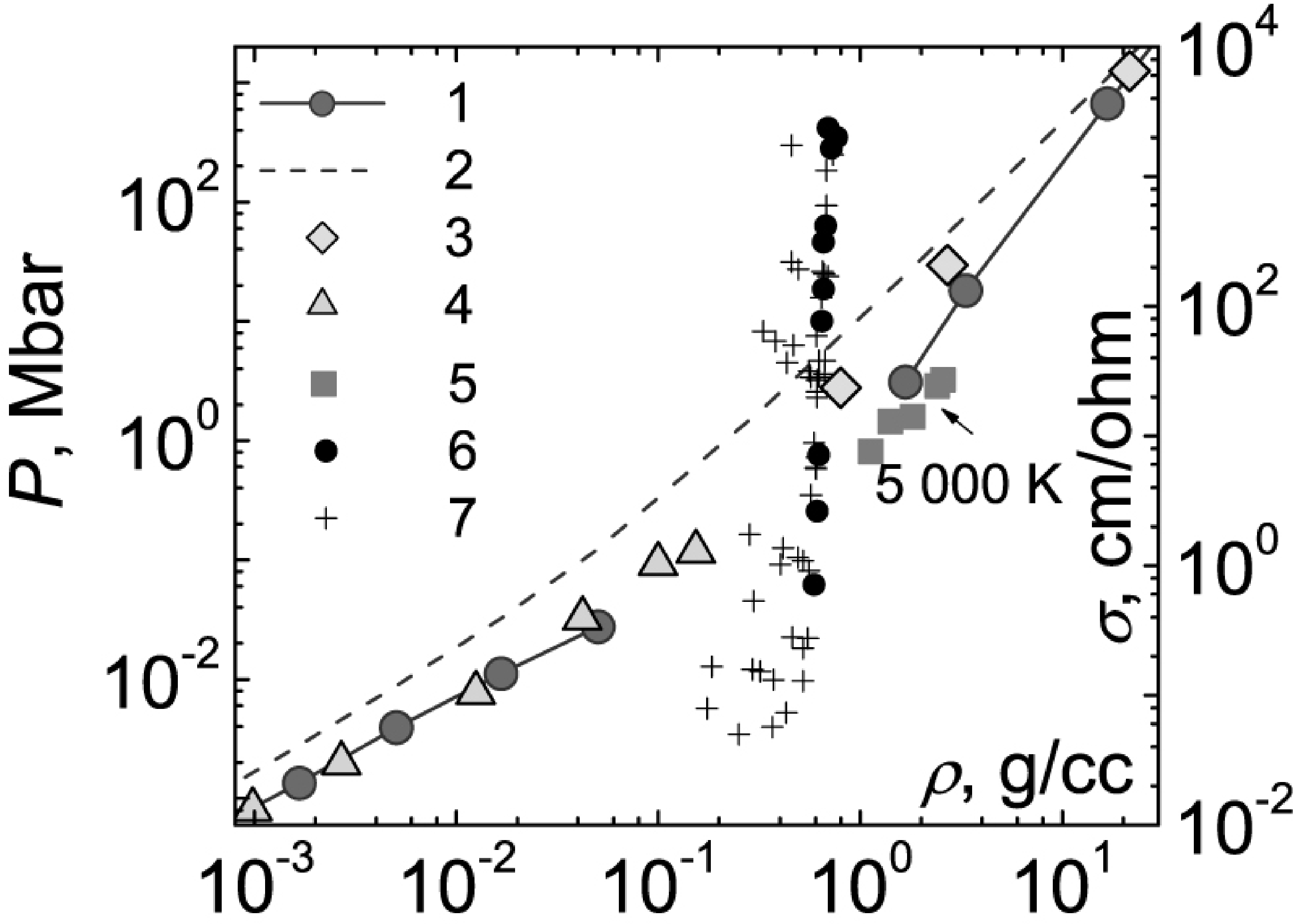
T=10000K



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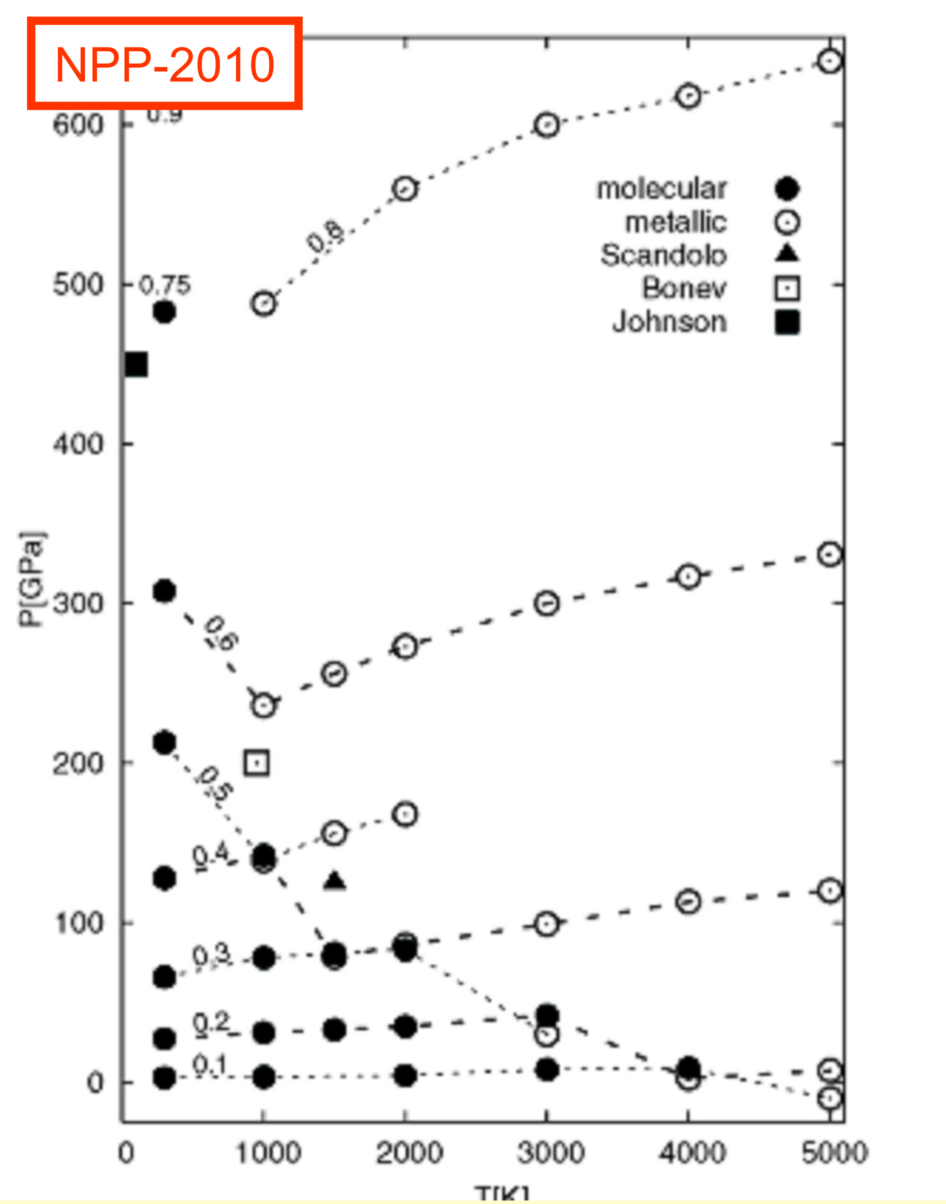

МФП+МД

Structure and Phase Boundaries of Compressed Liquid Hydrogen

Isaac Tamblyn* and Stanimir A. Bonev†

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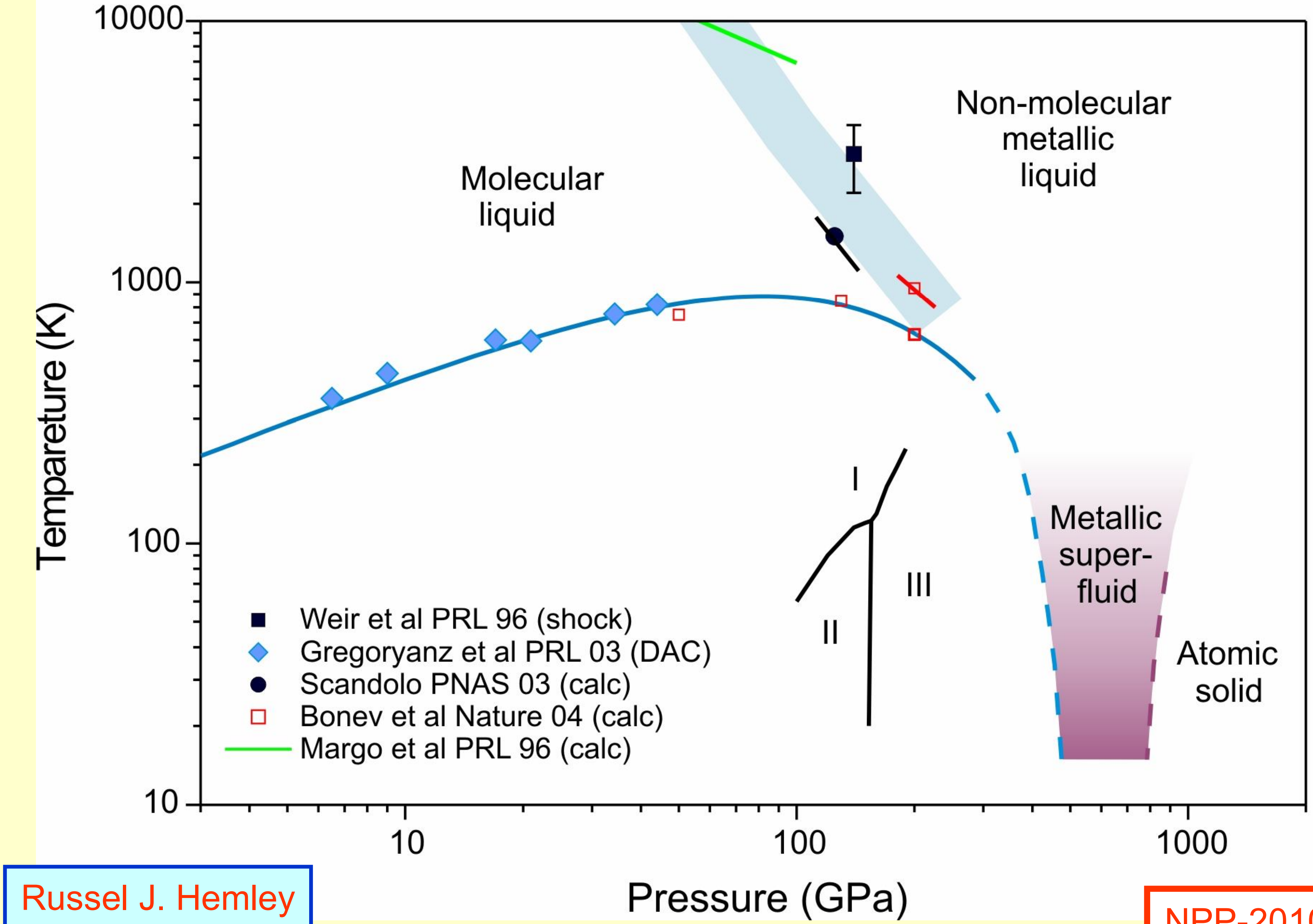
(Received 9 July 2009; published 11 February 2010)



Russel J. Hemley

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ТЕОРИЯ

1. Классическая статистическая теория жидкости,
развиваемая для атомарно-молекулярной смеси.
(М.Росс, Шауман и Шабрийе, Грязнов-Иосилевский, Редмер и др.)

Self-consistent fluid variational theory for pressure dissociation
in dense hydrogen
Hauke Juranek and Ronald Redmera)
Fachbereich Physik, Universita¨t Rostock, D-18051 Rostock, Germany
~Received 7 July 1999; accepted 18 November 1999!

JOURNAL OF CHEMICAL PHYSICS VOLUME 112, NUMBER 8
22 FEBRUARY 2000

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$$F = F_0 + F_{HS} + F_{INT}$$

$$F_0 = -N_a kT \ln\left(\frac{eV}{N_a \lambda_a^3}\right) - N_m kT \ln\left(\frac{eV\Sigma_m}{N_m \lambda_m^3}\right)$$

$$F_{HS} \rightarrow Mansoory, Carnahan, Starling$$

$$F_{INT} = \frac{1}{2}\sum_{i,j}\int V_{i,j}(r) g_{i,j}^{HS}(r)\,dr$$

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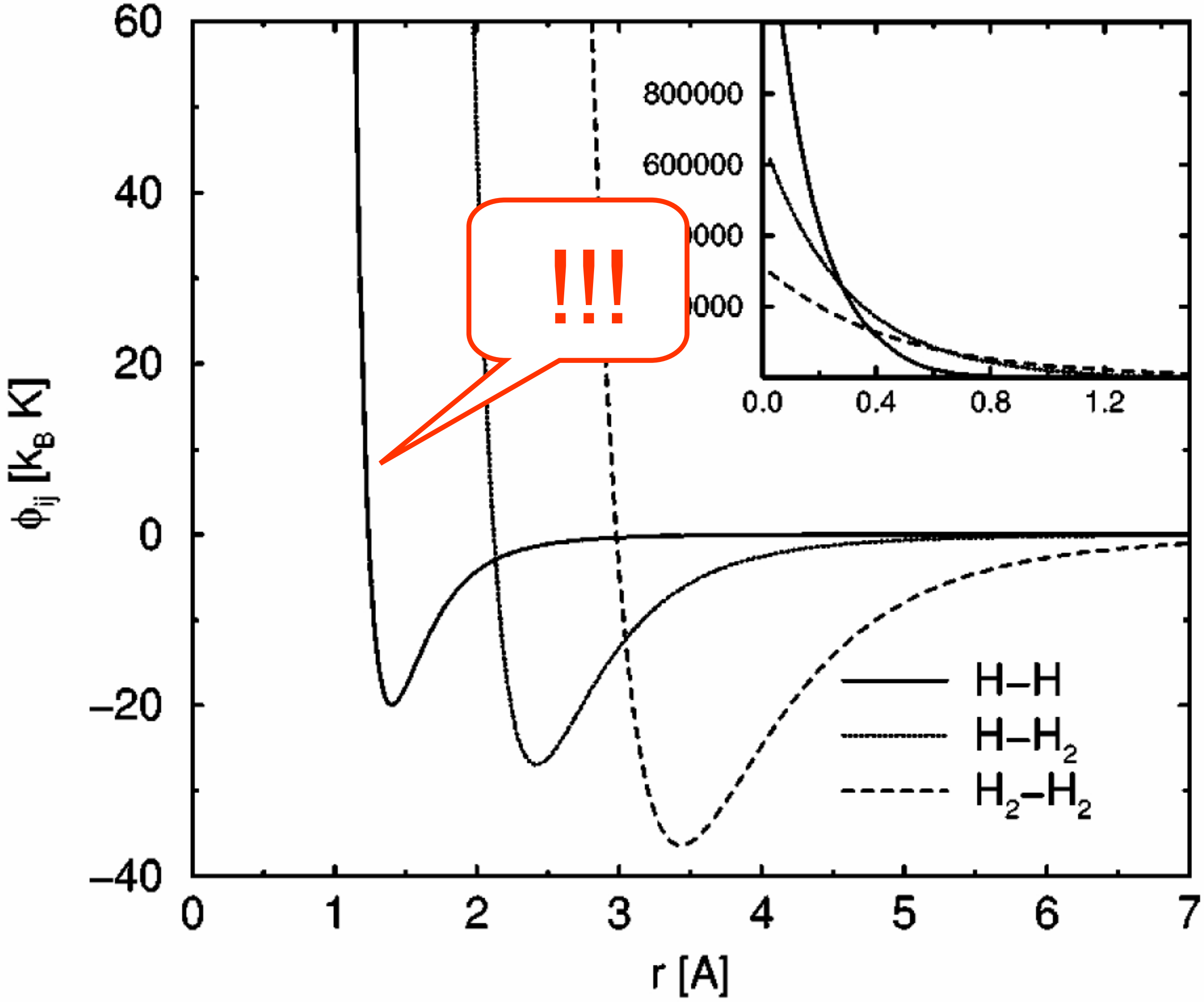

!!!

FIG. 1. Effective pair potentials for the H–H_2 mixture.

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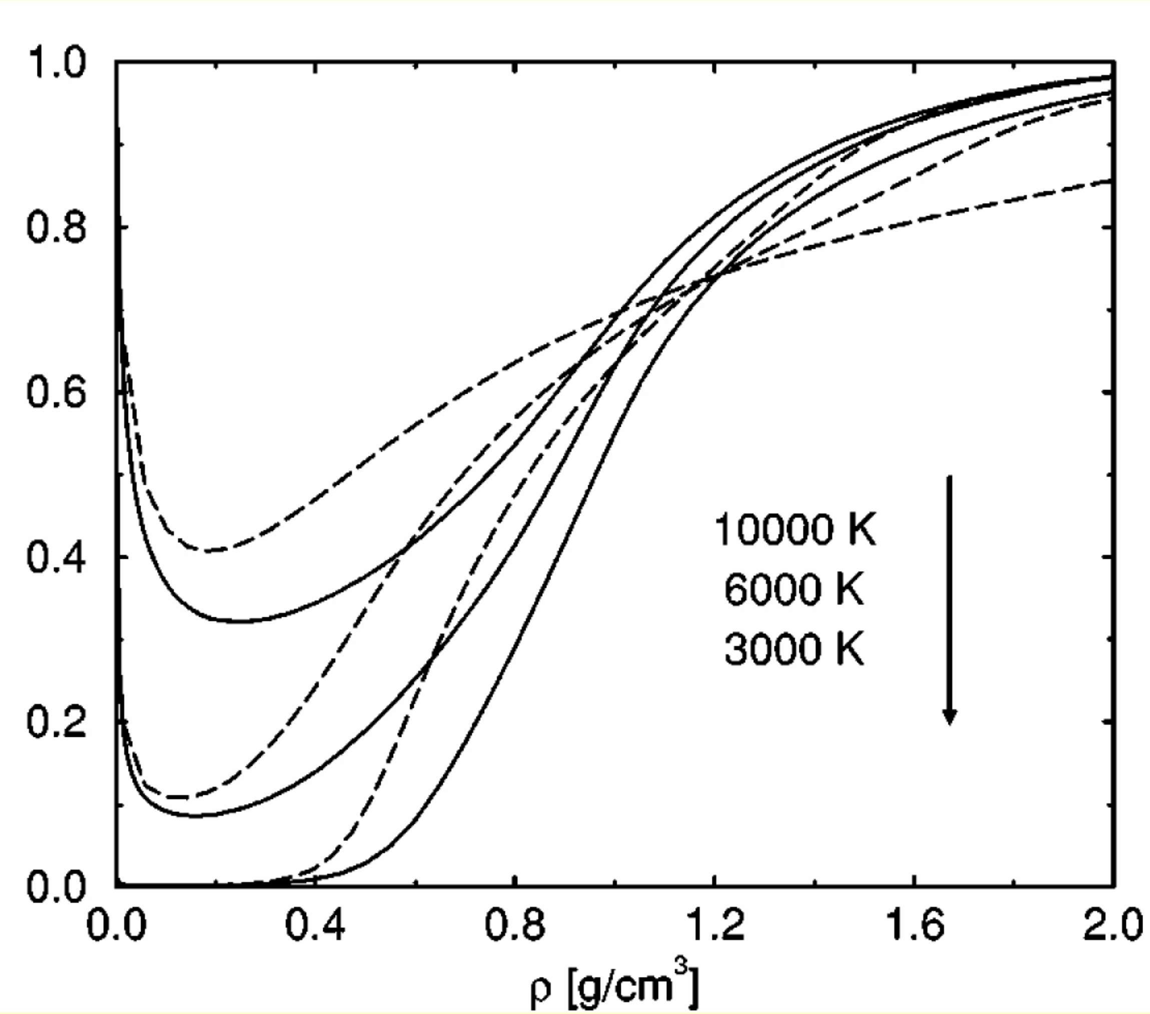
Степень диссоциации водорода α

$$\alpha = \frac{N_a}{N_a + N_m}$$



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Основные предположения

1. Атомы и молекулы имеют твердую сердцевину и формируют исключенный объем.

2. Потенциально взаимодействуют между собой только свободные атомы

3. Свободные атомы в плотном диссоциированном флюиде образуют квазижидкостную структуру

4. Взаимодействие между атомами осуществляетя квантовым электронным обменом, который ведет к возникновению знергии связи (cohesive energy)

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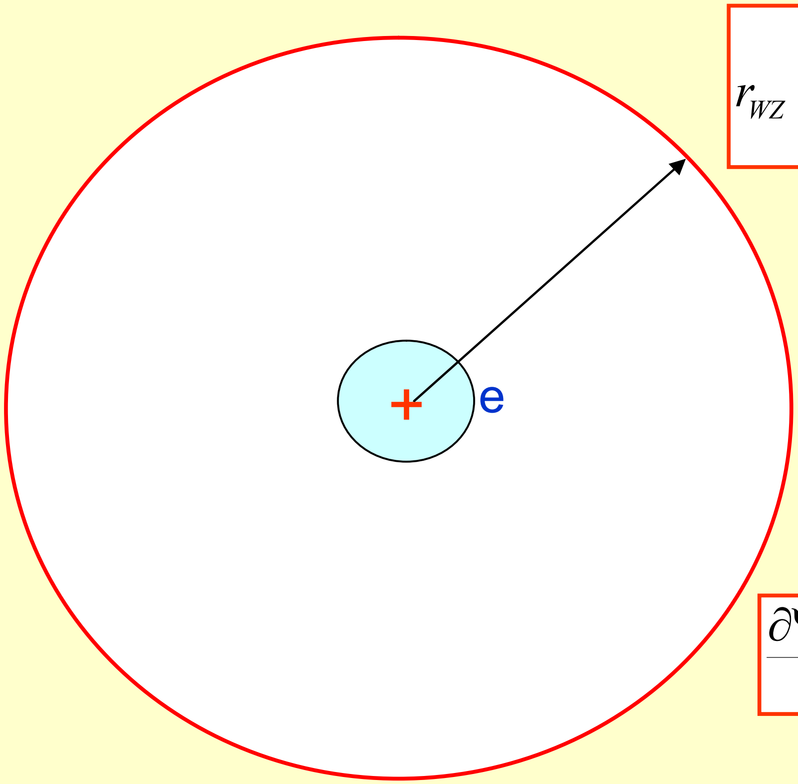
Энергия основного состояния атома в квазижидкости



$$r_{WZ} = \left(\frac{3}{4\pi n_a}\right)^{1/3}$$

Wigner-Seitz cell

$$\left.\frac{\partial \Psi(r)}{\partial r}\right|_{r=r_{WZ}} = 0$$

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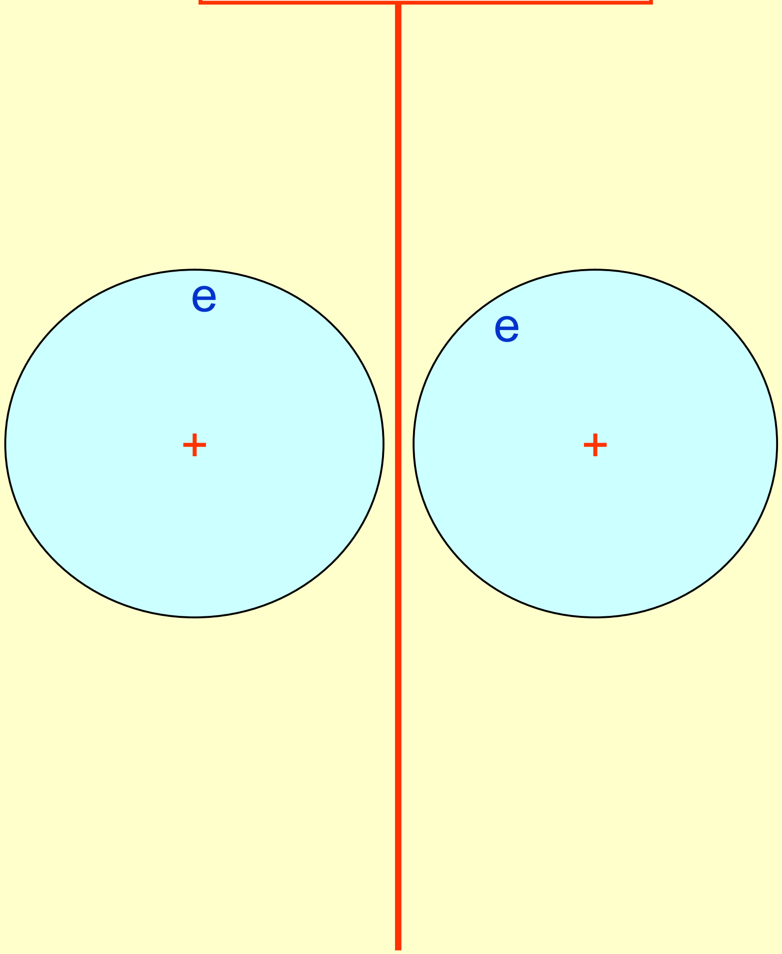
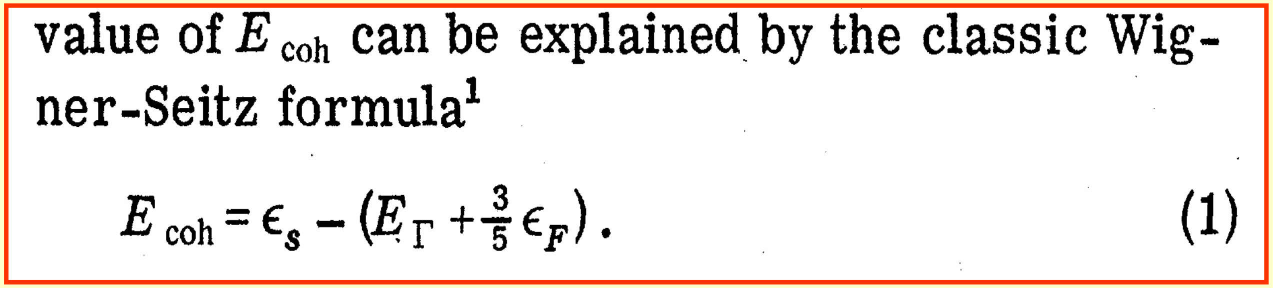
$$\left.\frac{\partial \Psi(r)}{\partial r}\right|_{r=r_m} = 0$$





value of E_{coh} can be explained by the classic Wigner-Seitz formula[1]

$$E_{\text{coh}} = \epsilon_s - \left(E_{\Gamma} + \tfrac{3}{5}\epsilon_F\right). \tag{1}$$

JULY, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6
An Improved Calculation of the Energies of Metallic Li and N a
J. BARDEEN*
Harvard University, Cambridge, Massachusetts
(Received April 13, 1938)

$$E_k = E_0 + \alpha \frac{p^2}{2m}$$

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$$E_a = E_0 + \alpha \frac{3}{5} E_F$$

$$E_{coh} = E_a + Ry$$

$$\alpha = \left[\frac{4\pi}{3} R_0^2(r_c) \right] \left[\frac{r}{R_1(r)} \frac{dR_1(r)}{dr} \right]_{r=r_c}$$

$$R_l(r) = A_l \exp(-kr)\, r^l F(l+1-1/ka_0, 2l+2, 2kr)$$

$$k^2 = 2m|E|/\hbar^2$$

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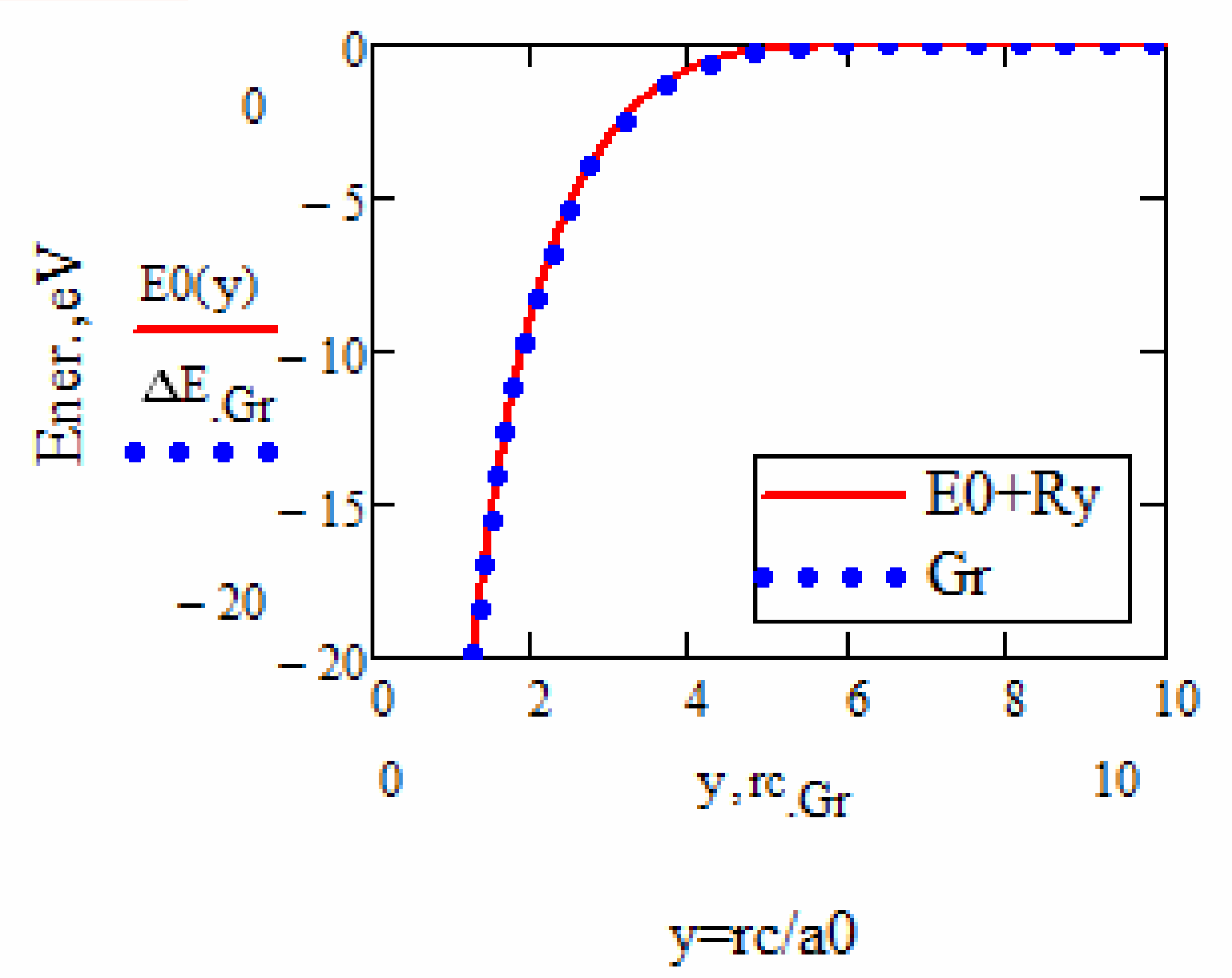

Ener.,eV
E0(y)
ΔE.Gr
0
−5
−10
−15
−20
0
−20
0
2
4
6
8
10
0
y, rc.Gr
10
E0+Ry
Gr
y=rc/a0

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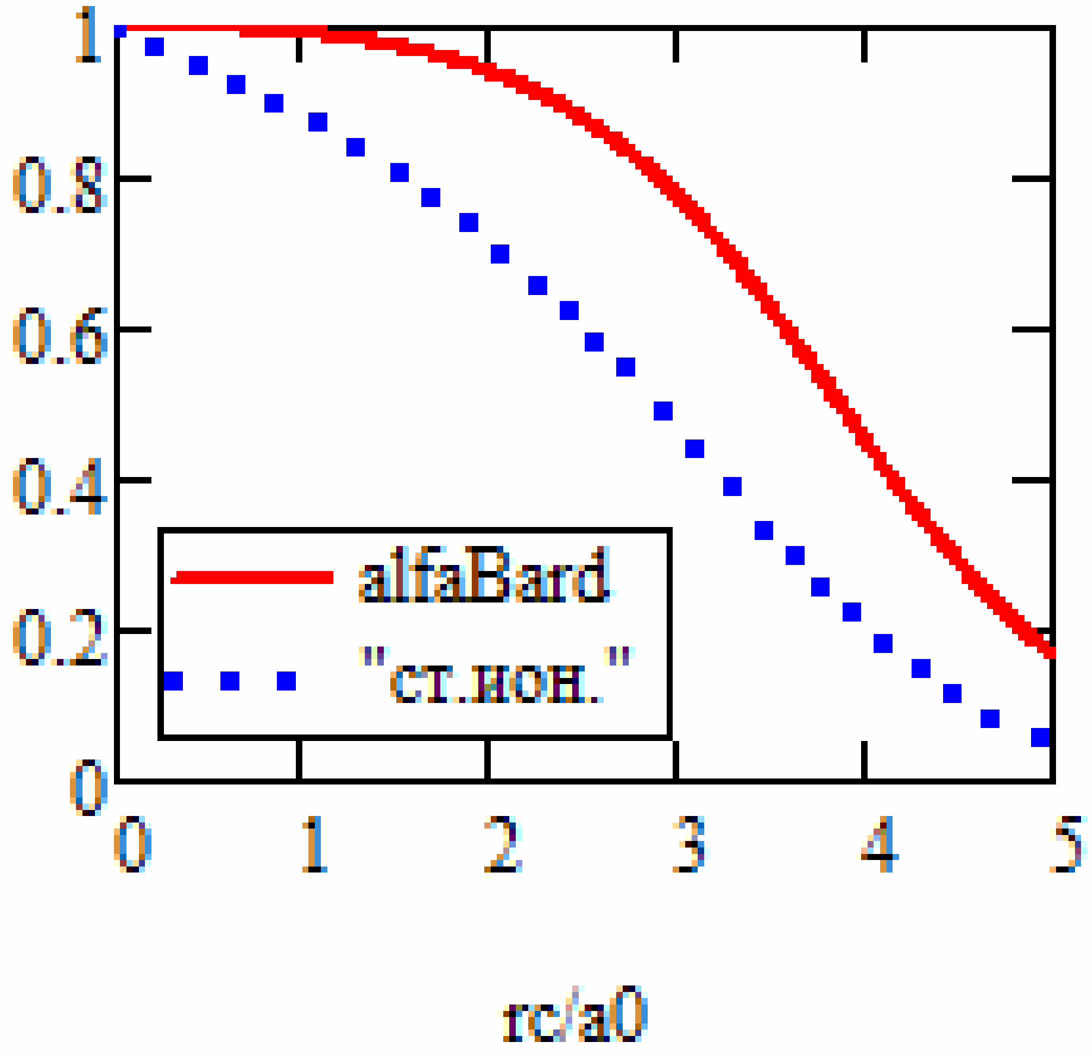

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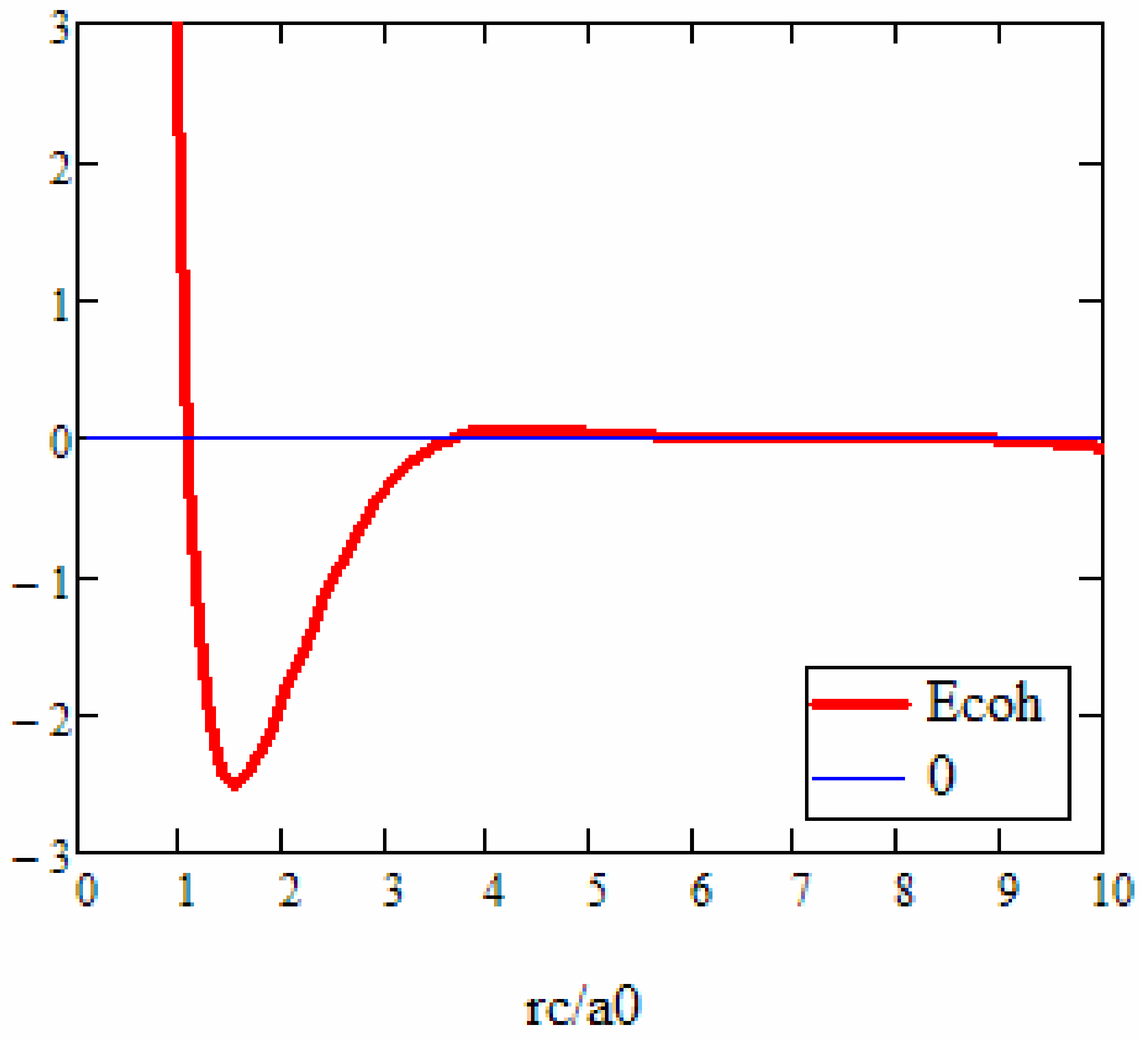

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$$F = F_0 + F_{HS} + F_{INT}$$

$$F_0 = -N_a kT \ln\left(\frac{eV}{N_a \lambda_a^3}\right) - N_m kT \ln\left(\frac{eV\Sigma_m}{N_m \lambda_m^3}\right)$$

$$F_{HS} = (N_a + N_m) kT \, \frac{4\eta - 3\eta^2}{(1-\eta)^2}$$

$$F_{INT} = \frac{1}{2} N_a E_{coh}(y)$$

$$y = r_{WS} / a_0 \qquad\qquad \eta = \frac{4}{3}\pi \left[\frac{N_m}{V} r_m^3 + \frac{N_a}{V} r_a^3(y) \right]$$

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$$P = P_{IG} + P_{HS} + P_{INT}$$

$$P_{IG} = kT\left(\frac{N_a + N_m}{V}\right)$$

$$P_{HS} = kT\left(\frac{N_a + N_m}{V}\right)\frac{4\eta - 3\eta^2}{(1-\eta)^2}(\eta - \frac{4}{3}\pi\frac{N_a}{V}r_a^3(\frac{y}{r_a}\frac{\partial r_a}{\partial y}))$$

$$P_{INT} = -\frac{1}{2}\frac{N_a}{V}\frac{\partial E_{coh}(y)}{\partial y}\frac{y}{3}$$

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$$\beta\mu_m = \beta\mu_m^0 + \beta\Delta\mu_m$$

$$\beta\mu_a = \beta\mu_a^0 + \beta\Delta\mu_a$$

$$\beta\mu_{m,a}^0 = -\ln\left(\frac{Vg_{m,a}\Sigma_{m.a}}{N_{m,a}\lambda_{m,a}^3}\right), \quad \Sigma_a = 1$$

$$\beta\Delta\mu_m = \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \left(\frac{N_a + N_m}{V}\right)\frac{4\pi}{3}r_m^3\frac{4-2\eta}{(1-\eta)^3}$$

$$\beta\Delta\mu_a = \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \left(\frac{N_a + N_m}{V}\right)\frac{4\pi}{3}r_a^3\frac{4-2\eta}{(1-\eta)^3}\left(1 - \frac{y}{r_a}\frac{\partial r_a}{\partial y}\right) + \frac{\beta E_{coh}}{2}\left(1 - \frac{y}{3E_{coh}}\frac{\partial E_{coh}}{\partial y}\right)$$

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$$K(n,\gamma,T) = n\,\lambda_a^3 \frac{1}{\sqrt{2}} \Sigma_m \exp(-\beta\Delta\mu_m + 2\beta\Delta\mu_a)$$

$$\gamma = n_a / n$$

$$G(n,\gamma,T) = 1 - \gamma - 2\gamma^2 K(n,\gamma,T) = 0$$

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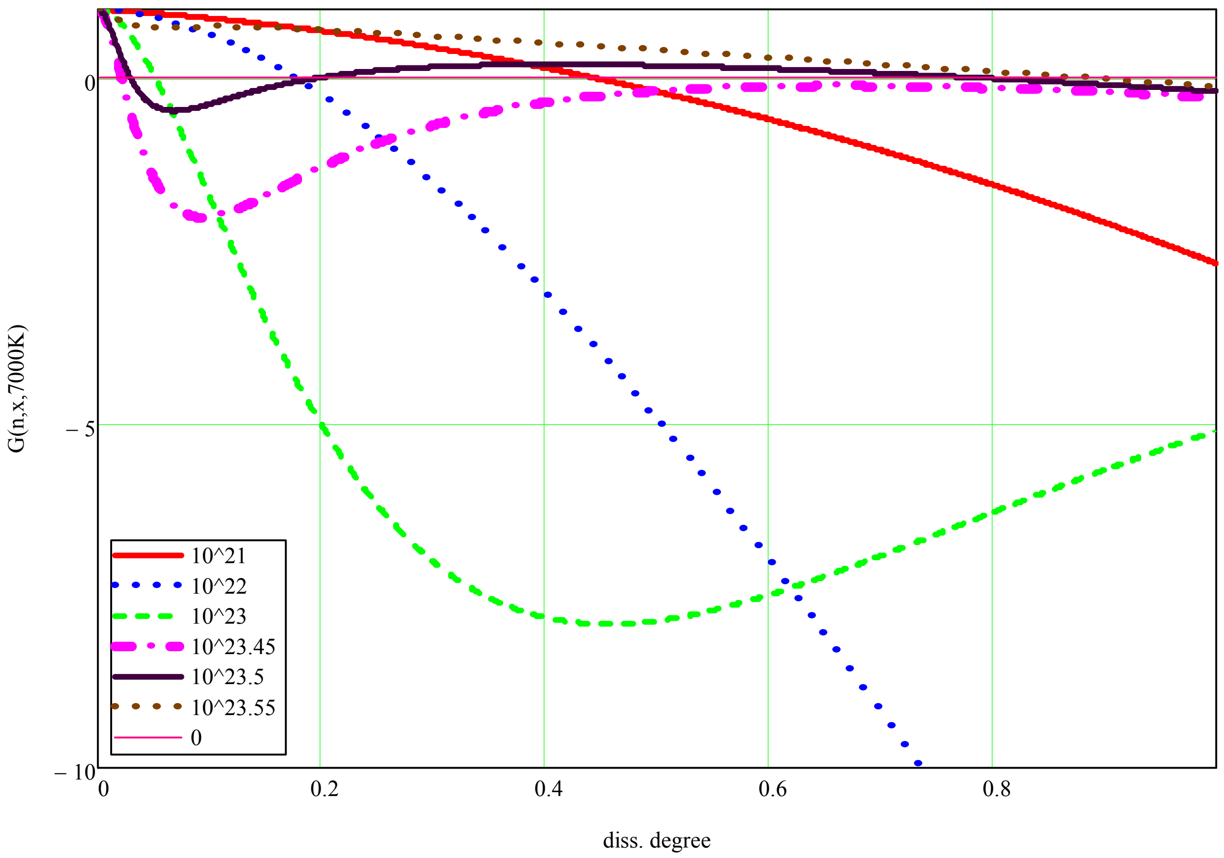
$$G(n,x,T) = 1 - x - 2x^2 K(n,x,T)$$



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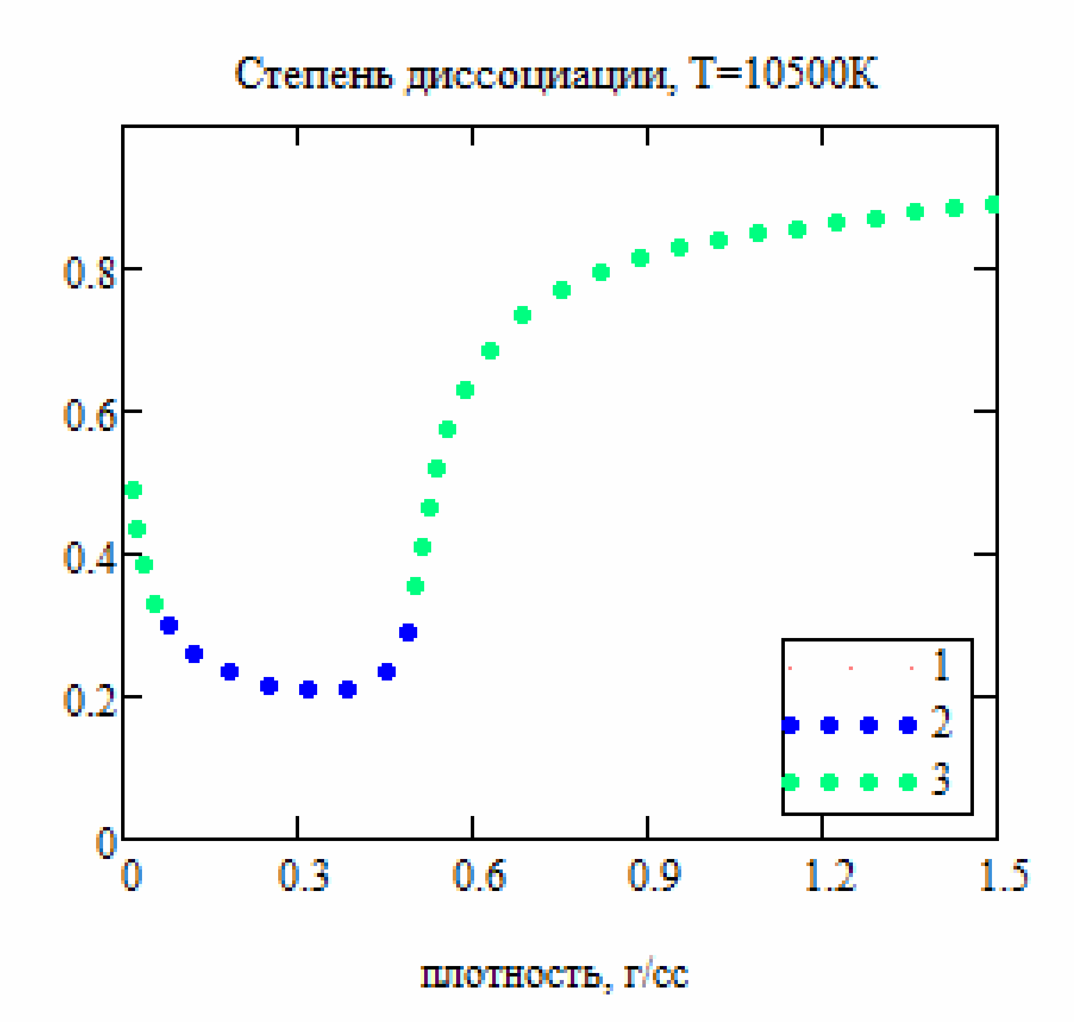
Степень диссоциации, T=10500K
0.8
0.6
0.4
0.2
0
0
0.3
0.6
0.9
1.2
1.5
1
2
3
плотность, г/сс

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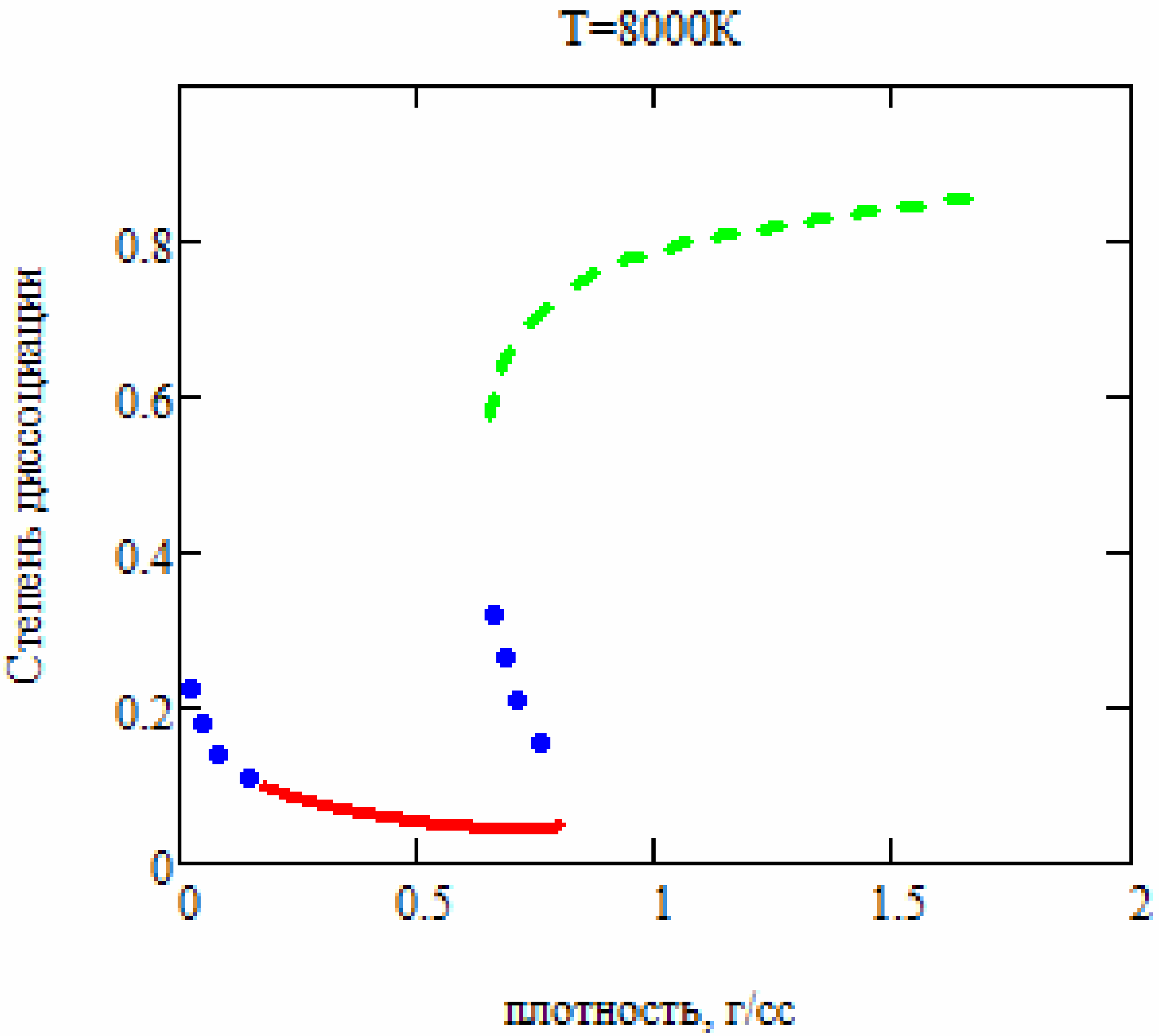
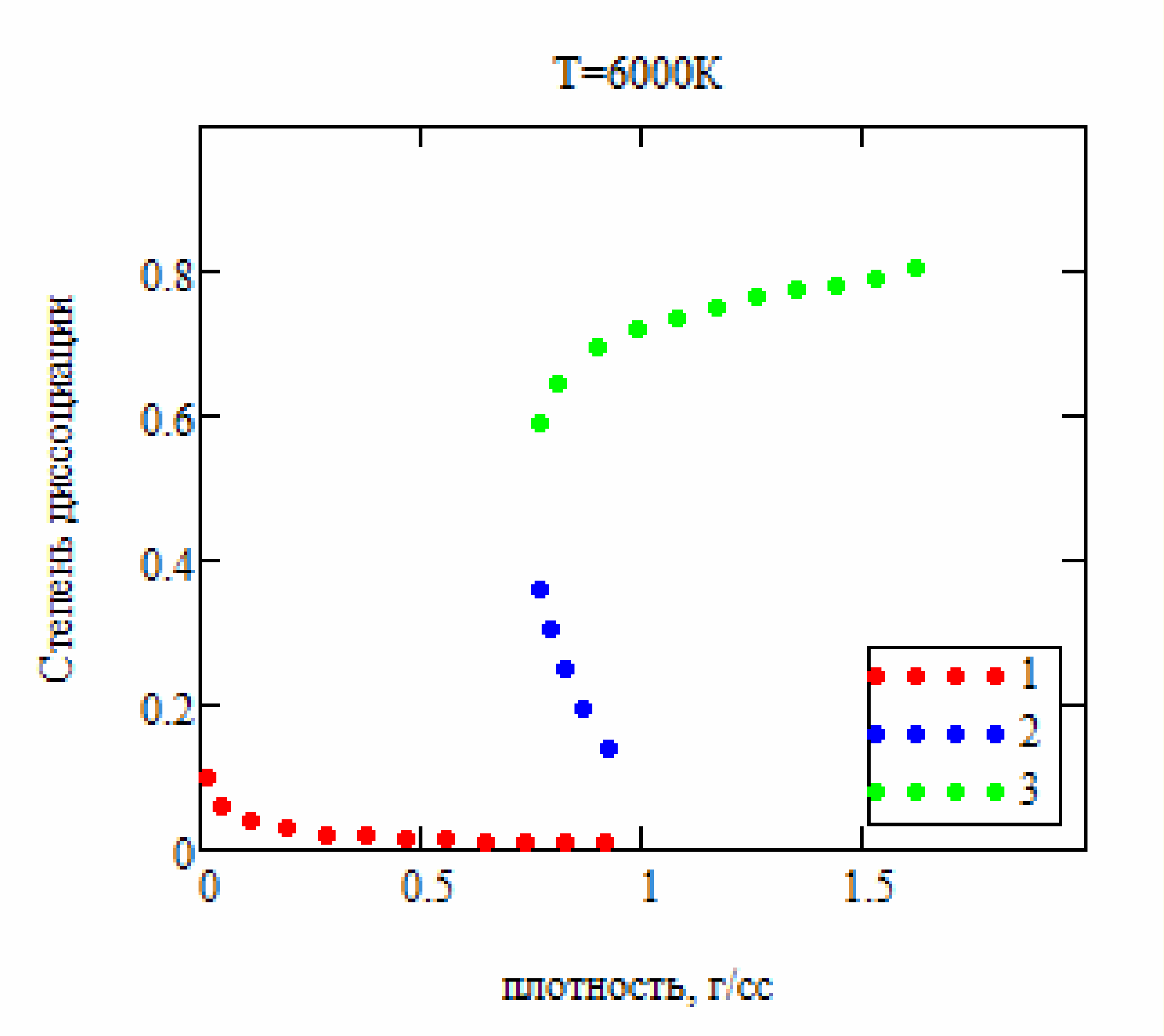
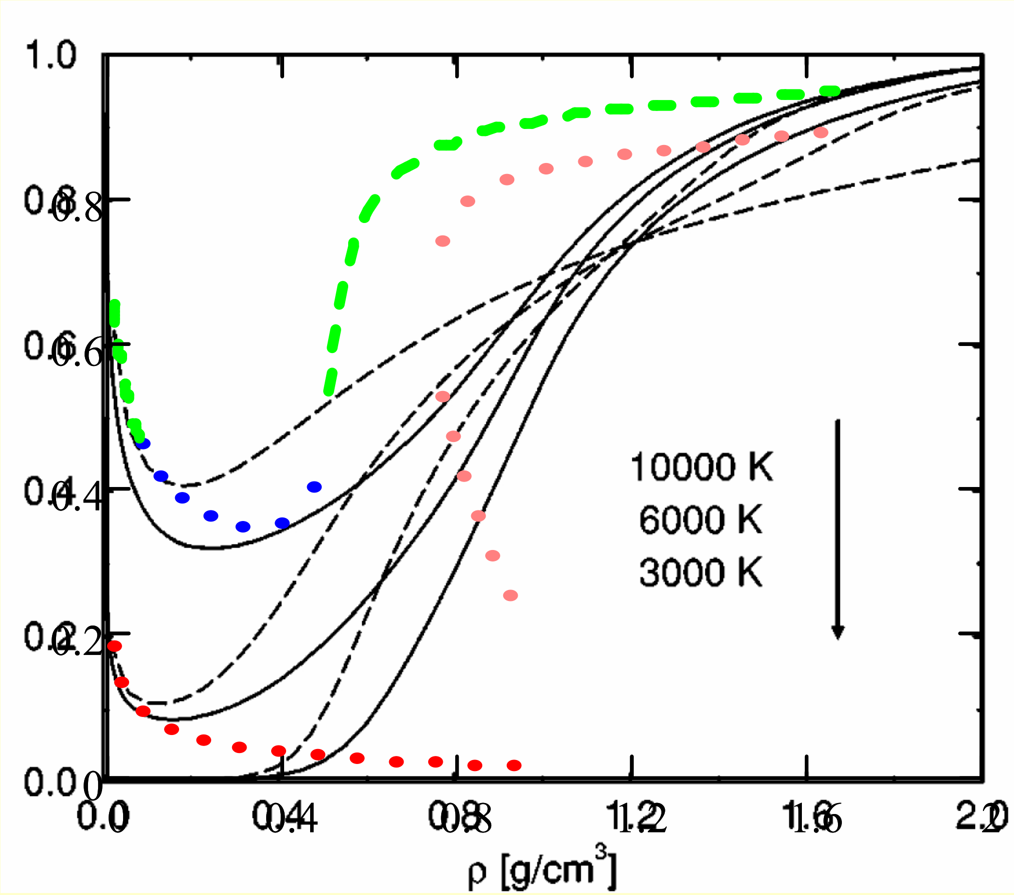

T=8000K
Степень диссоциации
плотность, г/сс
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2

NPP-2010



T=6000K
Степень диссоциации
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
плотность, г/сс
1
2
3

NPP-2010



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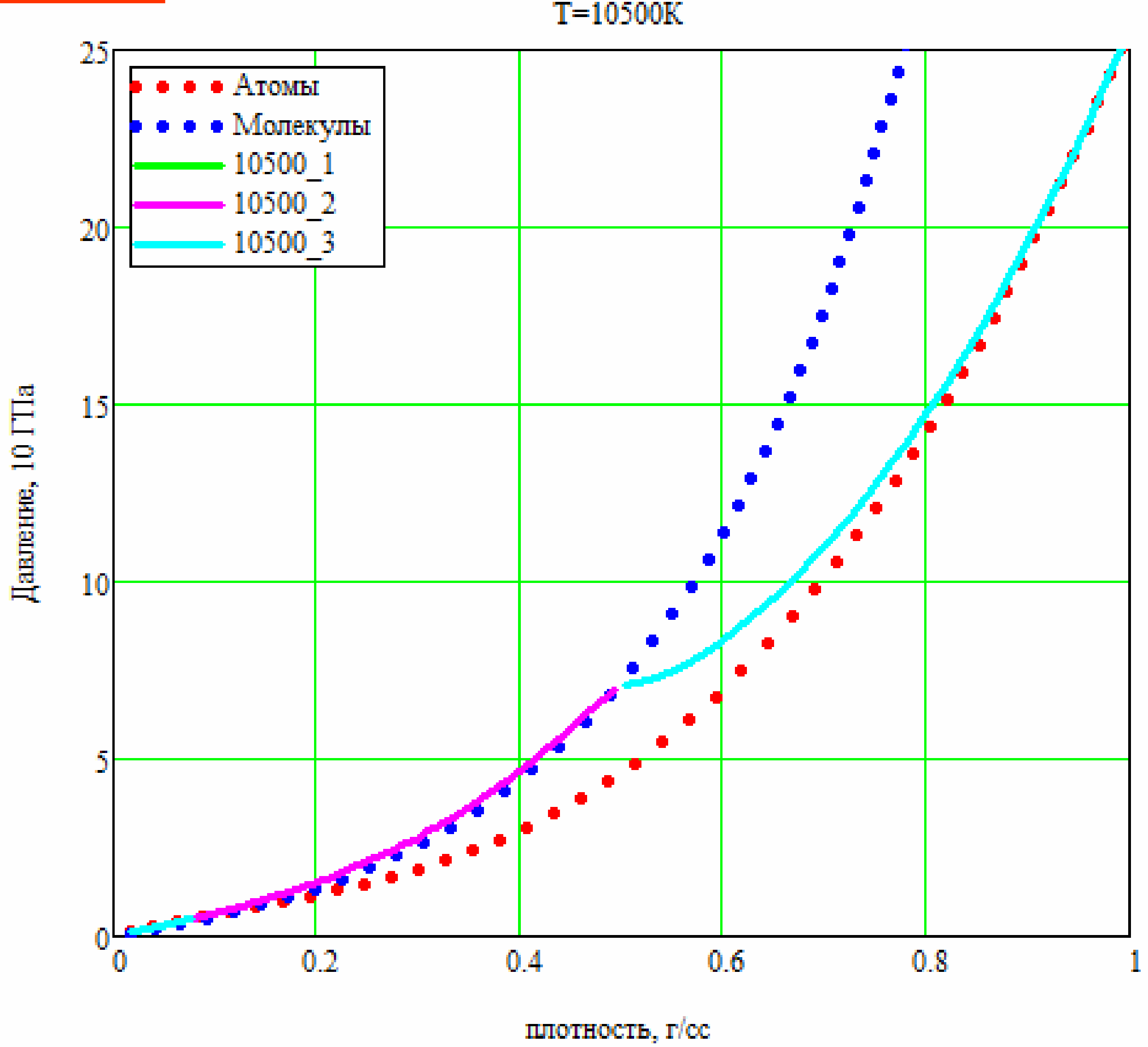
T=10500K
Атомы
Молекулы
10500_1
10500_2
10500_3
Давление, 10 ГПа
0
5
10
15
20
25
0
0.2
0.4
0.6
0.8
1
плотность, г/сс

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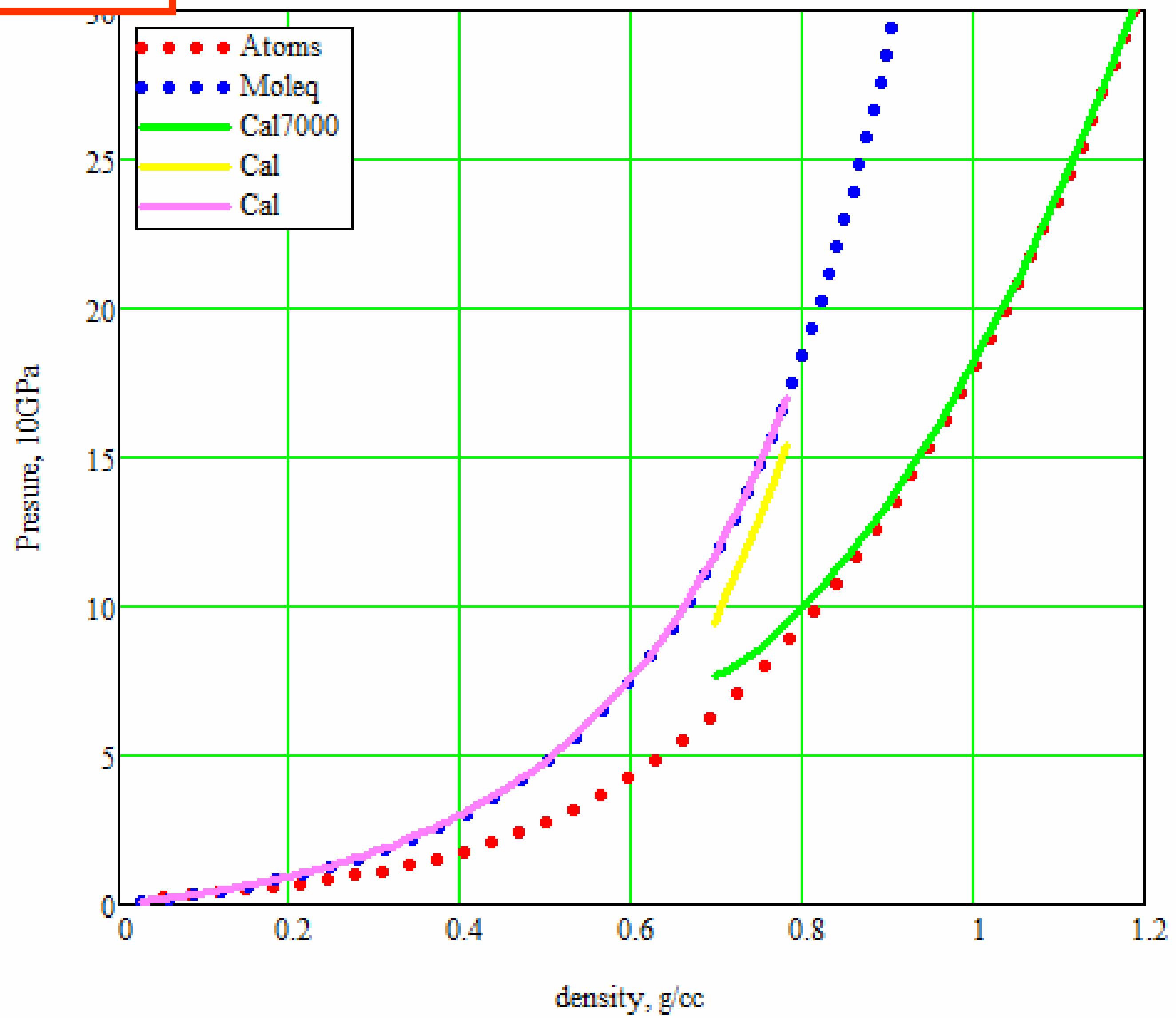

Atoms
Moleq
Cal7000
Cal
Cal
Presure, 10GPa
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
density, g/cc

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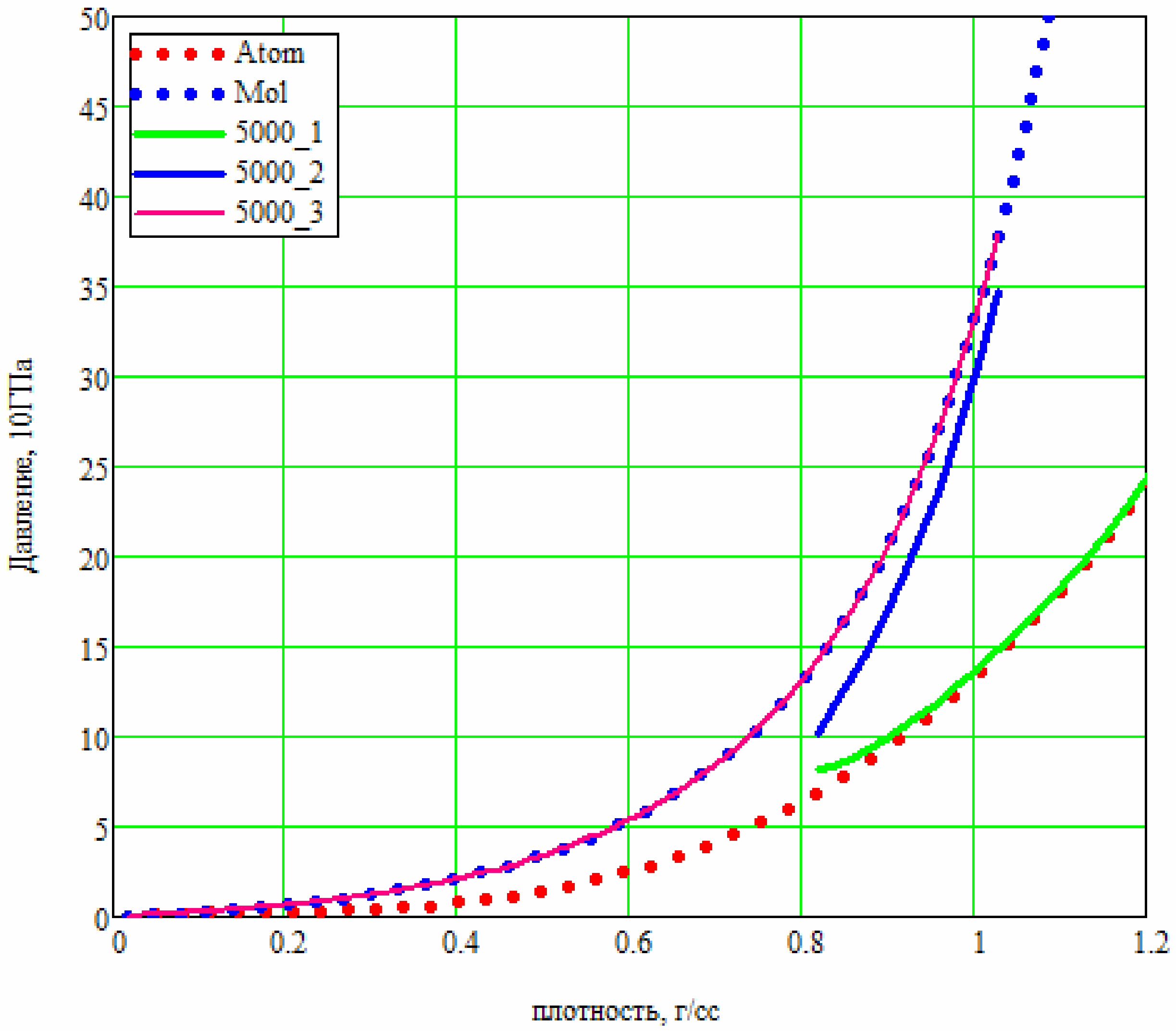
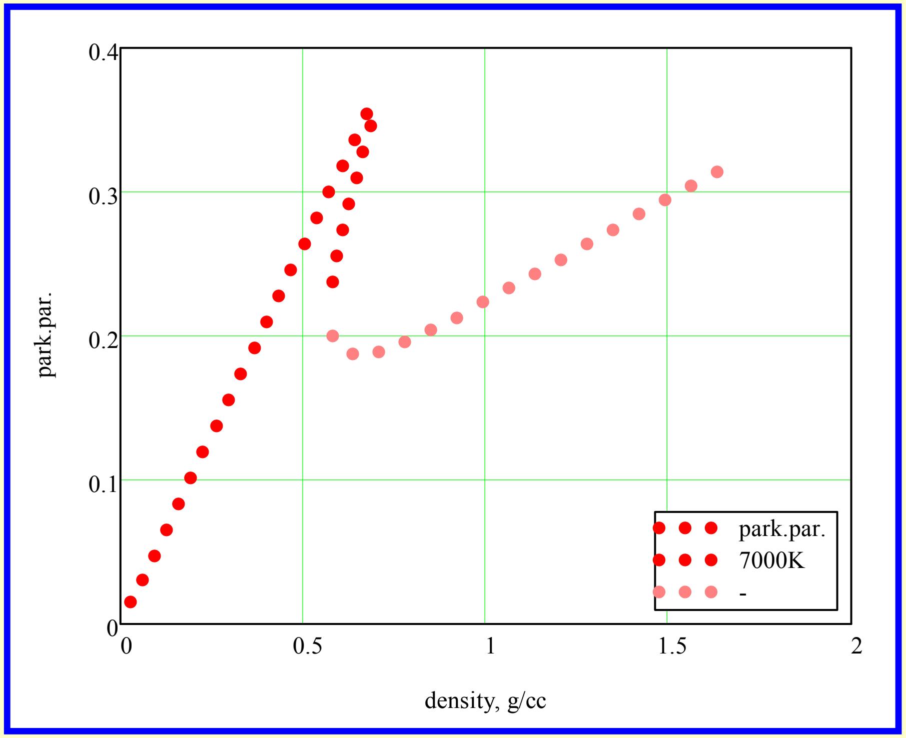

Atom
Mol
5000_1
5000_2
5000_3
Давление, 10ГПа
плотность, г/сс
0
5
10
15
20
25
30
35
40
45
50
0
0.2
0.4
0.6
0.8
1
1.2



7000K

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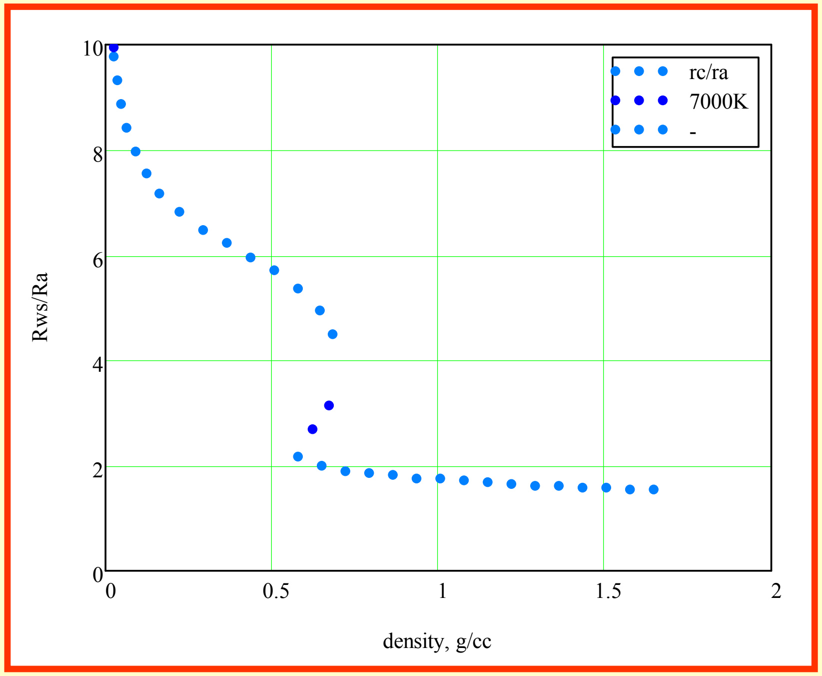
η(ρ)

$$\frac{r_{WZ}}{r_a}(\rho)$$



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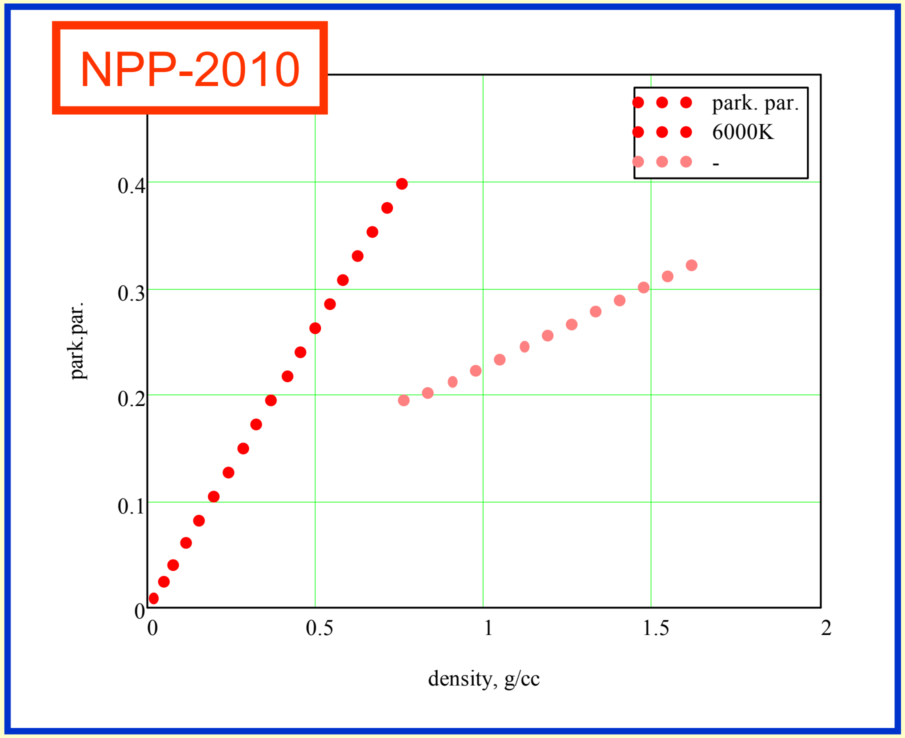
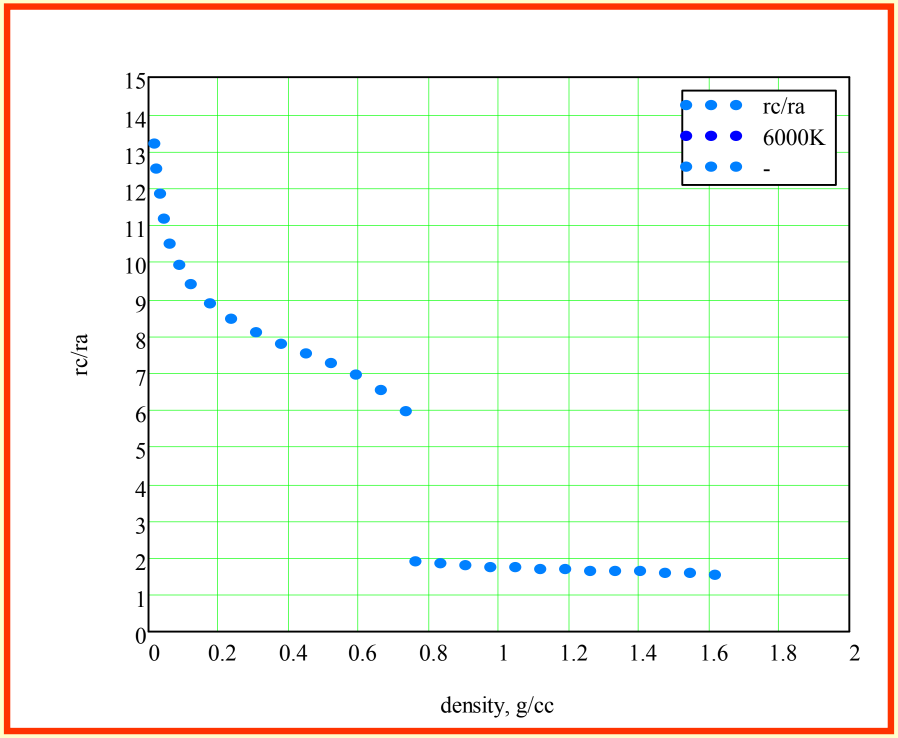


6000K

$\eta(\rho)$

$$\frac{r_{WZ}}{r_a}(\rho)$$



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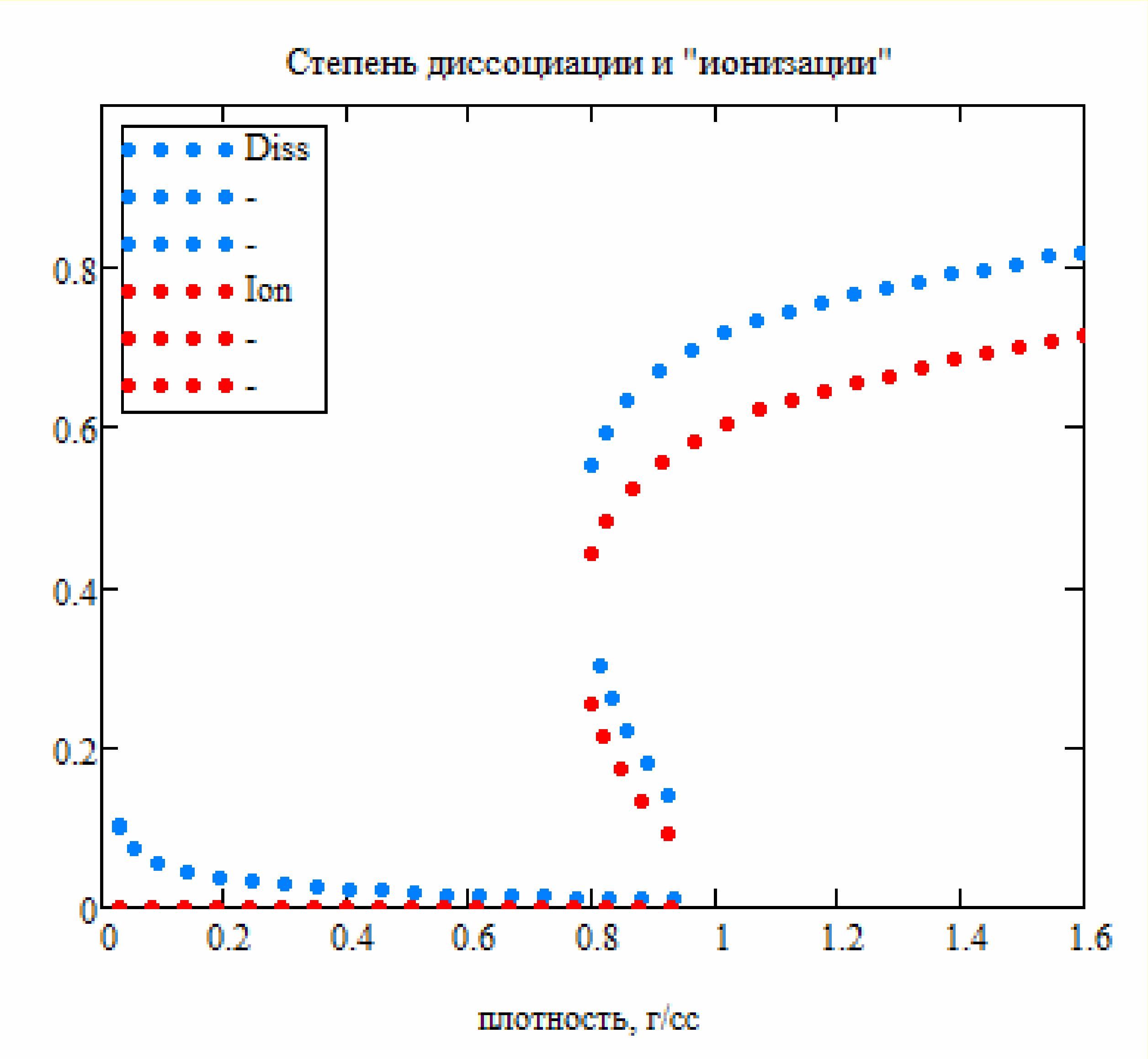
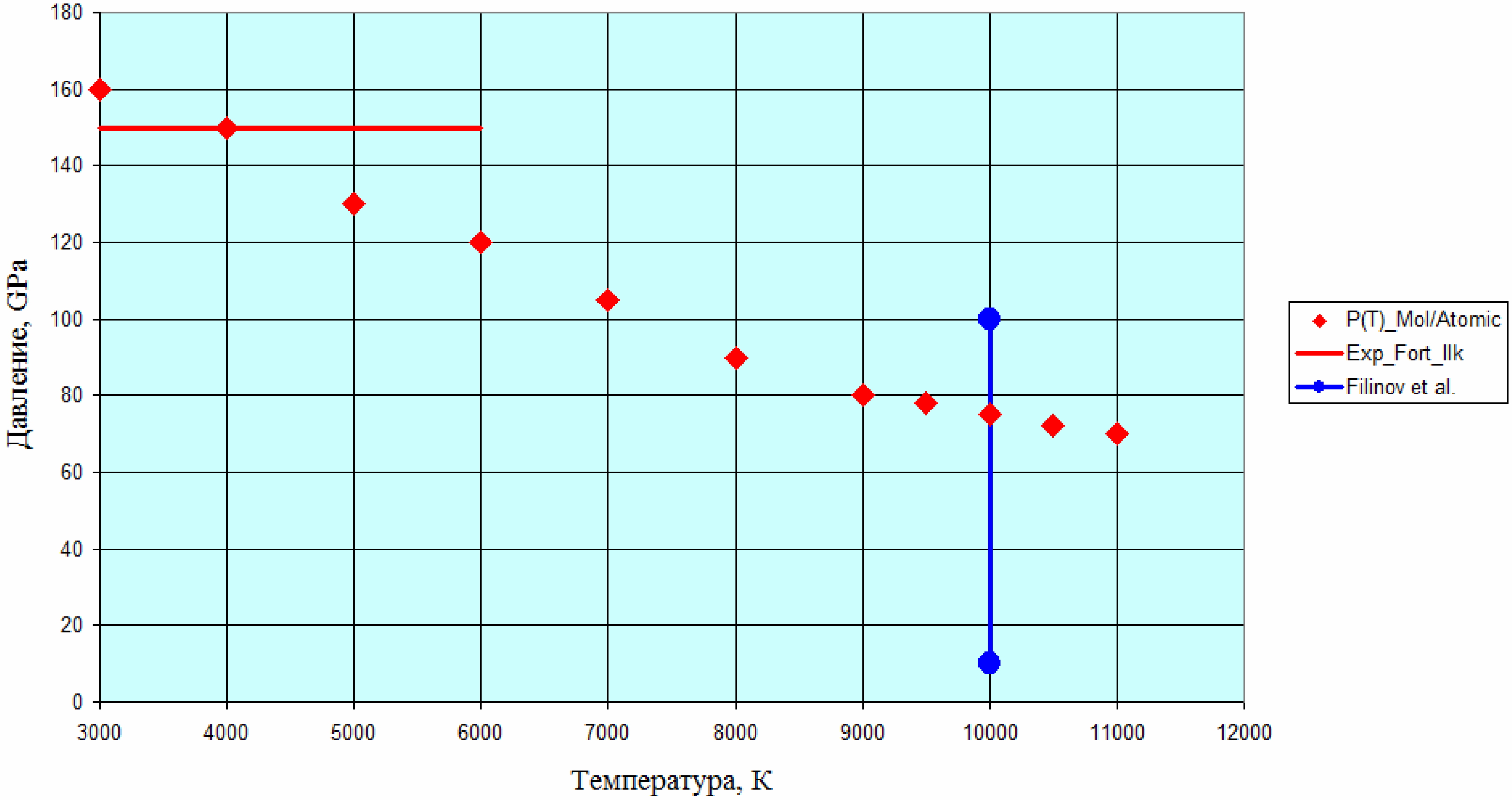


T=6000K

Линия сосуществования ДФП



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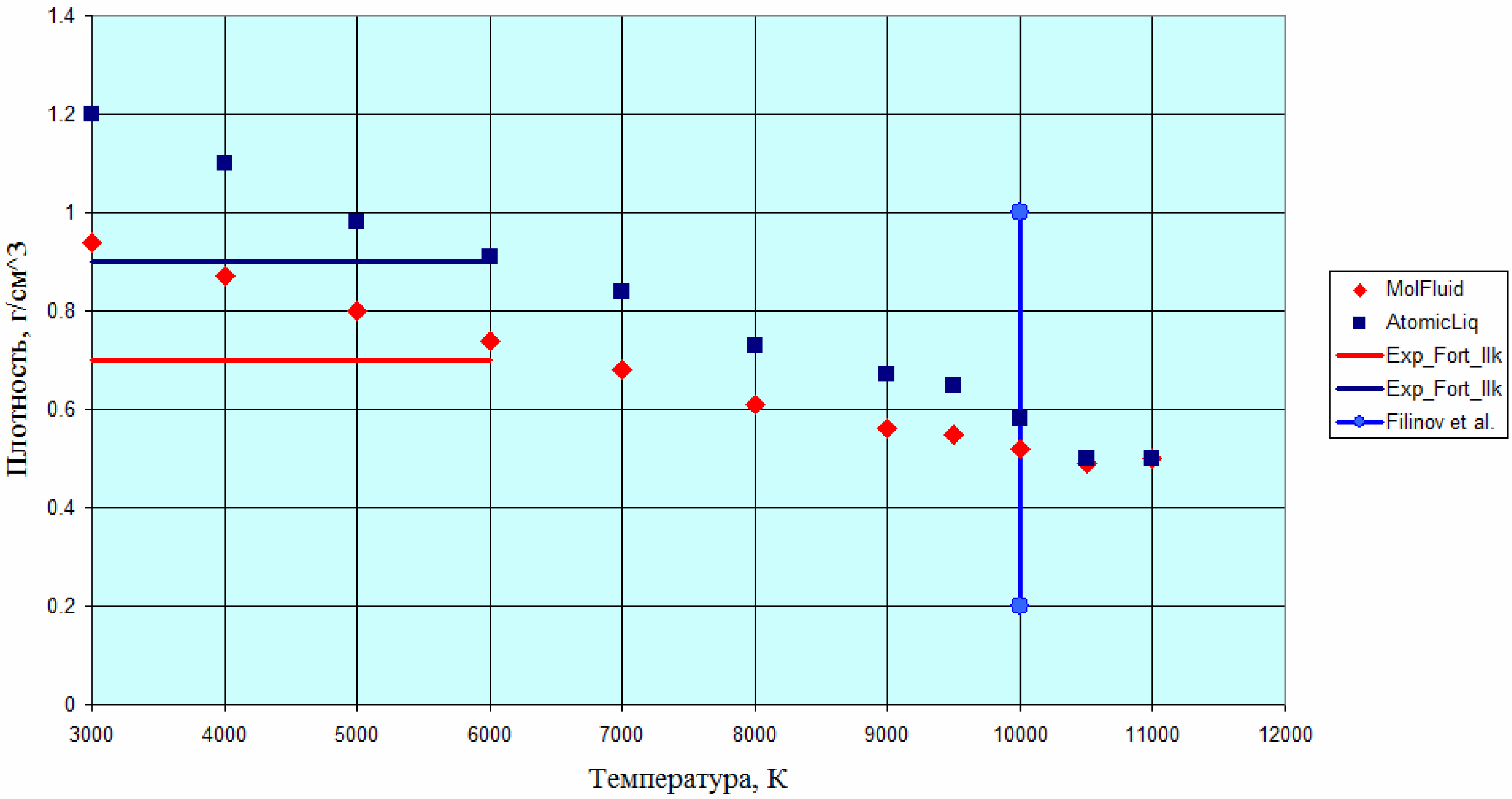
Бинодаль ДФП



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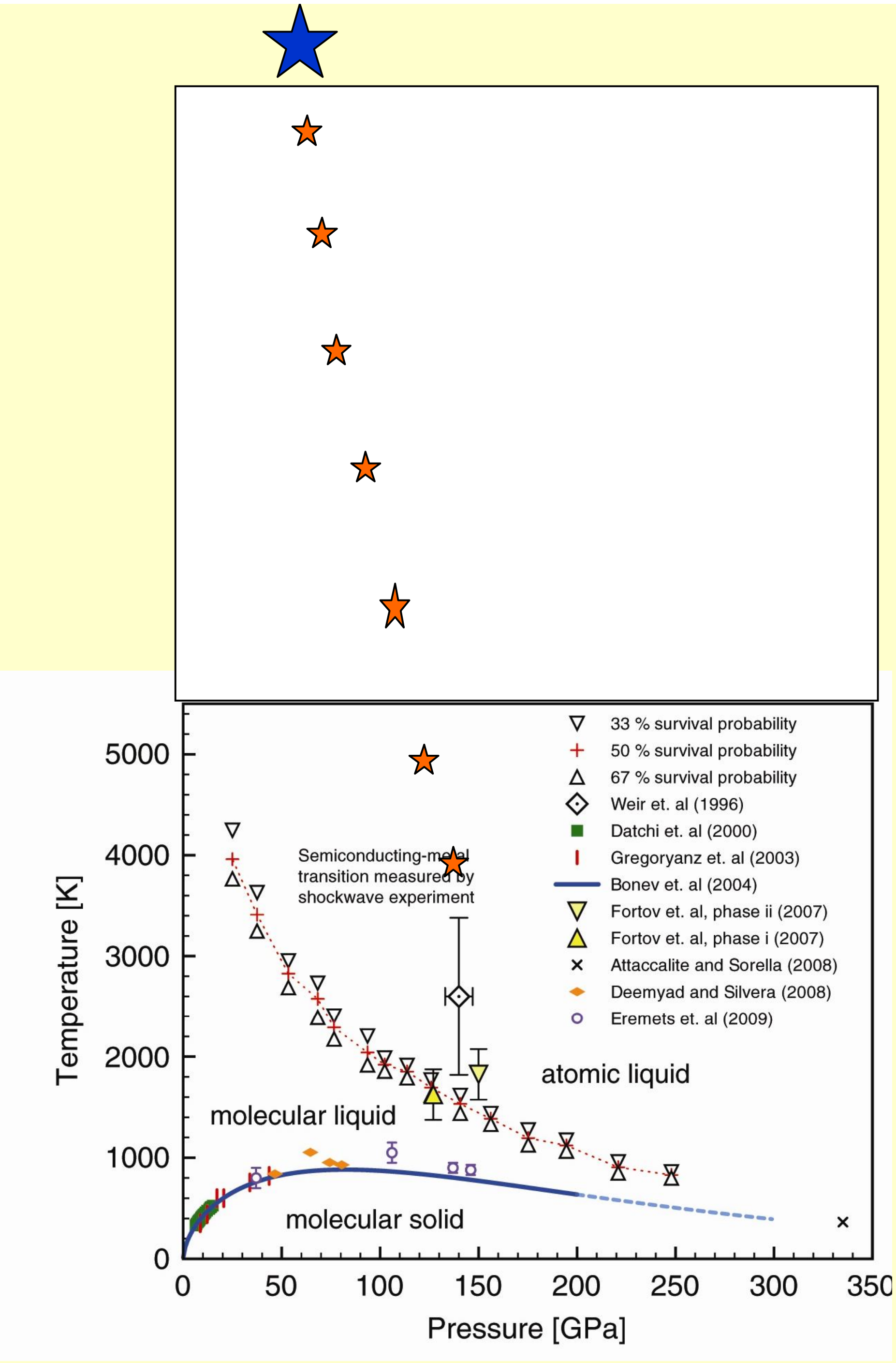
T_{cr}=10500 K

P_{cr}=72GPa



Structure and Phase Boundaries of Compressed Liquid Hydrogen

Isaac Tamblyn* and Stanimir A. Bonev†

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(Received 9 July 2009; published 11 February 2010)

PRL 104, 065702 (2010)

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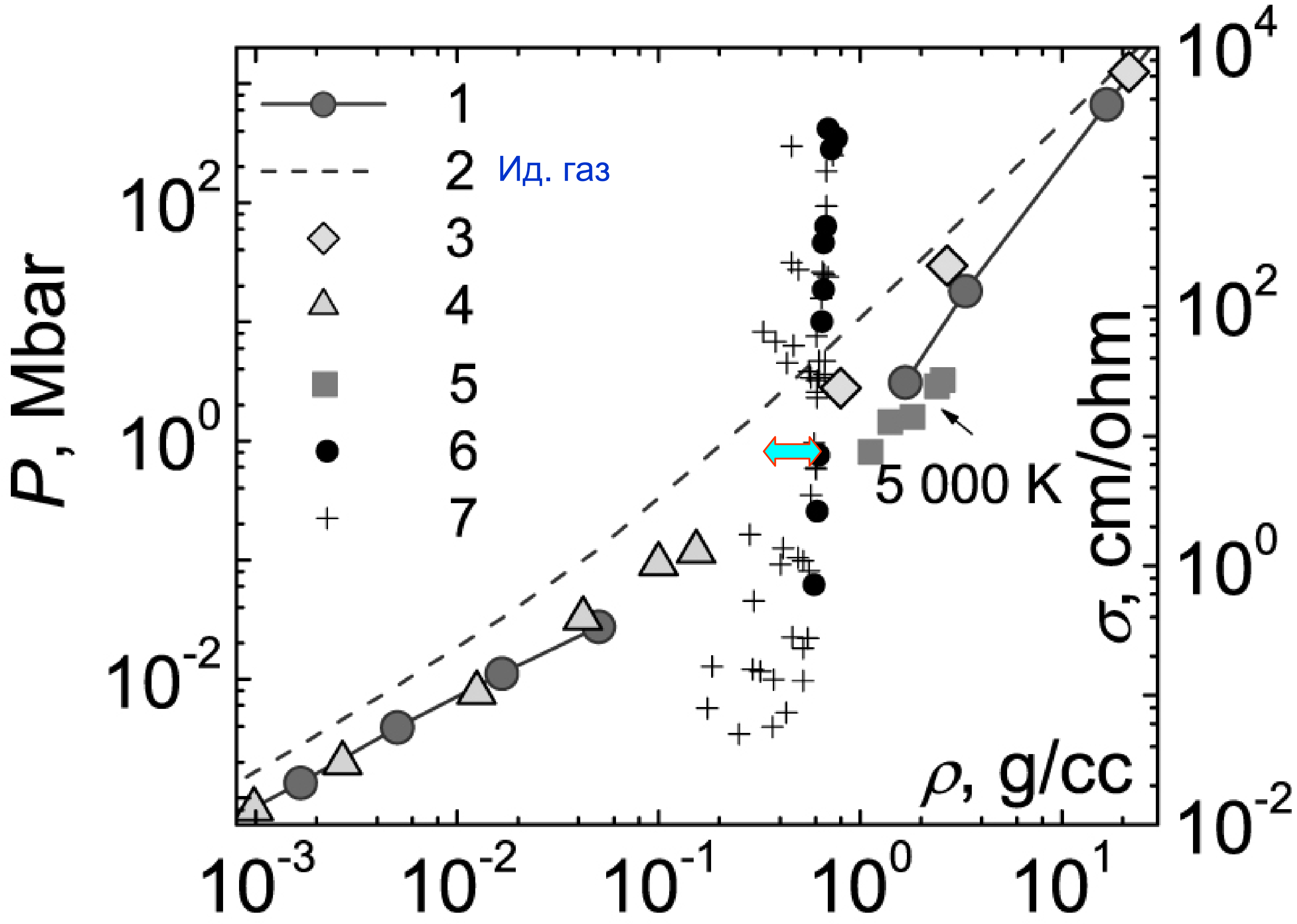

T=10000K

Филинов

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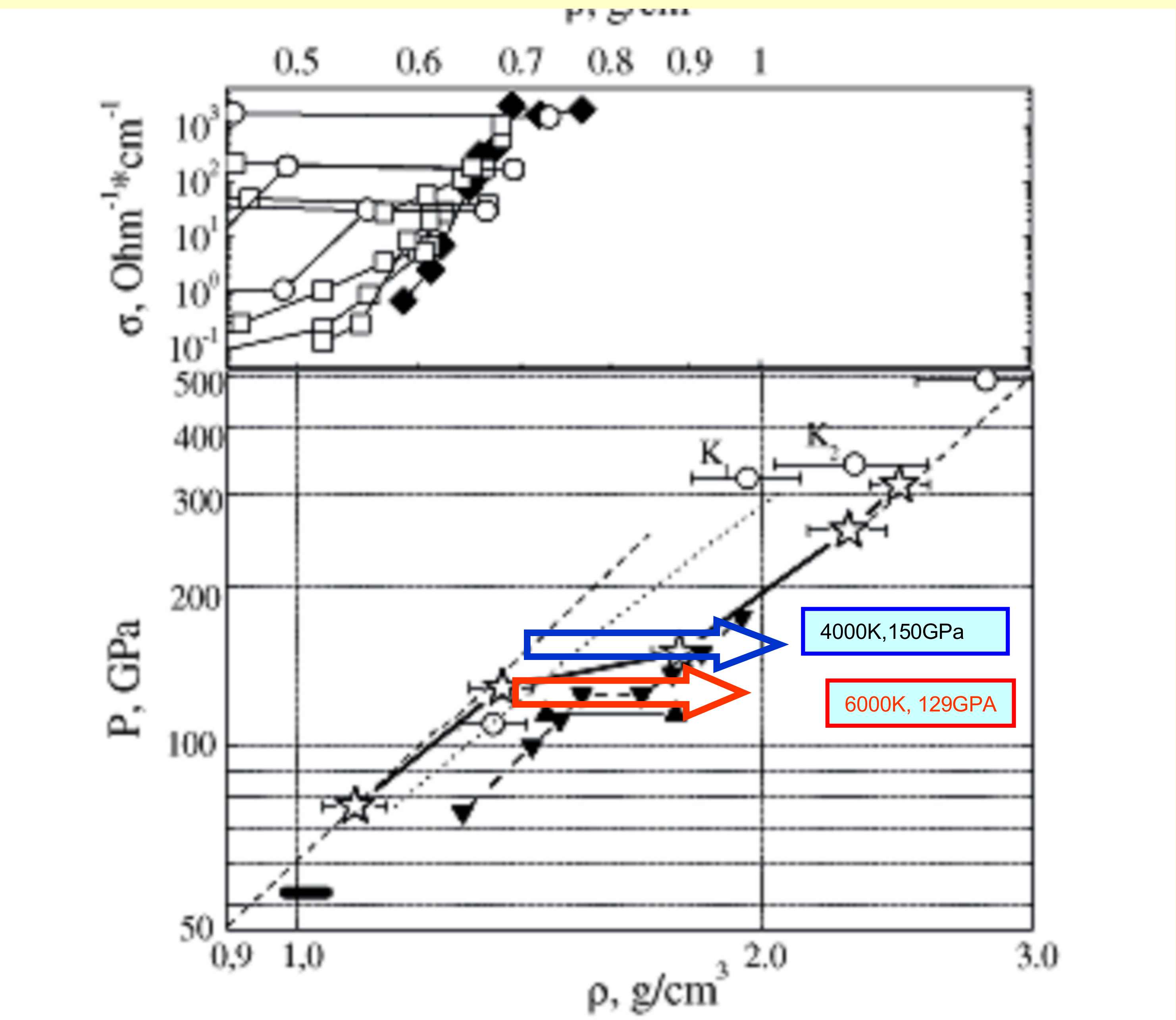
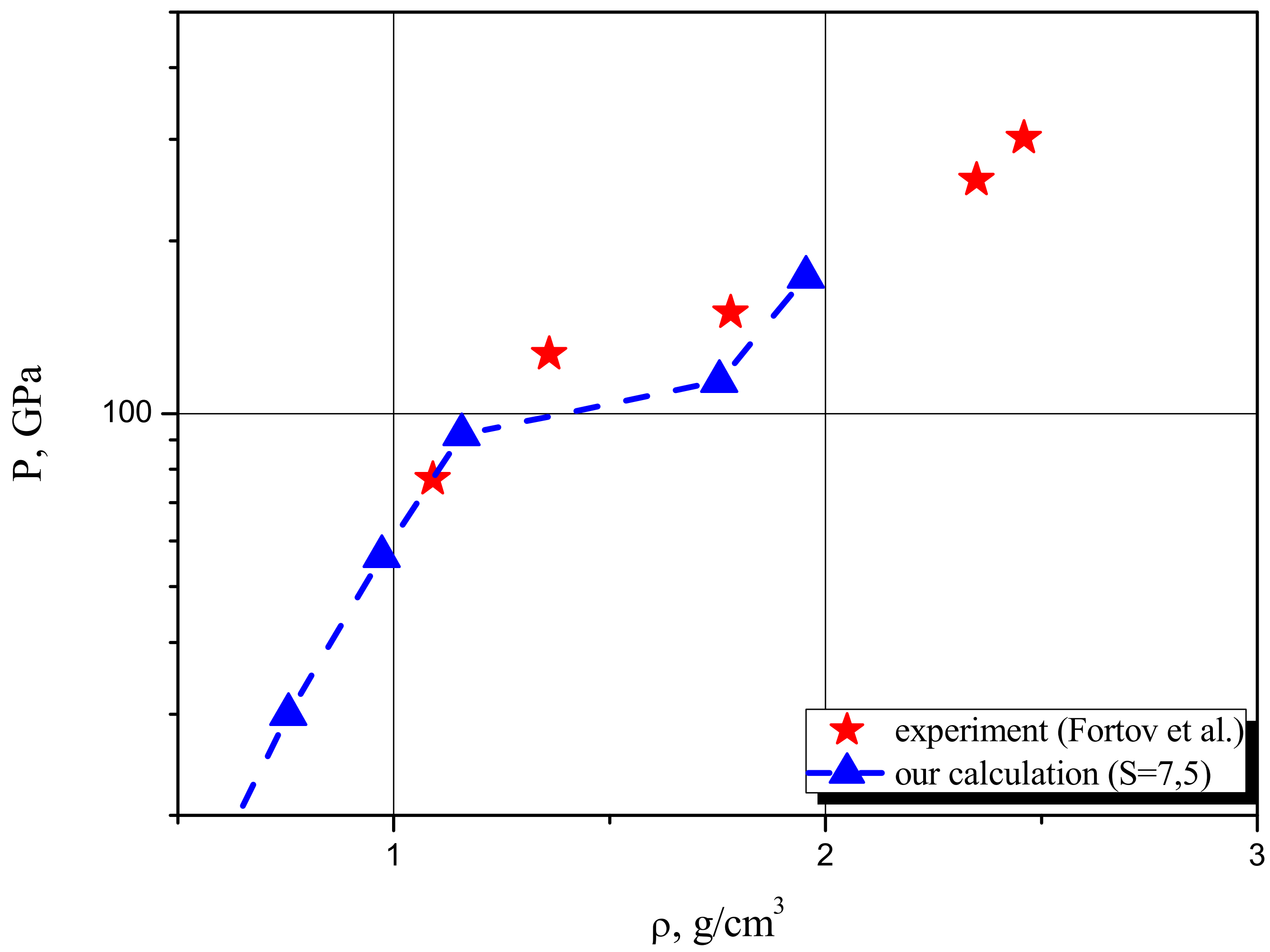
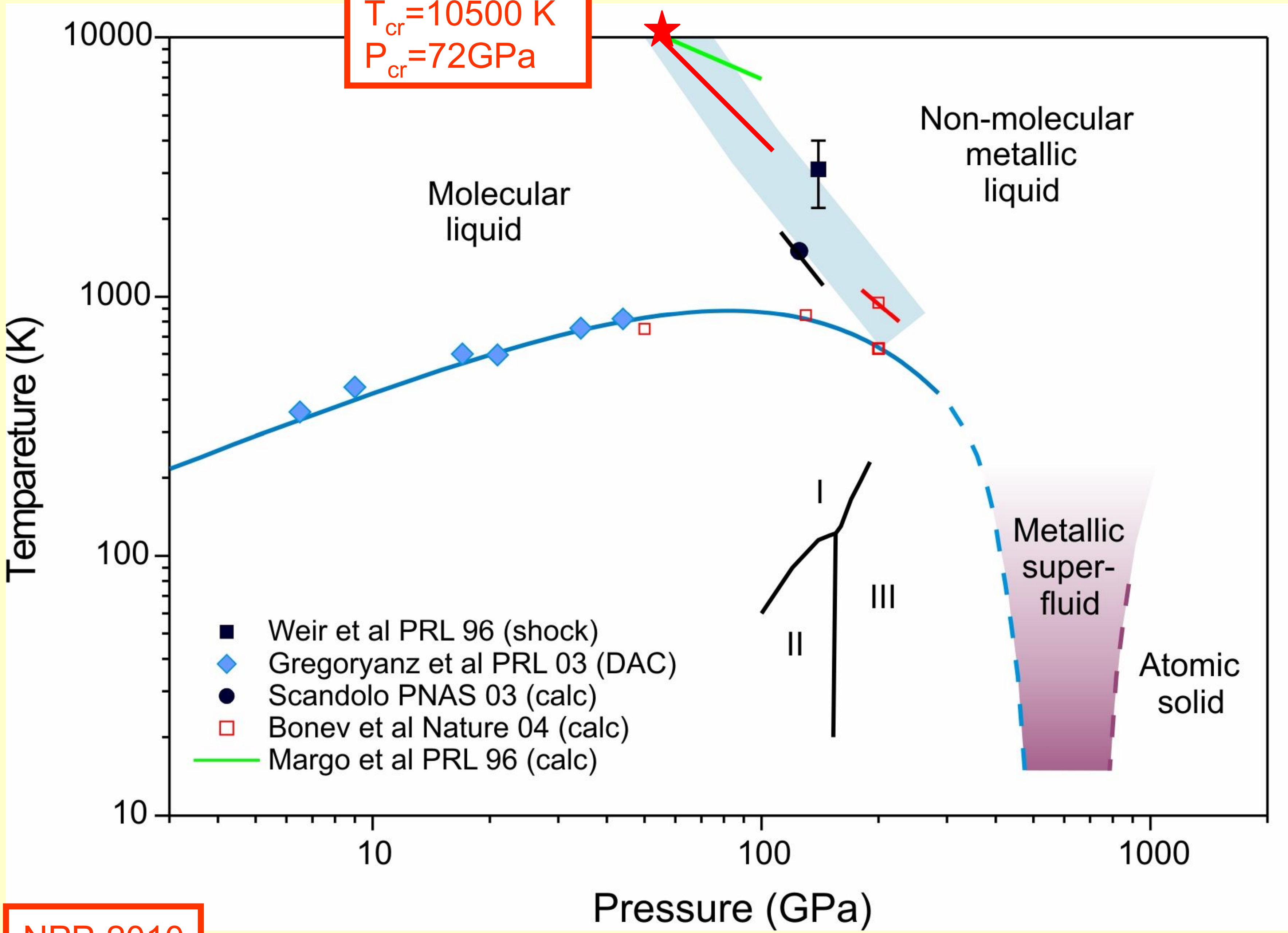


4000K,150GPa

6000K, 129GPA


P, GPa
100
1
2
3
ρ, g/cm^3
experiment (Fortov et al.)
our calculation (S=7,5)



T_{cr}=10500 K
P_{cr}=72GPa

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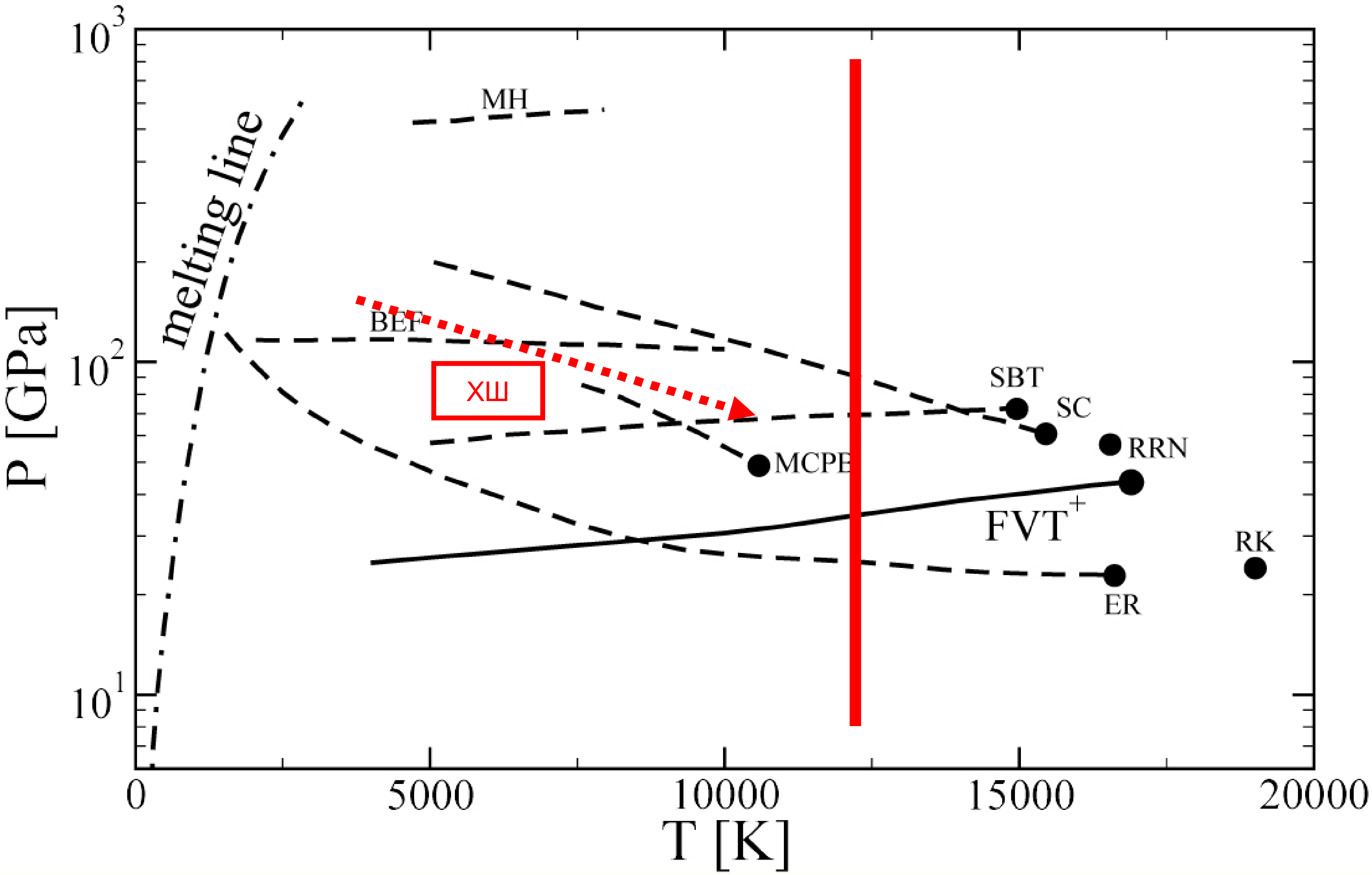
MH
melting line
BEF
ХШ
SBT
SC
RRN
MCPE
FVT+
RK
ER
P [GPa]
10^3
10^2
10^1
0
5000
10000
15000
20000
T [K]

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ВЫВОДЫ:

Предложена простая физическая модель диссоциирующего плотного флюида водорода. Предположено, что свободные атомы взаимодействуют путем квантового межэлектронного обмена аналогичного взаимодействию в жидкометаллической фазе щелочных металлов. Вычислена плотностная зависимость энергия связи атома водорода в такой квазижидкости. Показано, что переход из молекулярного флюида в водородную жидкость имеет характер фазового перехода первого рода. Найдены критические параметры перехода: $P_c = 72\,GPa$, $T_c = 10500\,K$, $\rho_c = 0.5\,g/cc$. Обнаружена возможность метастабильного существования атомарной жидкости водорода в диссоциирующем молекулярном флюиде при разгрузке давления.

СПАСИБО ЗА ВНИМАНИЕ !!!

ОСОБАЯ, ЛИЧНАЯ БЛАГОДОНОСТЬ:

ФОРТОВУ В.Е.

ГРЯЗНОВУ В.К.

ВОРОБЬЕВУ В.С.

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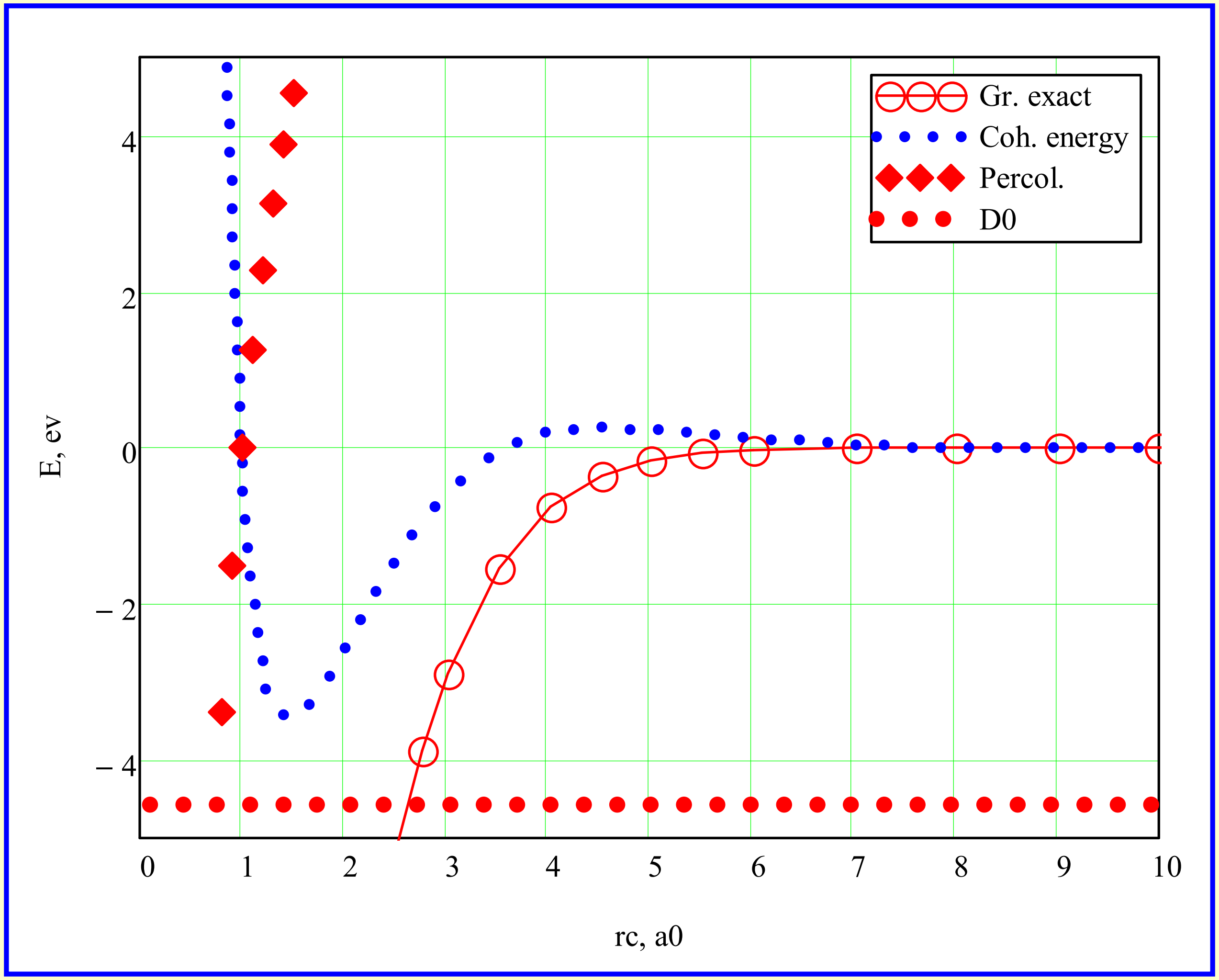

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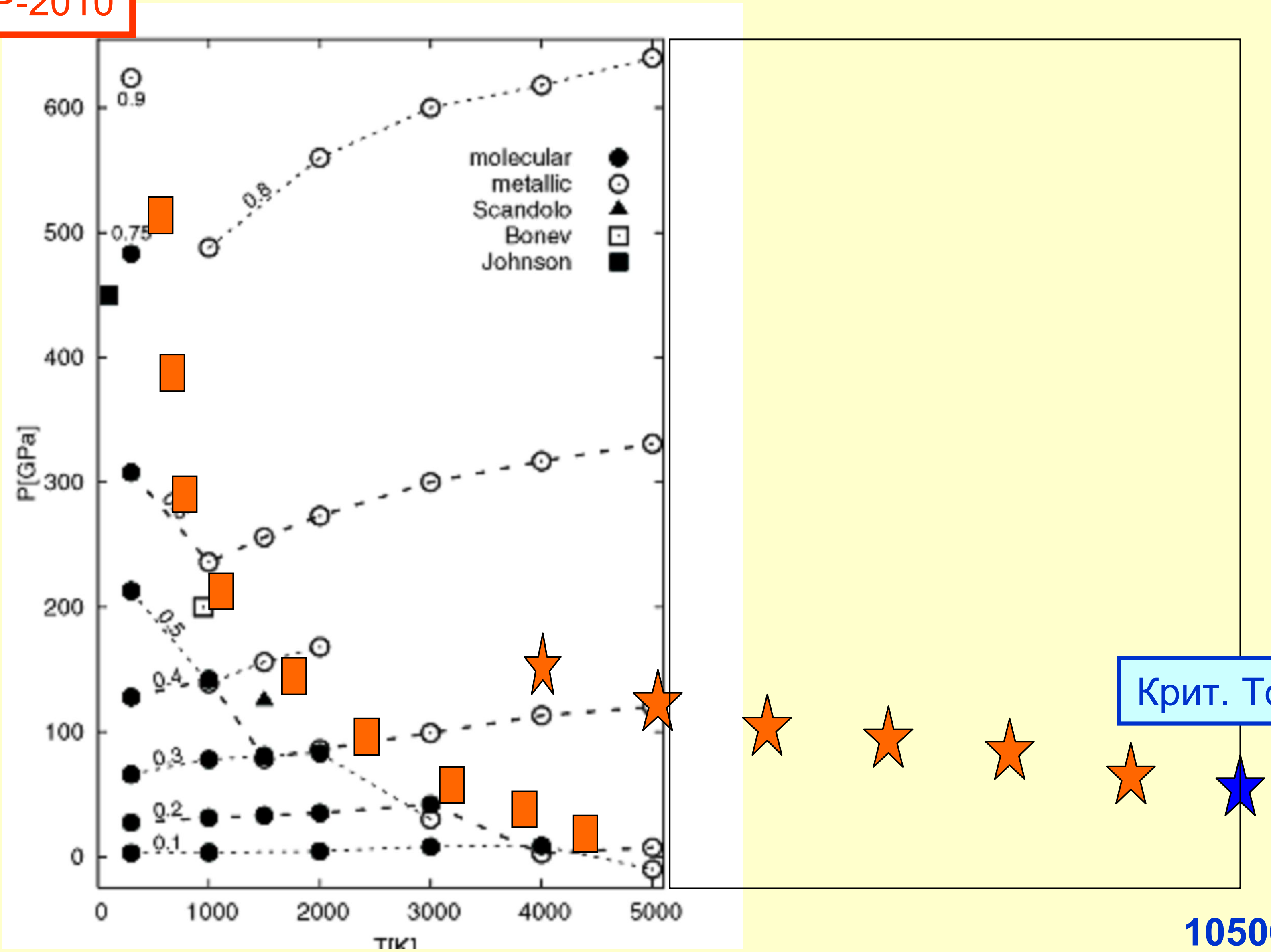

Крит. Точка

10500 К

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$$MHS_{.a}(\eta,n,y) := \frac{4\cdot\eta - 3\cdot\eta^{2}}{(1-\eta)^{2}} + n\cdot\frac{4\cdot\pi}{3}\cdot R1_{.a}(y)^{3}\cdot\left(1-\frac{y}{R1_{.a}(y)}\cdot DR_{.a}(y)\right)\cdot\frac{4-2\cdot\eta}{(1-\eta)^{3}}\cdot a_{.0}{}^{3}$$

$$MHS_{.m}(\eta,n) := \frac{4\cdot\eta - 3\cdot\eta^{2}}{(1-\eta)^{2}} + n\cdot\frac{4\cdot\pi}{3}\cdot R_{.m}{}^{3}\cdot\frac{4-2\cdot\eta}{(1-\eta)^{3}}$$

$$\Delta\mu HS\,(n,\alpha,T) := MHS_{.m}(n,\alpha) - 2\cdot MHS_{.a}(n,\alpha)$$

$$K(n,\alpha,T) := n\cdot\lambda_{.a}(T)^{3}\cdot\frac{2}{\sqrt{2}}\cdot\exp\left(\frac{D0+\Delta D0\,(n,\alpha)\cdot 11605}{T} - \Delta\mu HS\,(n,\alpha,T)\right)\cdot\sigma_{.int}(T)$$

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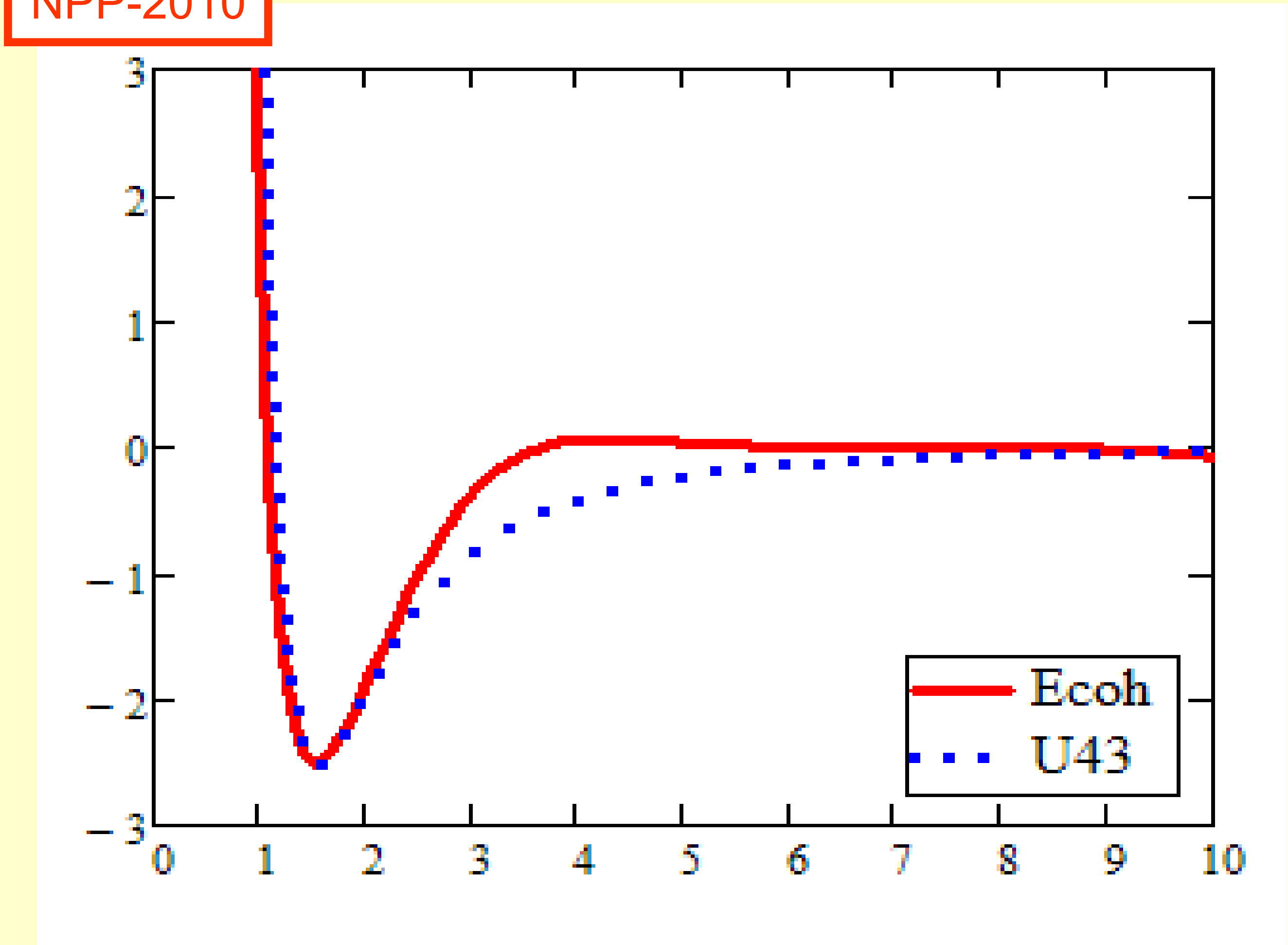

$$U(y) = 10.152\left[\frac{3}{4}\left(\frac{1.53}{y}\right)^4 - \left(\frac{1.43}{y}\right)^3\right]$$

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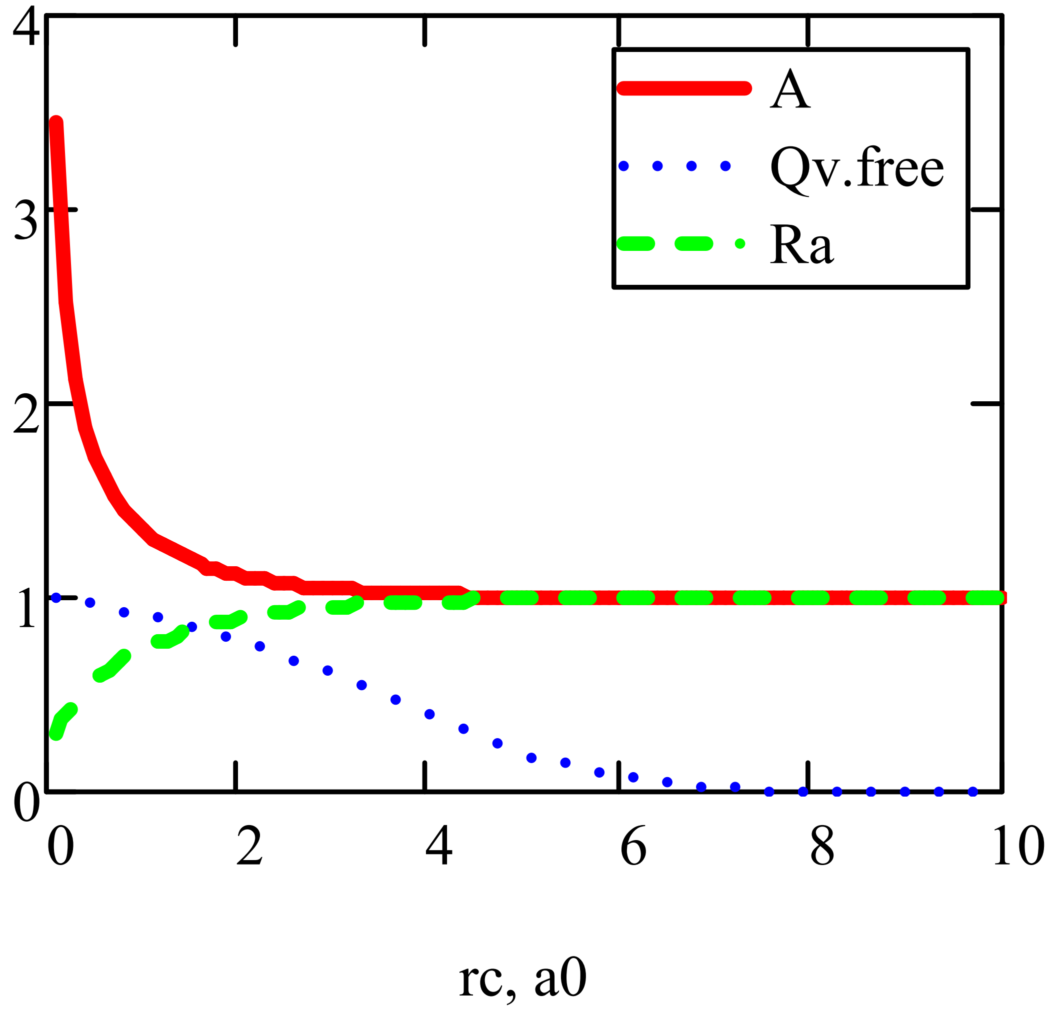

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$$E_{CE}(r_{WS}) = E_{BS}(r_{WS}) + \frac{3}{5}E_F(r_{WS}) + Ry$$

$$E_F(r_{WS}) = \left(3\pi^2\right)^{3/2}\frac{\hbar^2}{2m_e}n_e^{qf}(r_{WS})$$

$$n_e^{qf}(r_{WS}) = n_a \frac{\Psi^2(r_{WS})4\pi\, r_{WS}^3 / 3}{\int\limits_0^{r_{WS}} 4\pi\Psi^2(r)r^2dr}$$

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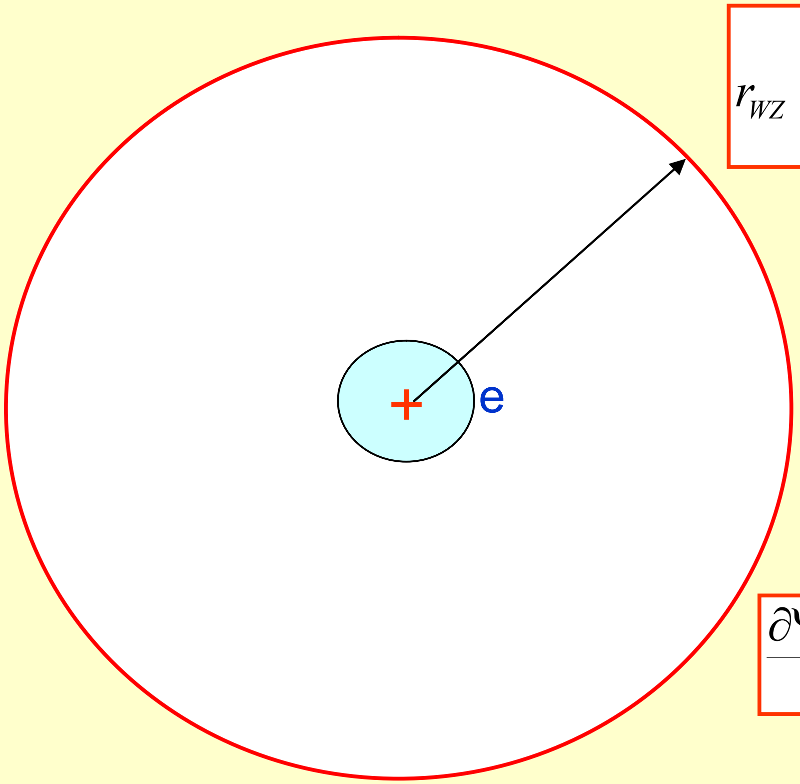
ргия основного состояния атома в квазижидкости

Wigner-Seitz cell



$$r_{WZ} = \left(\frac{3}{4\pi n_a} \right)^{1/3}$$

$$\left. \frac{\partial \Psi(r)}{\partial r} \right|_{r=r_{WZ}} = 0$$

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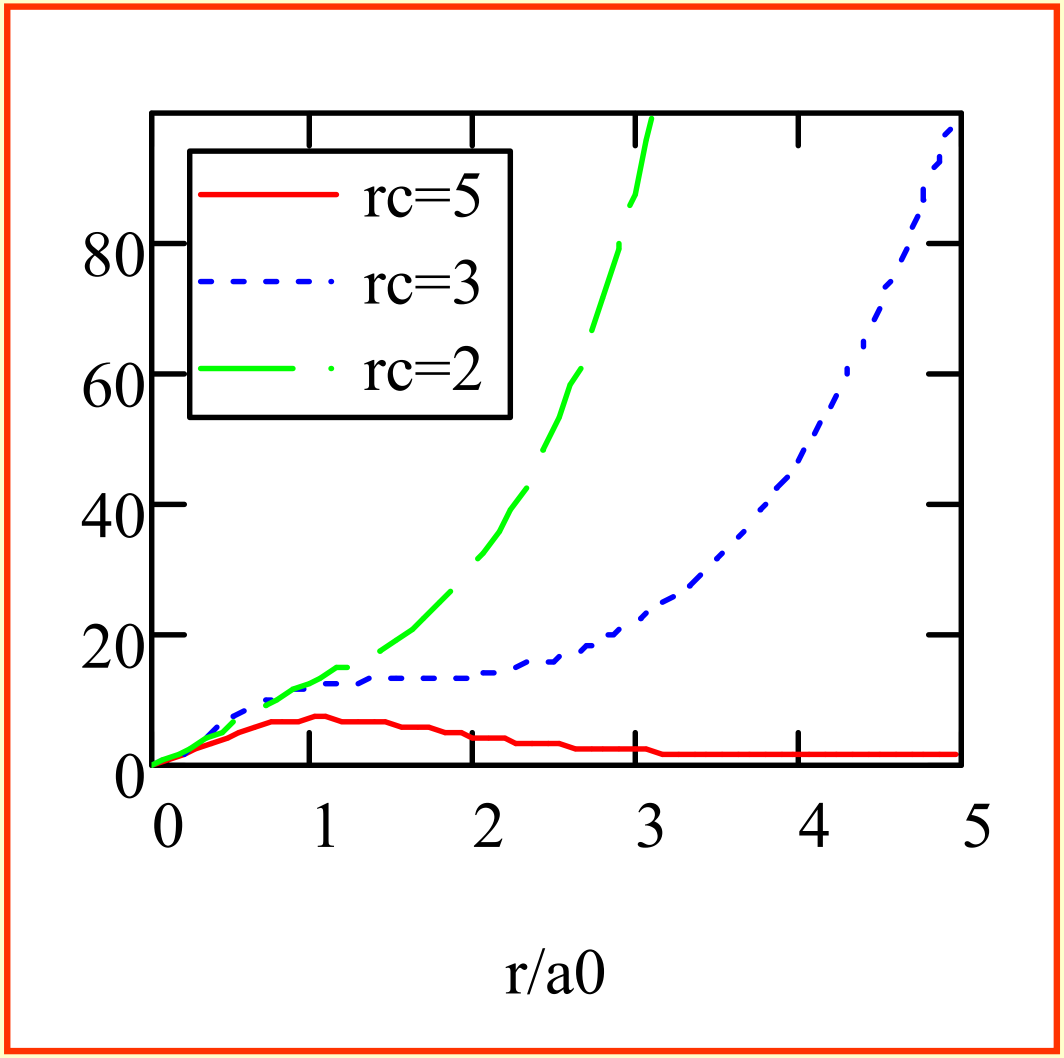
$$4\pi r^2 \Psi^2 (r, r_{WS})$$



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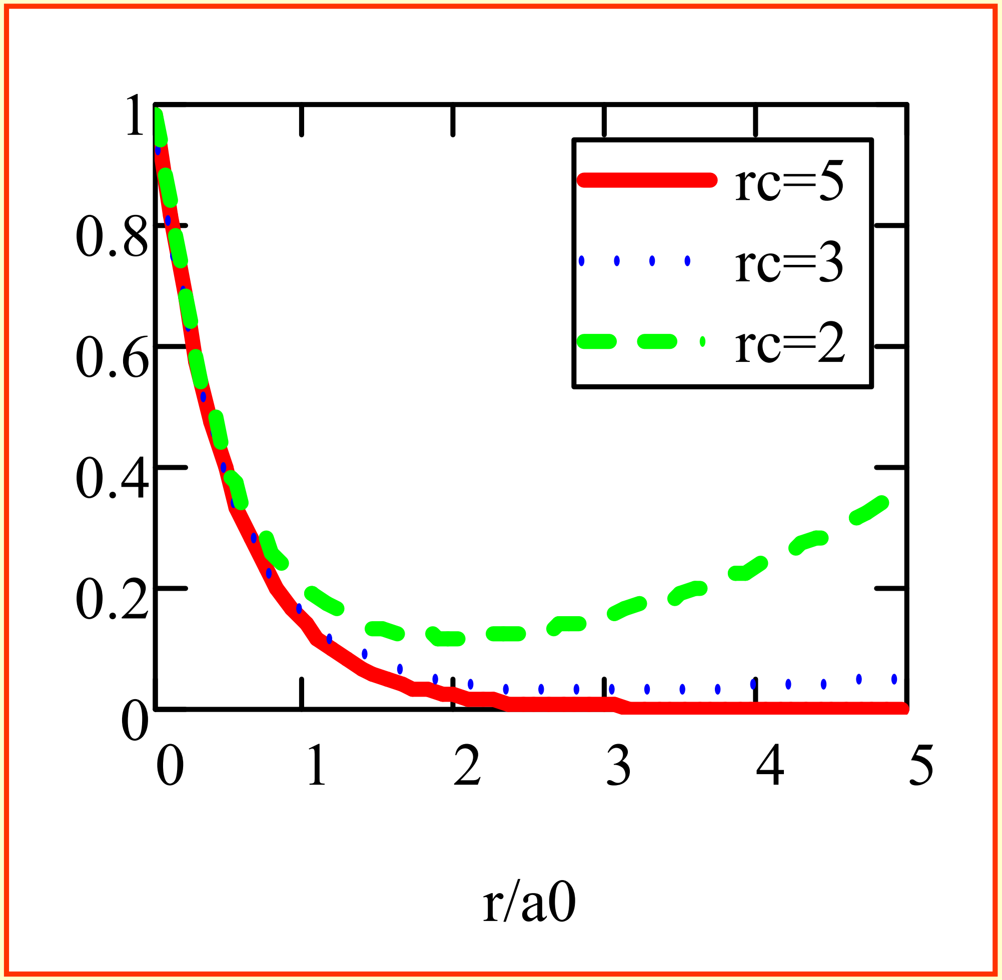
$$\Psi^2(r, r_{WS})$$



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$$a_0 = \hbar^2 / me^2$$

$$\left.\frac{dR_0(r)}{dr}\right|_{r=r_c} = 0$$

$$R_1(r) = A_1 \exp(-k_0 r) r\, F(2 - 1/k_0 r, 4, 2k_0 r)$$

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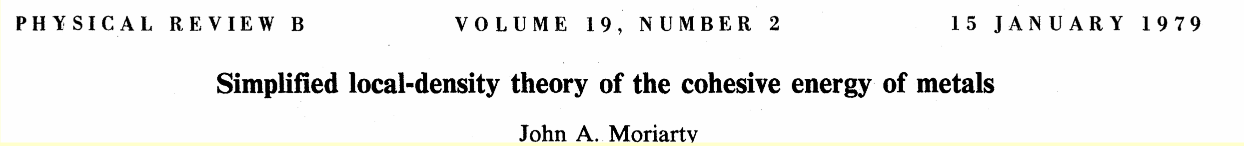
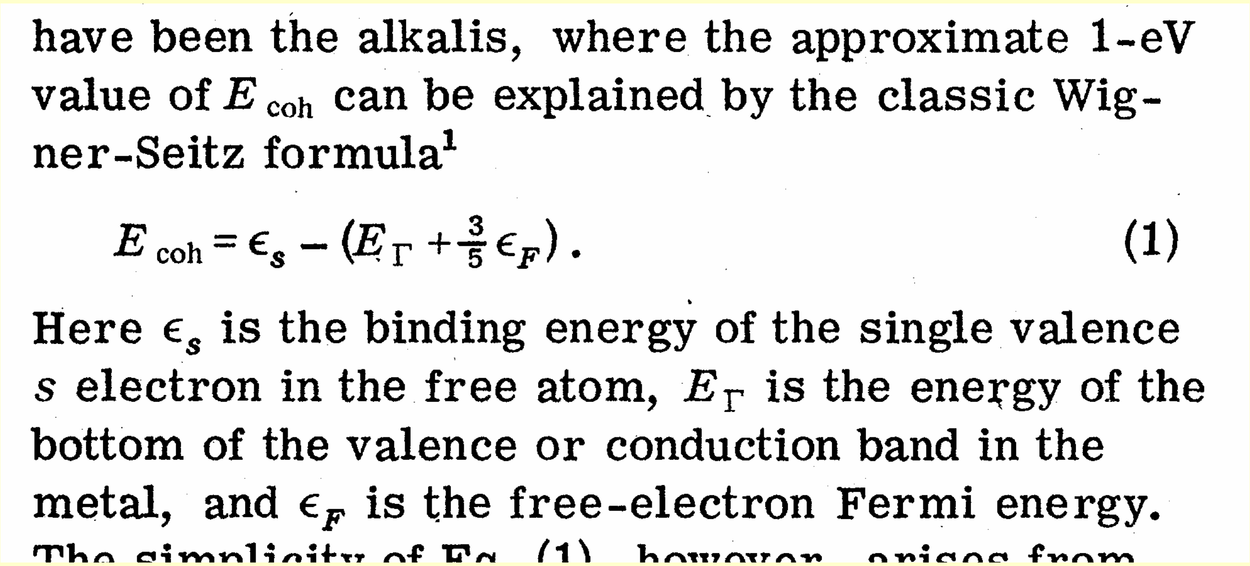


PHYSICAL REVIEW B VOLUME 19, NUMBER 2 15 JANUARY 1979

Simplified local-density theory of the cohesive energy of metals

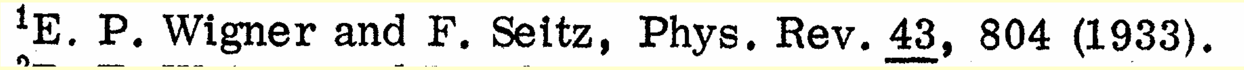
John A. Moriarty



have been the alkalis, where the approximate 1-eV value of E_{coh} can be explained by the classic Wigner-Seitz formula[1]

$$E_{\text{coh}} = \epsilon_s - (E_\Gamma + \tfrac{3}{5}\epsilon_F) . \tag{1}$$

Here ϵ_s is the binding energy of the single valence s electron in the free atom, E_Γ is the energy of the bottom of the valence or conduction band in the metal, and ϵ_F is the free-electron Fermi energy. The simplicity of Eq. (1), however, arises from



[1] E. P. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).

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Однокомпонентные вещества

$$F = F_0 + F_{HS} + F_{\text{int}}$$

$$F_0 = -NkT\ln\left(\frac{eV}{N\lambda^3}\right)$$

$$F_{HS} = NkT\frac{4\eta - 3\eta^2}{(1-\eta)^2}$$

$$F_{INT} = \frac{1}{2}4\pi\int V(r)g^{HS}(r)r^2dr$$

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2. Ab Initio – расчеты
(Филинов, Цеперли, Бонев и др.)

Structure and Phase Boundaries of Compressed Liquid Hydrogen
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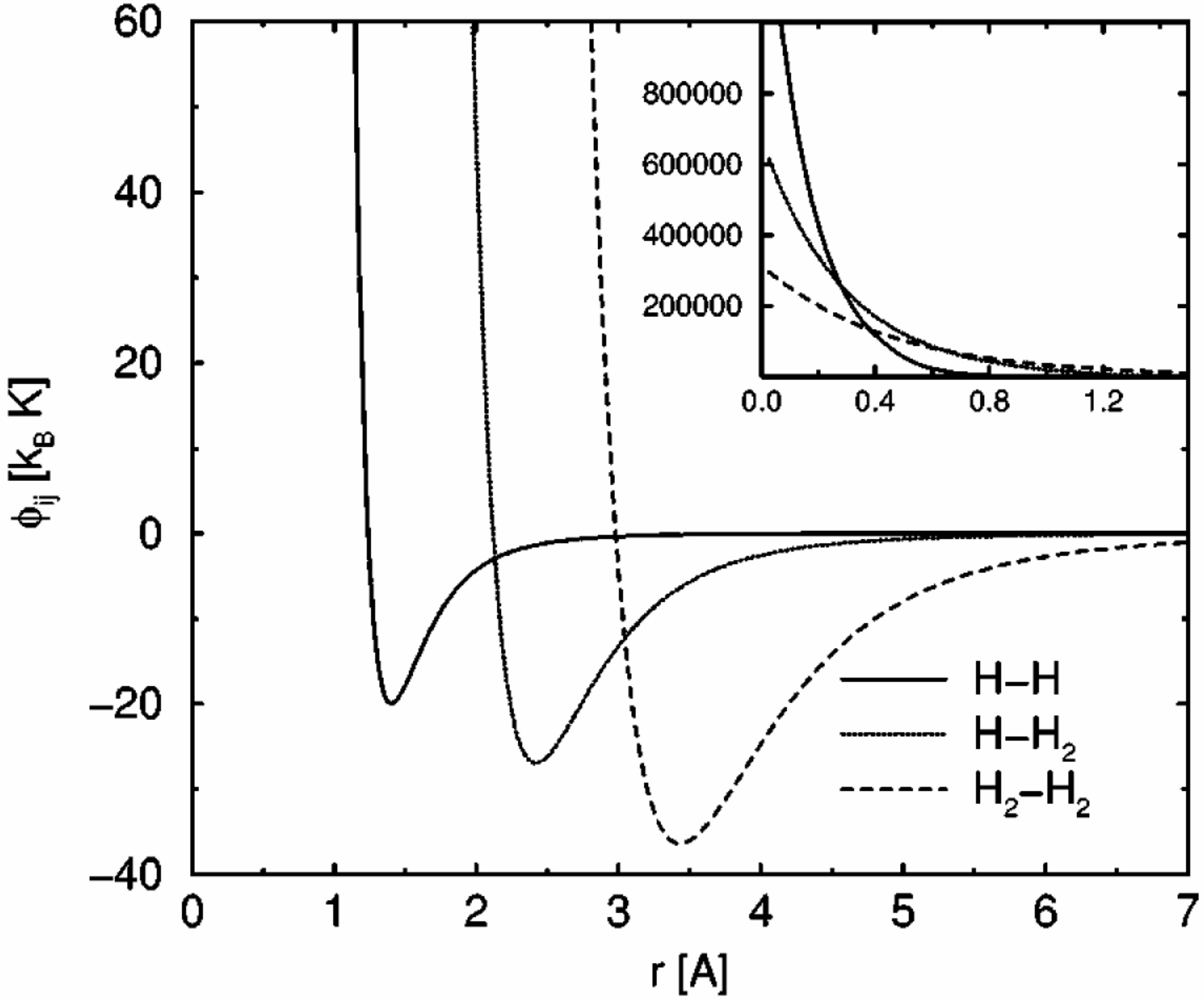

FIG. 1. Effective pair potentials for the H–H_2 mixture.