7th International EMMI Workshop

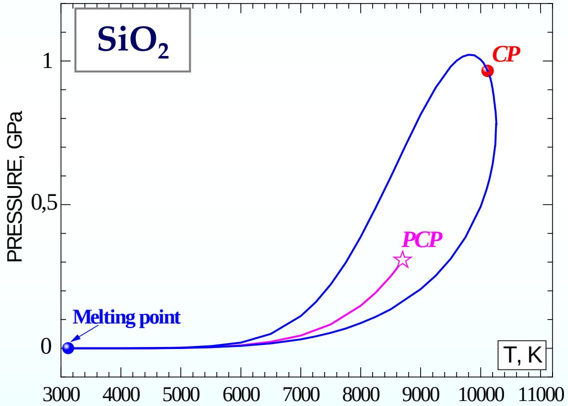
Plasma Physics & Intense Heavy Ion
& Laser Beams at FAIR

Moscow, Russia, December 2014

High-Temperature Phase Diagram

and

Critical Point Parameters *in* SiO_2



Igor Iosilevskiy *and* Victor Gryaznov

Joint Institute for High Temperature (Russian Academy of Science)
Institute of Problems Chemical Physics (Russian Academy of Science)
Moscow Institute of Physics and Technology (State University)

2014

2014

HIB for study of WDM thermophysical properties

what could we do and what should we do ?

Historical comments

“Day-One” experiments *with* volumetric HIB energy deposition

(**1997,** ITEPh)

$\Delta E \sim 1$ kJ/g	(1997)
....	
$\Delta E \sim 1$ kJ/g	(2001)
....	
$\Delta E \sim 1$ kJ/g	(2007)
....	
??	(**??**)

Boris Sharkov’s claim:

1997

? **What could we do** with $\Delta E \sim$ **1** kJ/g *and* $t_{HIB} \sim 100$ ns **?**

2014

“Day-One” experiments *with* HIB energy deposition *at* FAIR

? **What should we do** with $\Delta E \sim$ **5-10** kJ/g $t_{HIB} \sim 100$ ns **?**

I.I.’s proposals (1997 – 2014):

Study of thermophysical properties of WDM

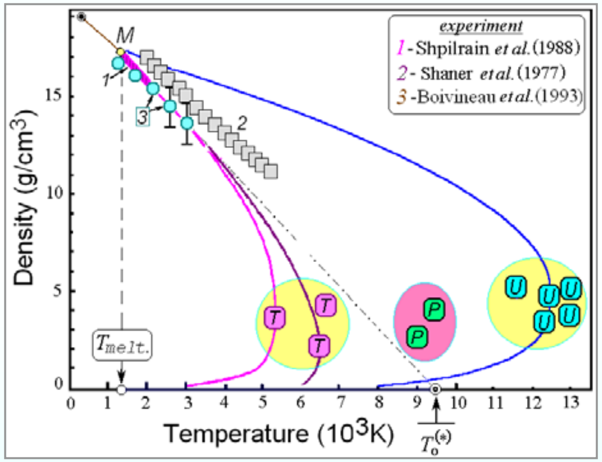
- What to study. Fundamental physical problem
- How to arrange HIB energy deposition
- How to arrange measurements

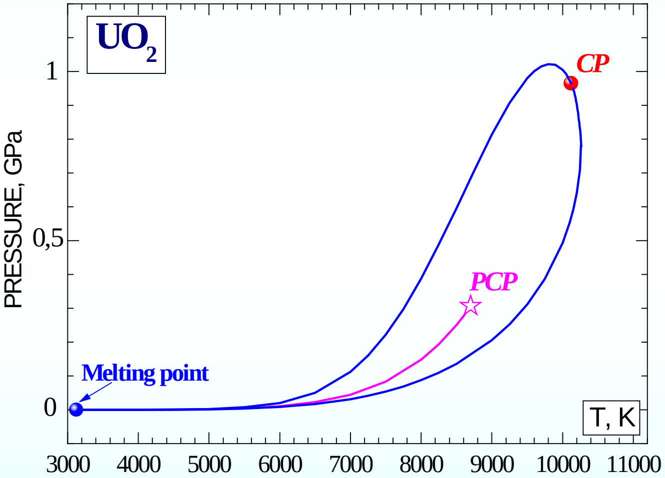
International Workshop on Physics of High Energy Density in Matter

*(Hirschegg – **2007**)*

HIB heating of porous samples:

why should we do it ?





Igor Iosilevskiy

Moscow Institute of Physics and Technology
(State University)

HIB for thermophysical investigations

(I.I. // Hirschegg – 2007 // GSI – 2007)

– How to arrange HIB energy deposition

Priorities

- Uniformity of heated material
- Thermodynamic equilibrium

– How to arrange measurements

Priorities

- Direct measurement of thermodynamic parameters
  without intermediate hydrodynamic re-calculations
- Energy deposition control

NB !

HIB heating of **highly dispersed** materials –

– very promising for **thermophysical investigations** (*)

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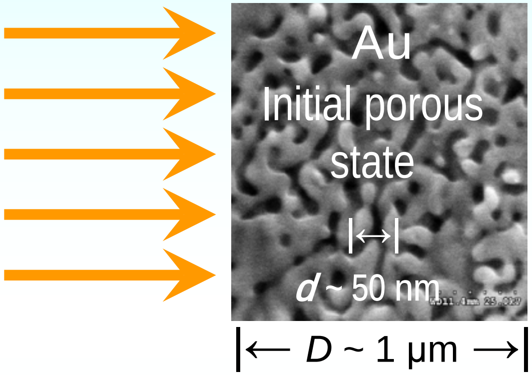
* Iosilevskiy I. // Int. Conf. *Intense Ion Beam Interaction with Ionized Matter* // Moscow, ITEP Publishing (**1999**) / arXiv:1005.4181
Iosilevskiy I., Gryaznov V. // XIV Int. Conf. *Heavy Ion & Inertial Fusion* // Moscow, ITEP Publishing (**2002**) / arXiv:1005.4192
Iosilevskiy I. // "*High Energy Density Physics with Intense Ion and Laser Beams*", GSI Annual Report 2006 /GSI-2007-2 /

HIB volumetric heating of porous sample

Acoustic time (*single grain*) $\tau_d \equiv d/c_s$ $<<$ τ_{HIB} $<<$ $\tau_D \equiv D/c_s$ (*whole sample*)



Real Experiment in GSI (2006)

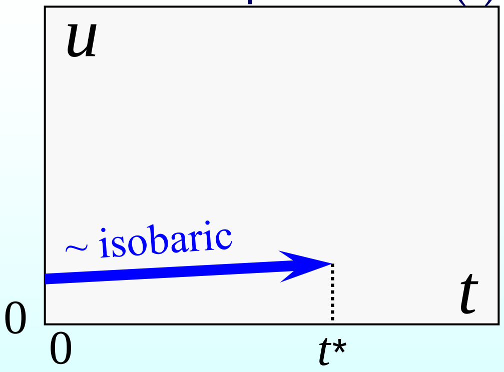
$d \sim 50$ nm, $D \sim 1$ mm, $\tau_{HIB} \sim 100$ ns

$a_{sound} \sim 2$ km/sec

$\tau_d \equiv d/a_s \sim$ **25** ps (!), $\tau_D \equiv D/a_s \sim$ **1** μs

$\tau_d <<< \tau_{HIB} < \tau_D$

Surface expansion: $u(t)$



Uniformity of heating

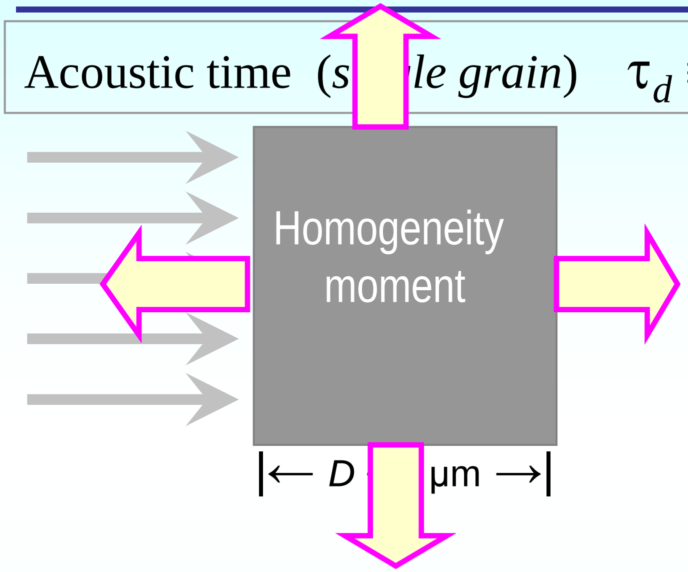
Porous sample: – Grain expansion is quasi-free (*isobaric*)

No surface movement up to **homogeneity moment !**

HIB heating of highly dispersed porous samples: *Why should we do it ?*

HIB volumetric heating of porous sample

Acoustic time (s le grain) $\tau_d \equiv d/c_s$ << τ_{HIB} << $\tau_D \equiv D/c_s$ (*whole sample*)



Real Experiment in GSI (2006)

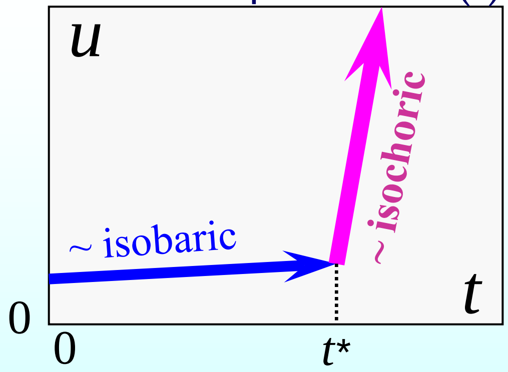
d ~ 50 nm, D ~ 1 mm, τ_{HIB} ~ 100 ns

a_{sound} ~ 2 km/sec

$\tau_d \equiv d/a_s$ ~ **25** ps (!), $\tau_D \equiv D/a_s$ ~ **1** μs

τ_d <<< τ_{HIB} < τ_D

Surface expansion: $u(t)$



Uniformity of heating

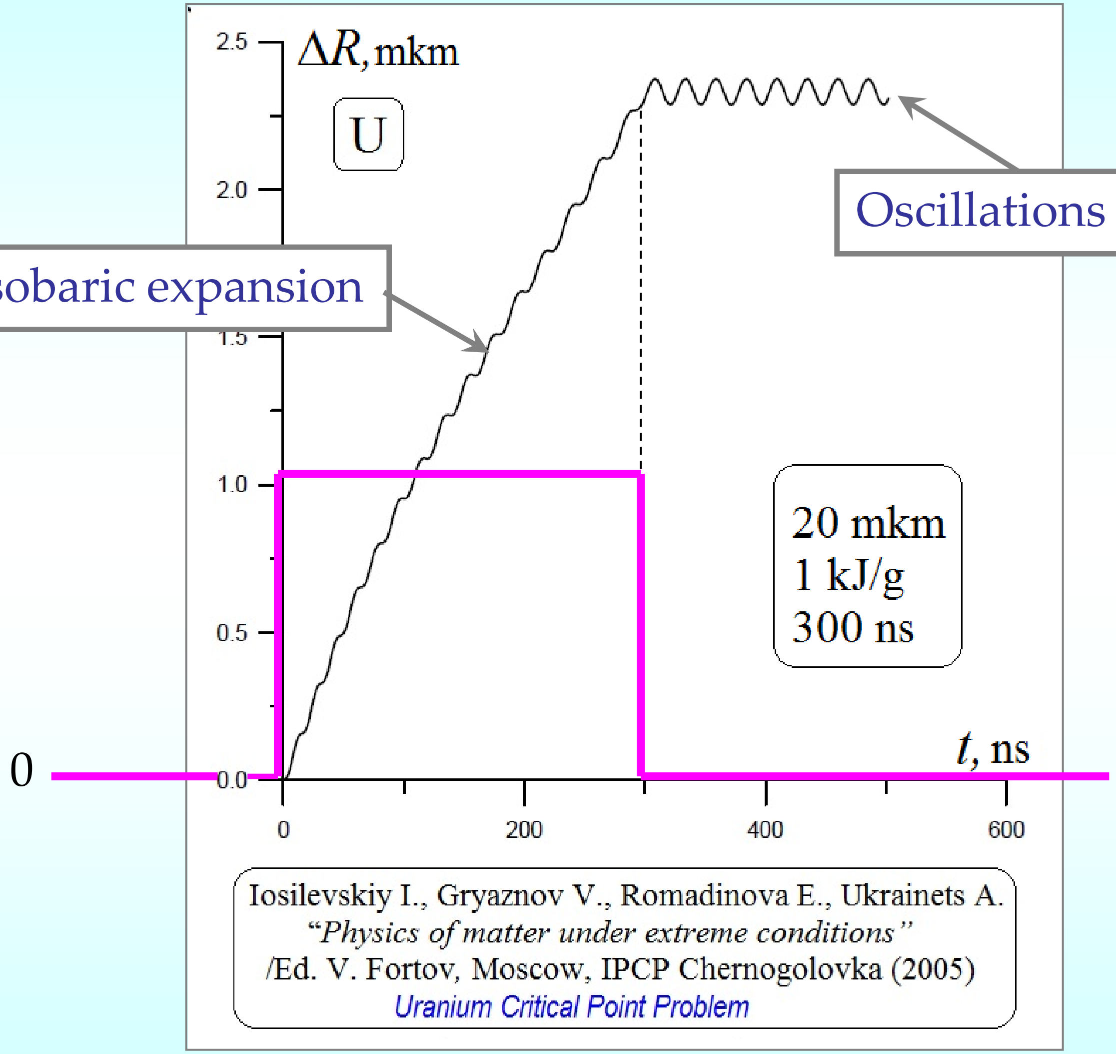
Porous sample: – Grain expansion is quasi-free (*isobaric*)

No surface movement up to **homogeneity moment !**

Fast surface expansion after homogeneity moment **!**

HIB heating of highly dispersed porous samples: *Why should we do it ?*

Quasi-isobaric thermal expansion *and* **oscillations** *of* **Uranium foil** *under* **volumetric HIB irradiation**



Quasi-isobaric expansion

Oscillations (ν ~10^8Hz, δx ~0.1μm)

HIB Energy deposition

Iosilevskiy I., Gryaznov V., Romadinova E., Ukrainets A.
"Physics of matter under extreme conditions"
/Ed. V. Fortov, Moscow, IPCP Chernogolovka (2005)
Uranium Critical Point Problem

Surface movement of uranium foil

(I.I. *et al* // Elbrus Conf. (Russia) – 2005)

Measurements of **thermal expansion** for **liquid SiO_2 under volumetric heavy ion beam irradiation (FAIR-GSI)**

Heating of stack target

The Sixth International Conference on Inertial Fusion Sciences and Applications IOP Publishing
Journal of Physics: Conference Series **244** (2010) 042021 doi:10.1088/1742-6596/244/4/042021

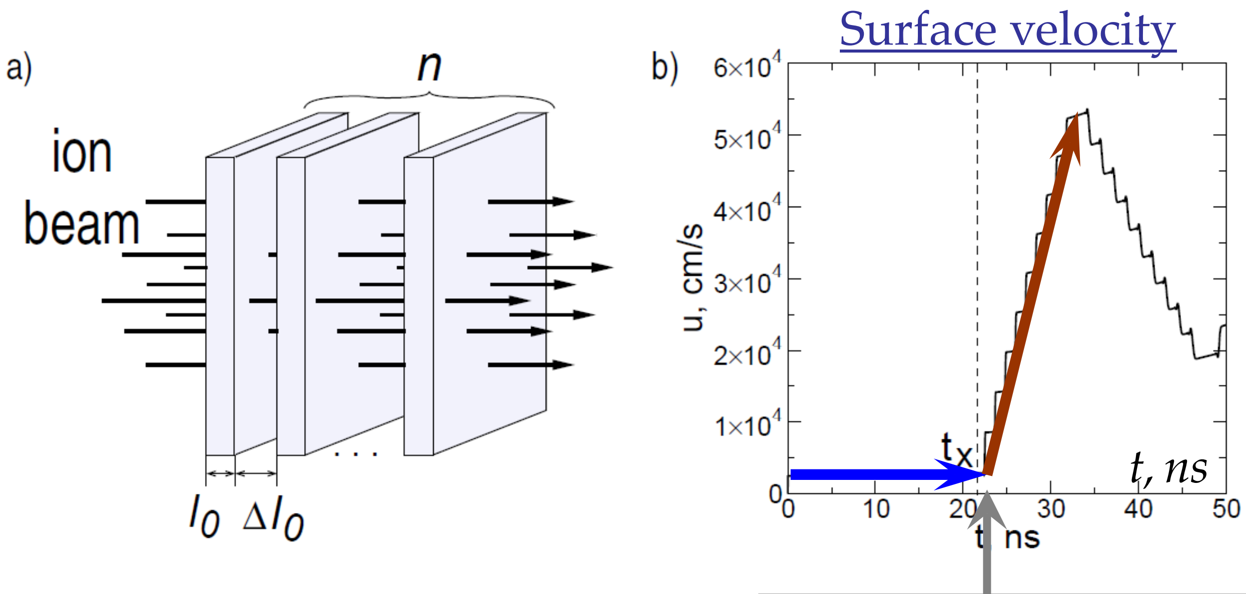


Figure 3. a) Stack target configuration. b) Surface vel
of 10 foils irradiated with an ion beam.

Homogeneity moment

Tauschwitz Ann., Basko M., Efremov V., Iosilevskiy I., Jacoby J., Maruhn J., Neumayer P., Novikov V., Tauschwitz And., Rosmej F.
Journal of Physics: Conference Series **244** 042021 (2010)
Outline of experimental schemes for measurements of thermophysical and transport properties in warm dense matter at GSI and FAIR

Anna Tauschwitz et al.

Dynamics of volumetrically heated matter passing through the liquid-vapor metastable states

Steffen Faik[1], Mikhail M. Basko[2,3], Anna Tauschwitz[1,2],
Igor Iosilevskiy[2,4,5], Joachim A. Maruhn[1,2]

(1) ITP, Goethe-Universität, Frankfurt am Main (2) EMMI, GSI, Darmstadt
(3) ITEP, Moscow (4) JIHT-RAS, Moscow (5) MIPT, Moscow region

PP-Seminar, GSI, Darmstadt, 17th April 2012

GOETHE UNIVERSITÄT FRANKFURT AM MAIN

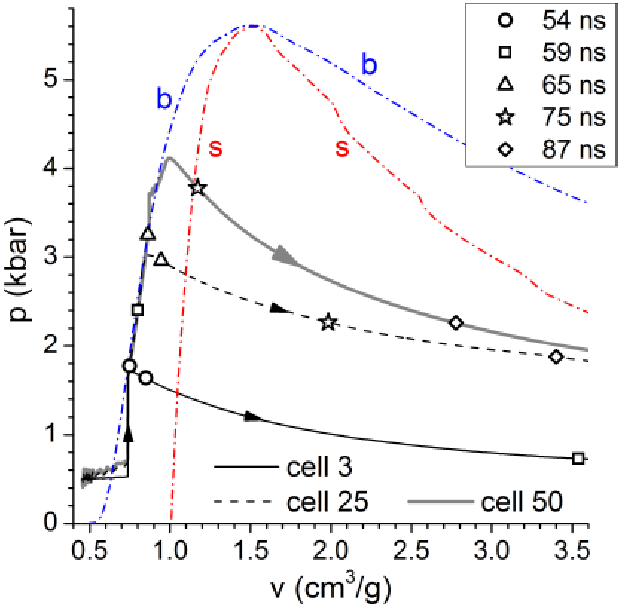
EMMI

GSI

Faik S. *et al.*/ *High Energy Density Physics,* **8,** 349 (2012) / arXiv:1205.2579v1

Simulation results (1/2)

v-p phase plane - MS case



Cell 3: Foil boundary

Cell 25: Half distance between center and boundary

Cell 50: Foil center

Evolution after boiling

The boundary relaxes to p_0.

The center elements follow for about 20 ns the binodal until the rarefaction wave arrives!

$c_{s,MS}/c_{s,EQ} \approx 30 \ldots 3$ on binodal $\Rightarrow$ Binodal becomes an attractor!

Faik S. *et al.*/ *High Energy Density Physics*, **8**, 349 (2012) / arXiv:1205.2579v1

HIB for thermophysical investigations

(I.I. // Hirschegg –2007 / GSI –2007)

- What to study
- How to arrange HIB energy deposition
- How to arrange measurements

Basic point

- Careful choice of investigated substance and physical problem

Criteria

- great uncertainty
- great applied importance
- fundamental physics

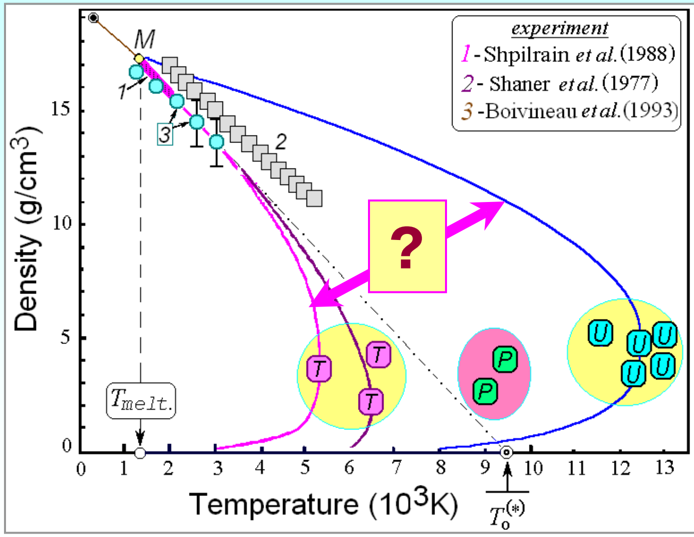
Heavy Ion Beam experiments – what should we study ?

Two outstanding goals

- **Uranium critical point location problem**
  - applied importance (++)
  - phenomenology (++)
  - fundamental physical problem (++)

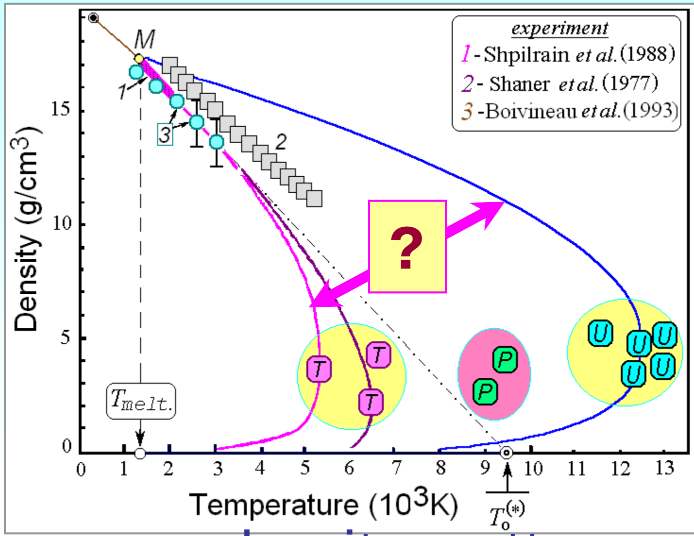
  Similar problem for refractory metals: **W, Mo, Co**…*etc*

  { e.g. Iosilevskiy I., Gryaznov V. *J. Nuclear Materials* **344,** (2005) }



- Iosilevskiy I., in: Int. Conference “*Intense Ion Beam Interaction with Ionized Matter*”, Moscow, 1999, (Proc., ITEP Publishing, p.159-173)
  Heavy Ion Beam for Investigation of Thermodynamic Properties // arXiv:1005.4181
- Iosilevskiy I., in: “*High Energy Density Physics with Intense Ion and Laser Beams*”, GSI Annual Report 2006 /GSI-2007-2, may 2007/
  Heavy Ion Beam in Resolution of the Critical Point Problem for Uranium and Uranium Dioxide.

Heavy Ion Beam experiments – what should we study ?



Two outstanding goals

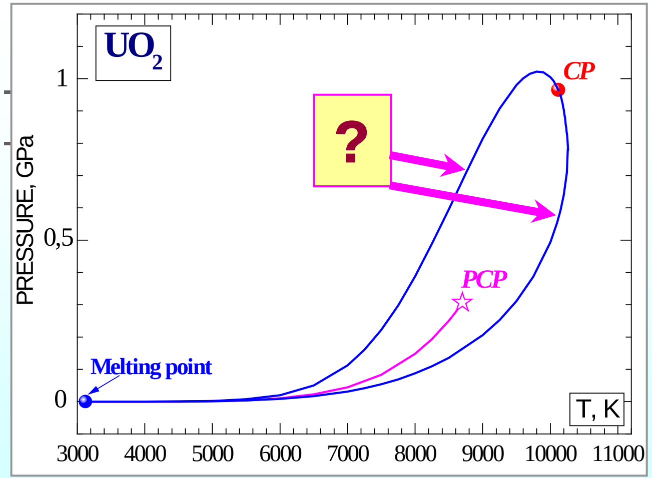
- **Uranium critical point location problem**
  - applied importance
  - phenomenology
  - fundamental physical problem

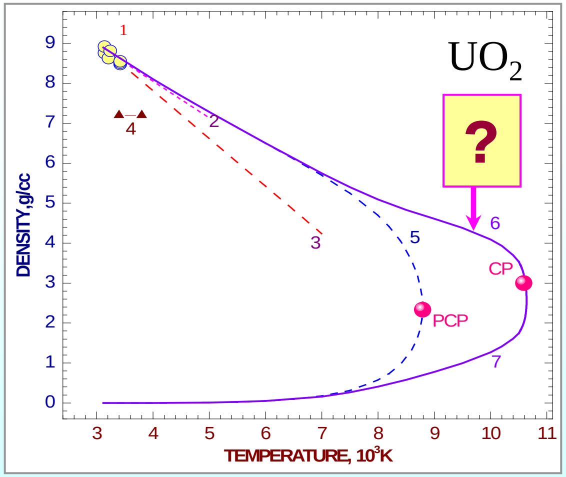
  Similar problem for refractory metals: **W, Mo, Co**…*etc*

  e.g. Iosilevskiy I., Gryaznov V. *J. Nuclear Materials* **344,** (2005)

- **Non-congruent phase transitions** in high energy density matter

  (*uranium-bearing fuels* (UO_2, UC, UN ...) *and other compounds* (SiO_2) *and mixtures*)





- applied importance (++)
- phenomenology (++)
- fundamental physics (++)

============

e.g. Iosilevskiy I. et al., *Trans. Amer. Nucl. Soc.* **81**, (1999)

- Iosilevskiy I., in: Int. Conference “*Intense Ion Beam Interaction with Ionized Matter*”, Moscow, 1999, (Proc., ITEP Publishing, p.159-173) *Heavy Ion Beam for Investigation of Thermodynamic Properties* // arXiv:1005.4181
- Iosilevskiy I., in: “*High Energy Density Physics with Intense Ion and Laser Beams*”, GSI Annual Report 2006 /GSI-2007-2, may 2007/ *Heavy Ion Beam in Resolution of the Critical Point Problem for Uranium and Uranium Dioxide.*

Great uncertainty in high-*T* density-temperature diagram and in parameters of Uranium critical point

Theoretical estimations

Thermal variants $\boxed{T}$

Yound & Shaner (1977)
Gathers et al. (1986)
Iosilevskiy (1991)
*Iosilevskiy & Gryaznov (**SAHA-T**)*

- - - - - - - - - - - - - - - -

Correlation

$T_C \Leftrightarrow$ Thermal expansion

Caloric variants $\boxed{U}$

Brout (1957)
Grosse (1961)
Morris (1964)
Yound & Alder (1971)
Gathers et al. (1974)
Fortov et al. (1975)
Hornung (1975).....
*Iosilevskiy & Gryaznov (code **SAHA-U**)*

- - - - - - - - - - - - - - -

Correlation

$T_C \Leftrightarrow$ Vaporization heat

Plasma Hypothesis $\boxed{P}$

Likalter (1981)
Likalter + Hess (1997)

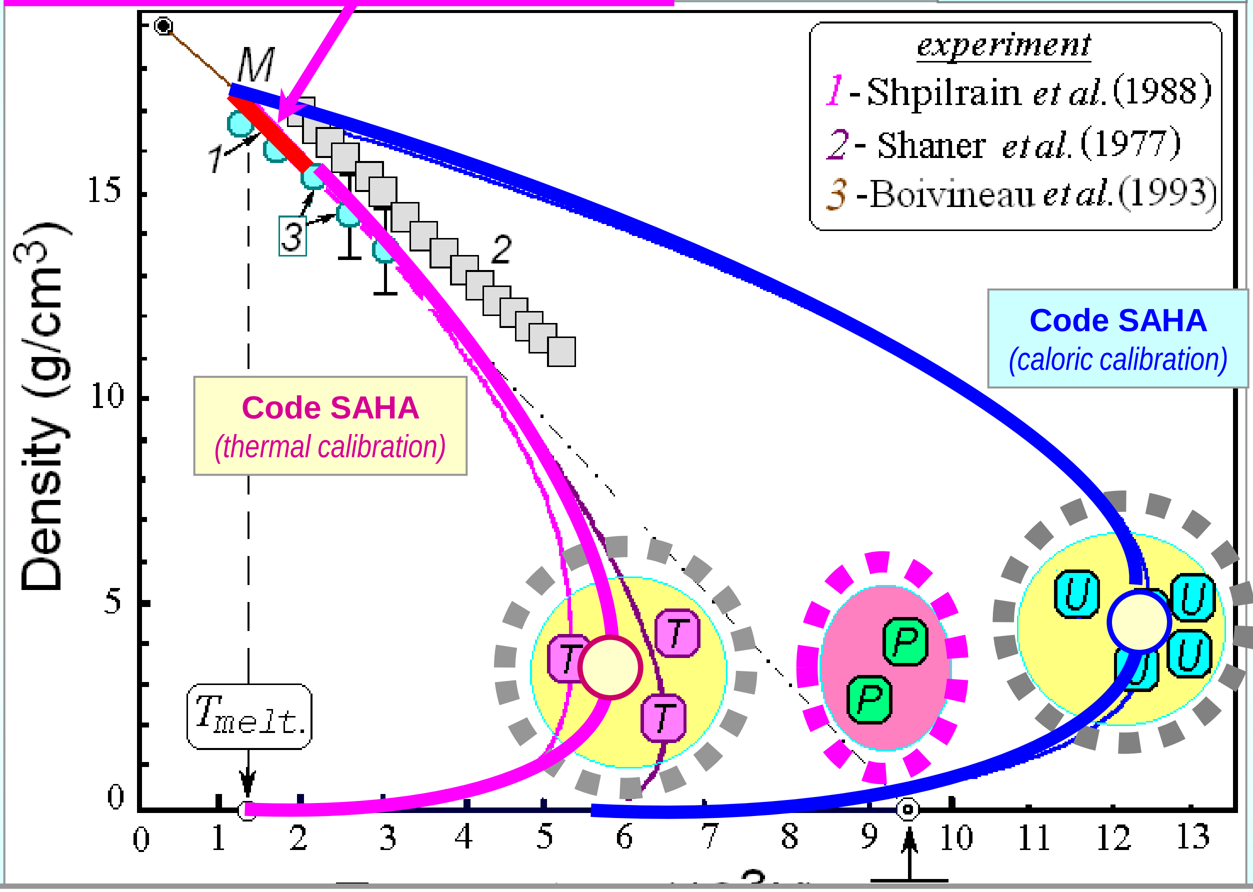
- - - - - - - - - - - - - - -

Correlation

$T_C \Leftrightarrow$ Ionization potential

Shpilrain *et al*. (1988)
Static experiment: - ρ_{liquid} (1400 < *T* < 2100 K)
accuracy – 0.7 % !!

arXiv:1312.7584



Code SAHA
(thermal calibration)

Code SAHA
(caloric calibration)

Extrapolation: (*i*) Guggenheim's formula, (*ii*) Law of Correspondent States (*Iosilevskiy, 1990*), *(iii)* SAHA-code (*Iosilevskiy & Gryaznov, 2005*)

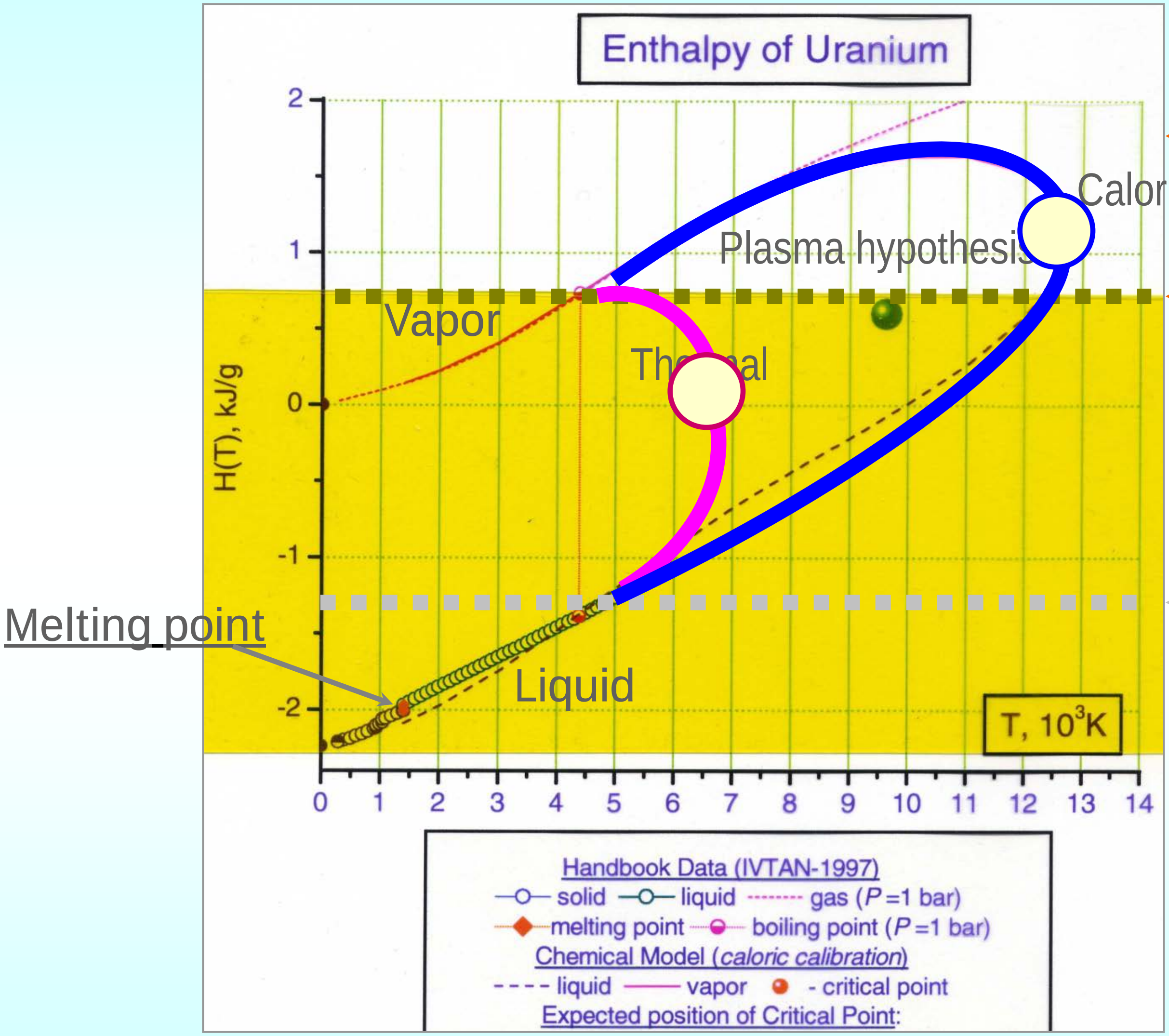
(*i*)

$$\frac{\rho_{l,v}}{\rho_c} = 1 + b_1(1 - \frac{T}{T_c}) \pm b_2(1 - \frac{T}{T_c})^{\beta}$$

(*ii*)

$$\left(\frac{\rho(T/T_{cr})}{\rho_{cr}}\right)_U = \left(\frac{\rho(T/T_{cr})}{\rho_{cr}}\right)_{Cs}$$

Uncertainty in high-*T* caloric phase diagram of Uranium



HIB energy

4 kJ/g

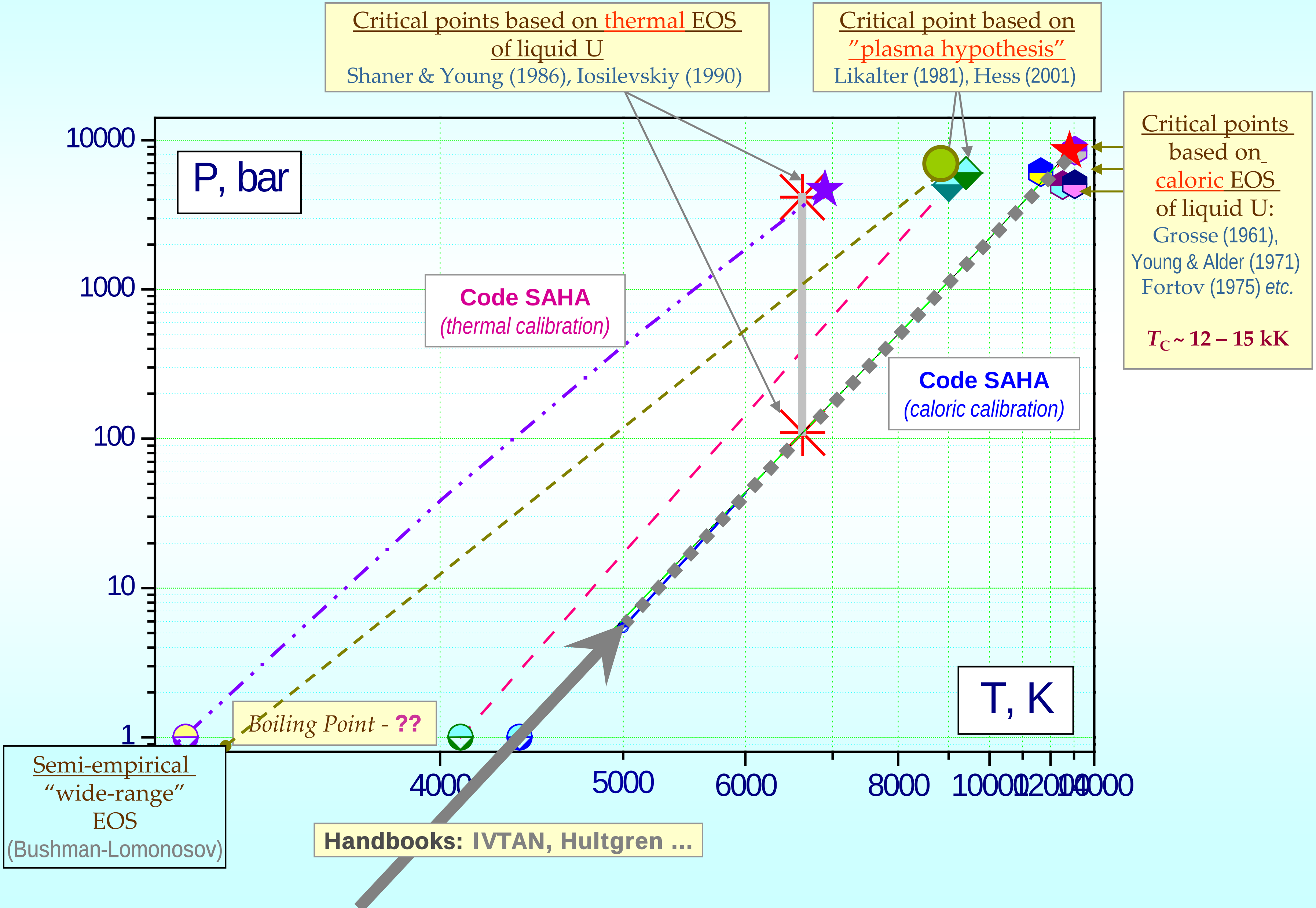
3 kJ/g

1 kJ/g

Iosilevskiy I. in "*Physics of Matter under Extreme Conditions*" IVTAN, Moscow, p.106 (**1991**)

Iosilevskiy I., Gryaznov V. *J. Nuclear Materials* 344, (**2005**) *Uranium Critical Point Location Problem*

Glaring contradiction *in* Uranium vapor pressure *and* critical point location



Critical points based on thermal EOS of liquid U
Shaner & Young (1986), Iosilevskiy (1990)

Critical point based on "plasma hypothesis"
Likalter (1981), Hess (2001)

Critical points based on caloric EOS of liquid U:
Grosse (1961),
Young & Alder (1971)
Fortov (1975) *etc.*

T_C ~ 12 – 15 kK

Code SAHA
(thermal calibration)

Code SAHA
(caloric calibration)

Boiling Point - ??

Semi-empirical "wide-range" EOS
(Bushman-Lomonosov)

Handbooks: IVTAN, Hultgren ...

Uranium critical point location problem

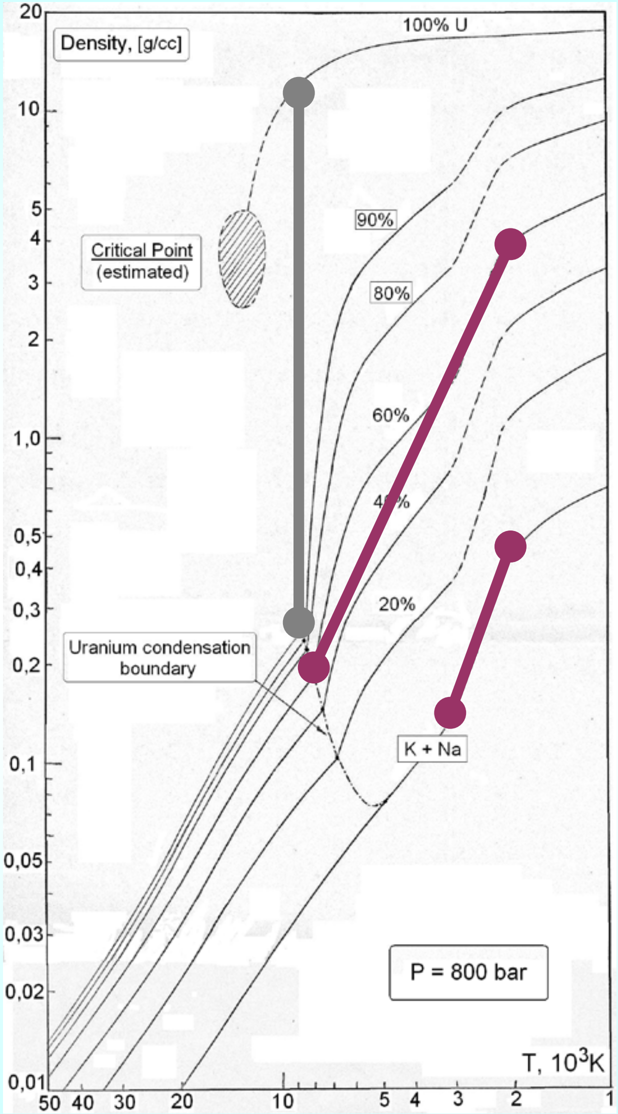
Extraordinary applied importance

What could we do and what should we do with HIB ?

Developments of Gas-Core Nuclear Reactor

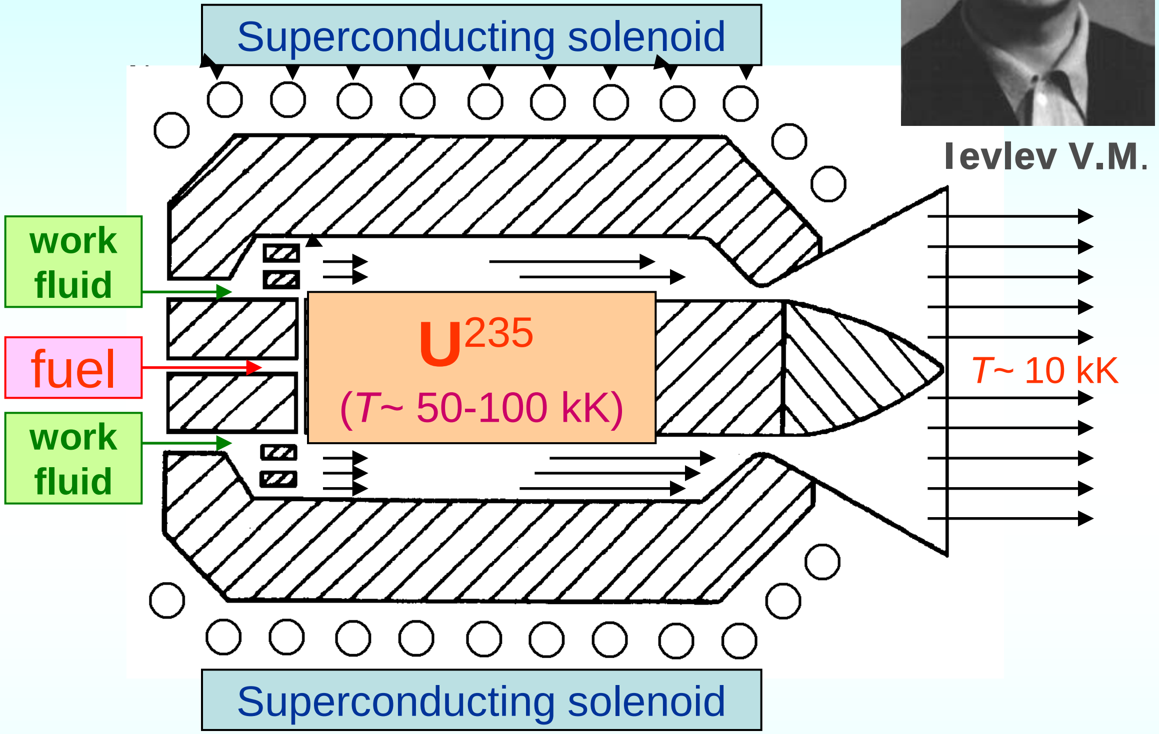
Ievlev V.M.

(1950-1980)



Phase diagram of mixture (U + K + Na)

Iosilevskiy et al. *ITPP Report*, 1972



High-temperature variant of GCNR

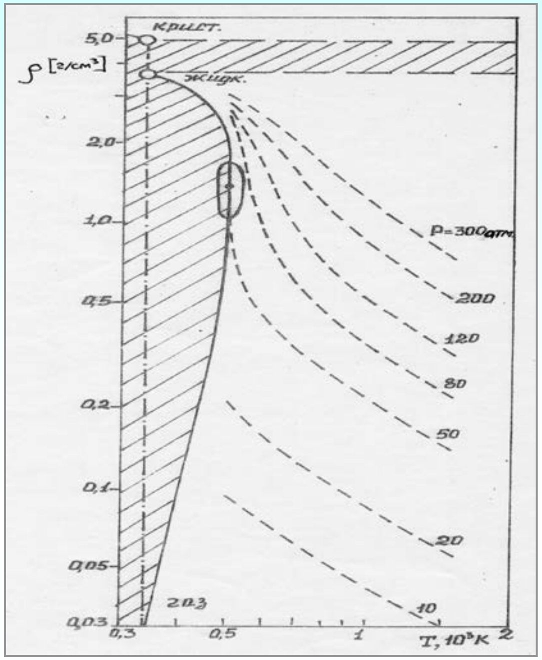
Ievlev V. *Bulletin of Russian Academy of Science* (Izvestia RAS), № **6**, (**1977**)

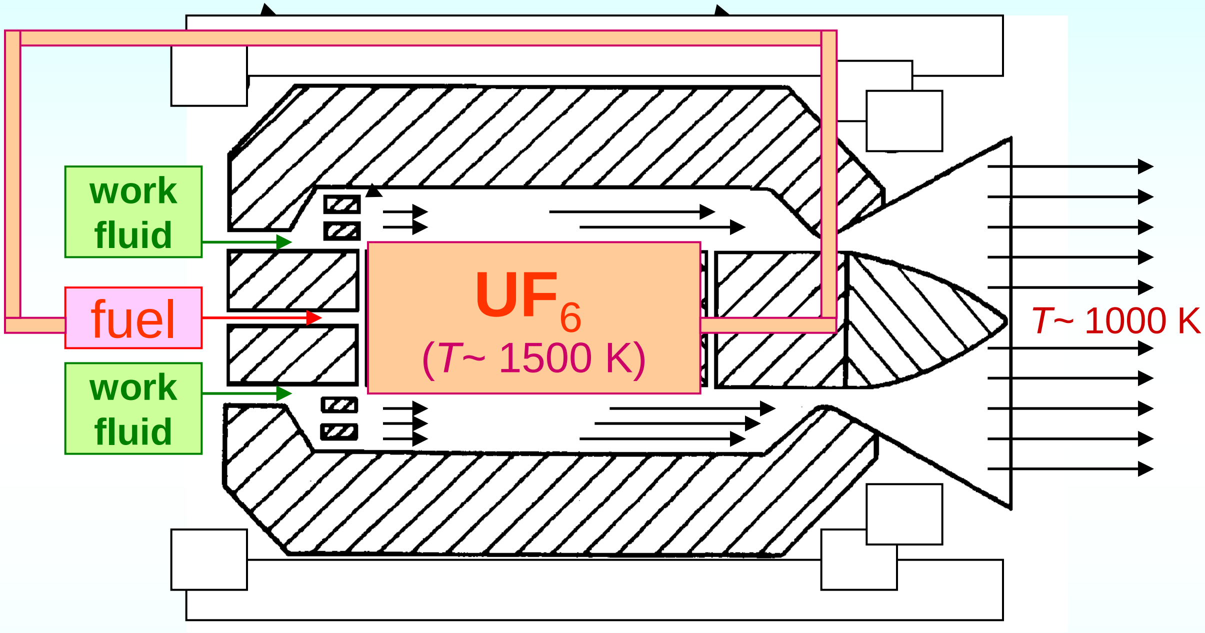
Gryaznov V, Iosilevskiy I, Fortov V, et al. "Thermophysics of gas-core nuclear reactor /Ed. V. Ievlev (**1980**) *(in Russian)*

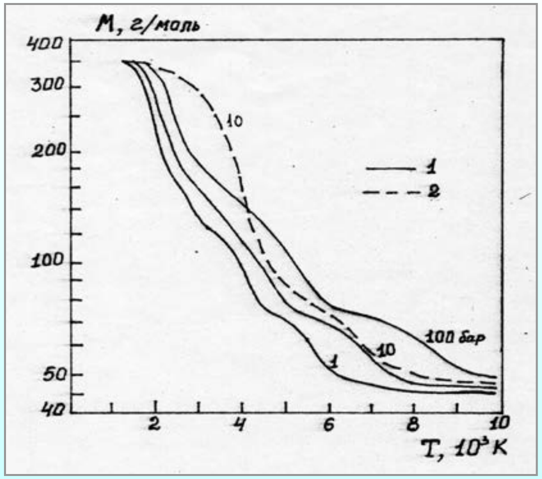
"Rocket engines and energy converters based on gas-core nuclear reactor", /Ed. A. Koroteev, "Mashinostroeniye" Publishing, Moscow, (2002), (in Russian)

Developments of Gas-Core Nuclear Reactor

(1950-1980)







Low-temperature variant of GCNR

Phase diagram // Mol. weight of UF_6

Iosilevskiy *et al*. 1982

Pavel'ev A., et al. *Space energy converters based on* UF_6
Space and Rocket Review, Ser.IV., N 1, NIITP, Moscow (1992), (in Russian);
Rocket engines and energy converters based on Gas-Core Nuclear Reactor
/Ed. A. Koroteev, "Mashinostroeniye" Publishing, Moscow, 2002, (in Russian)

What could we do and what should we do with HIB ?

Mixtures *and* ***compounds dominate*** *in our* ***interests***

Mixtures *and* **compounds dominate** *in our* **interests**

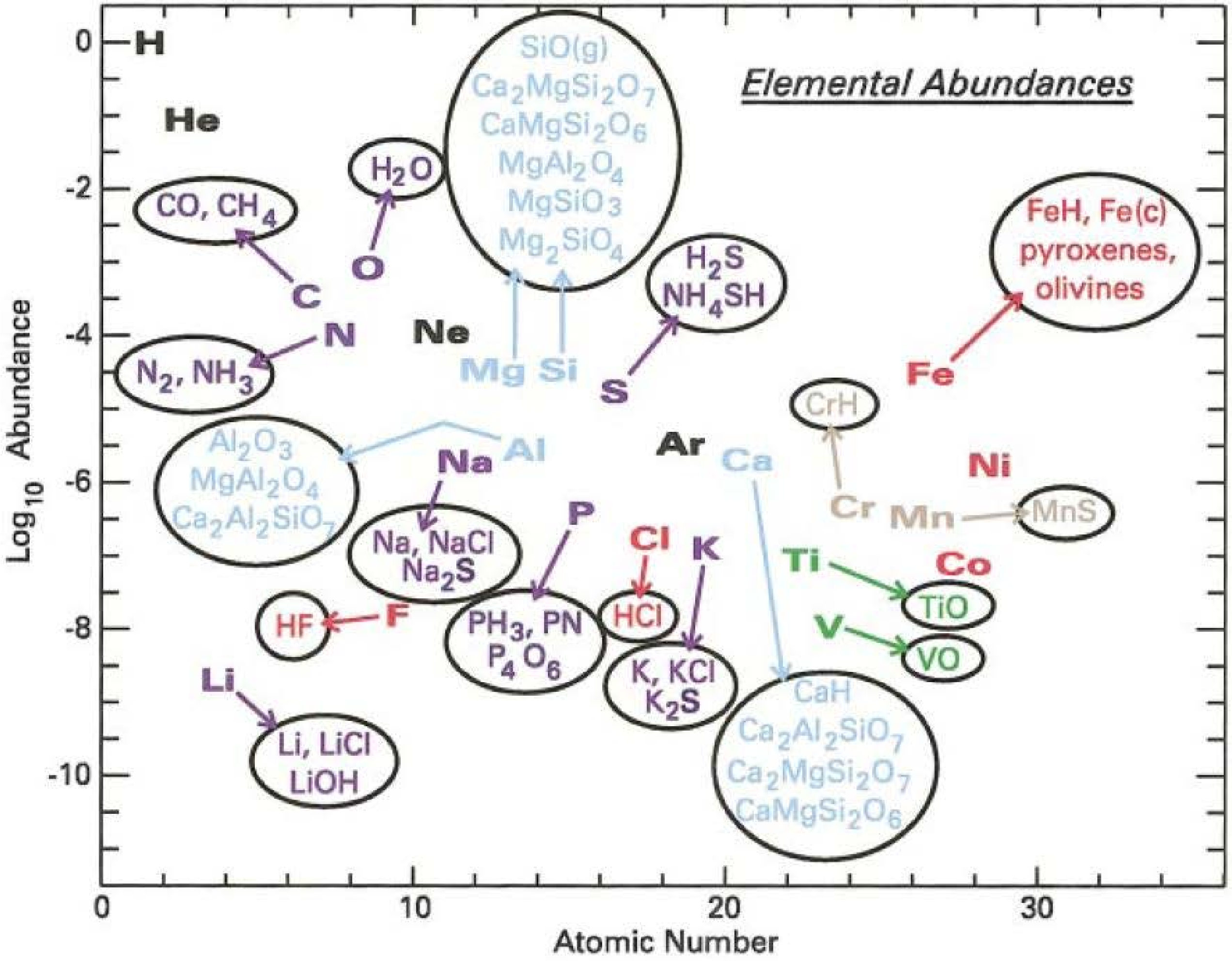
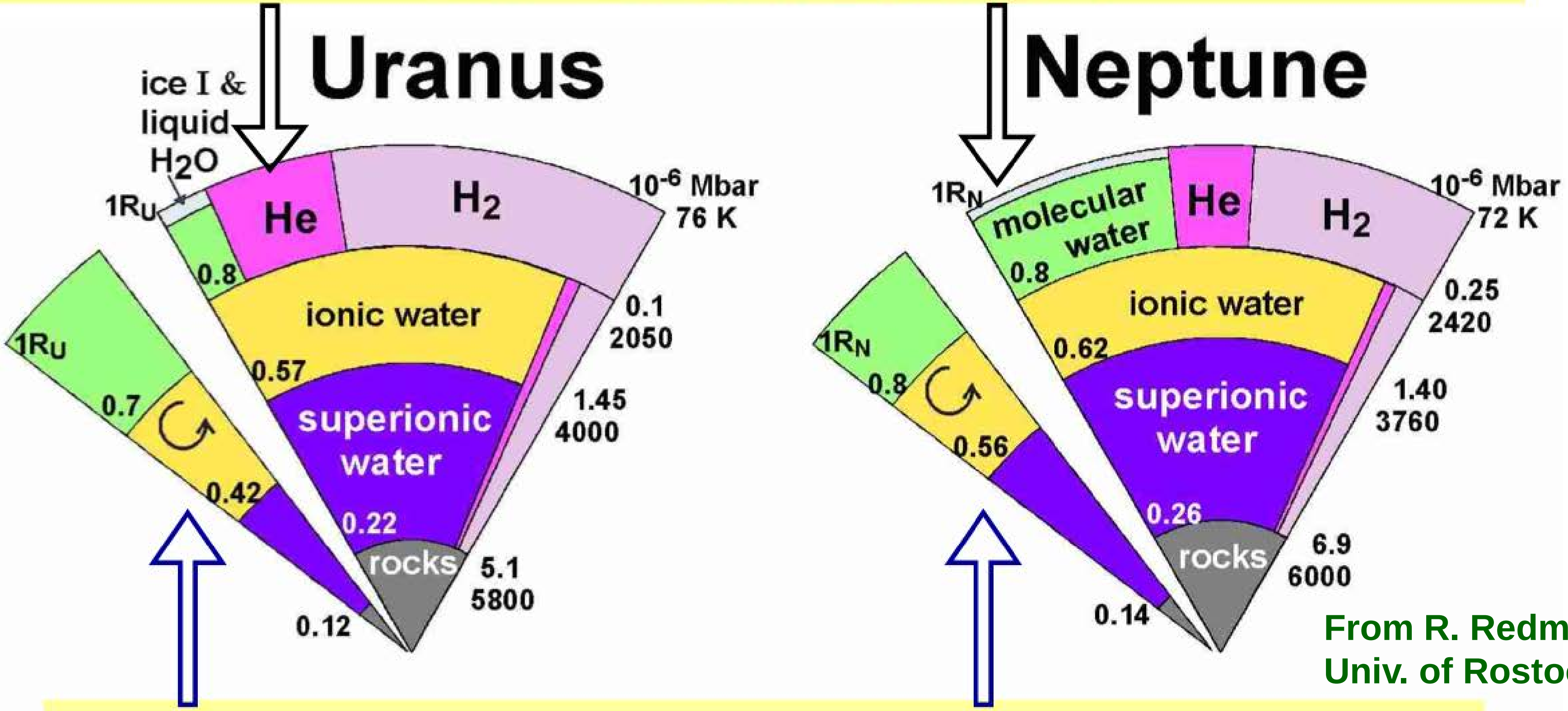


FIG. 10. A plot of the abundance of the elements vs atomic number. The position of the element name indicates its elemental abundance according to Anders and Grevesse (1989); see Table II. The balloons contain representative associated molecules/atoms/condensates of importance in brown dwarf and giant planet atmospheres. See Sec. V in text for discussion [Color].

Element abundance in cosmic materials

Interior of Neptune and Uranus

7th International Workshop on Warm Dense Matter (WDM)
Saint-Malo, France June 23-26, 2013



From R. Redmer
Univ. of Rostock

Slide from:

Marcus D. Knudson

Sandia National Laboratories,   Albuquerque

Probing planetary interiors:
Shock compression of water to 700 GPa and 3.8 g/cc

Non-congruent phase transitions in uranium dioxide

Extraordinary applied importance

Ronchi C., Iosilevskiy I., Yakub E. // Equation of State of Uranium Dioxide / Springer, Berlin, 2004

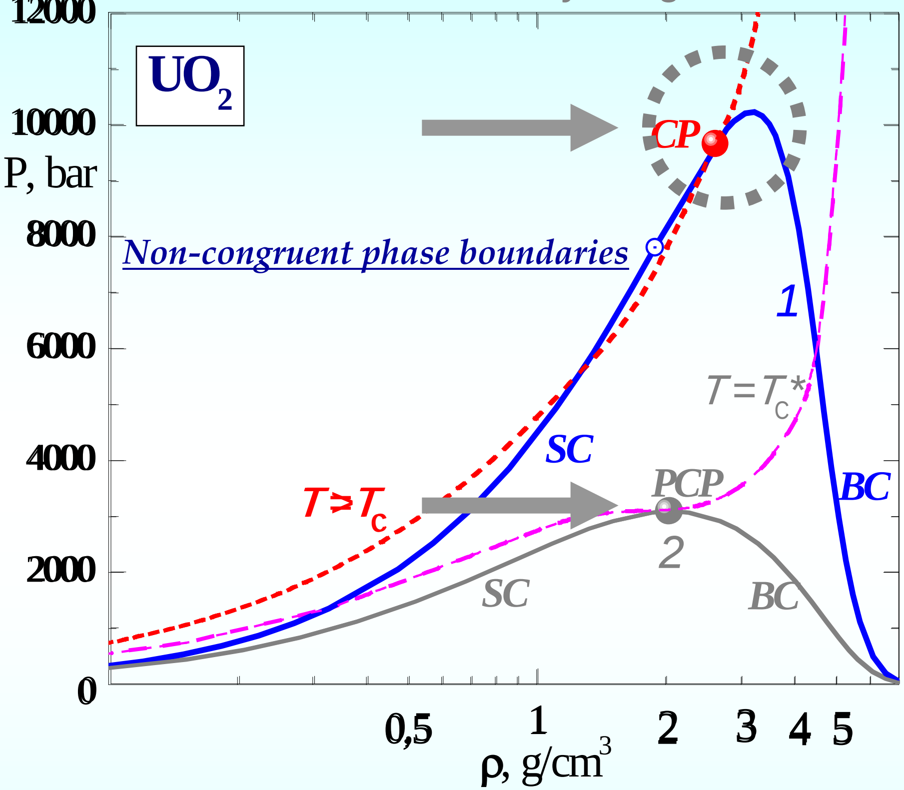
arXiv:1005.4181 / arXiv:1005.4186 /

What could we do and what should we do with HIB ?

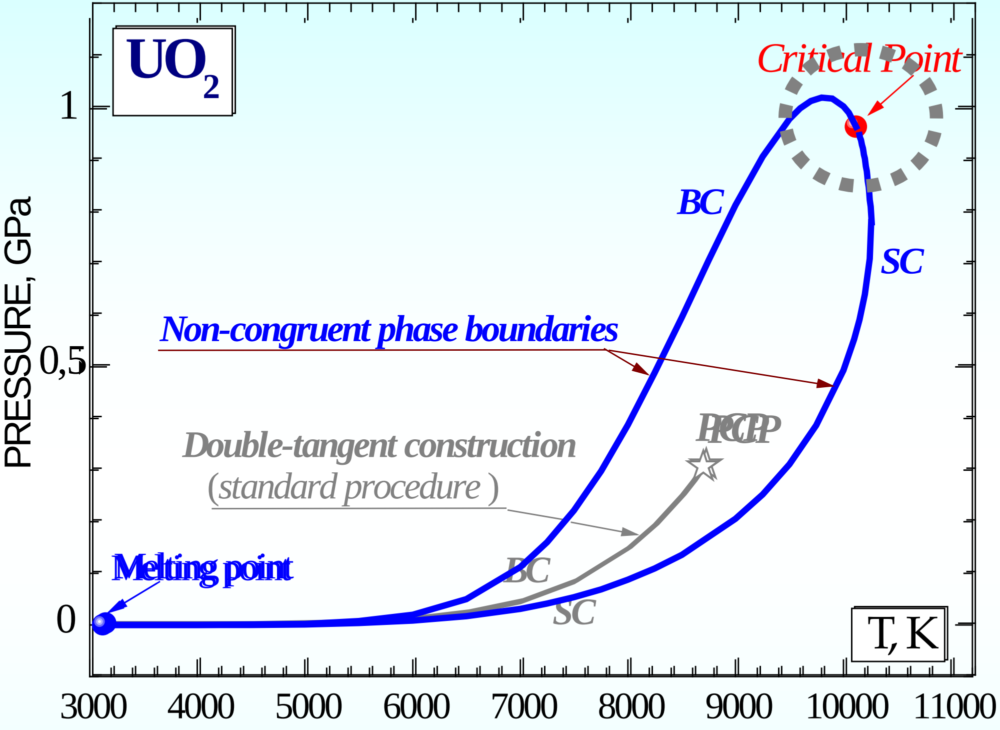
Non-congruent evaporation in U-O system

(*Gibbs - Guggenheim conditions*)

Pressure - Density Diagram



Pressure - Temperature Diagram



NB! **2-dimensional two-phase region** instead of standard *P-T* saturation curve

NB! **High pressure level** of non-congruent phase decomposition

NB! **Critical point** should be of **non-standard** type: $(\partial \boldsymbol{P}/\partial \boldsymbol{V})_T \neq 0$ $(\partial^2 \boldsymbol{P}/\partial \boldsymbol{V}^2)_T \neq 0$

It should be instead: $(O/U)_{liquid} = (O/U)_{vapor}$ and $\{\|\partial \boldsymbol{\mu_i}/\partial \boldsymbol{n_k}\|_T\}_{CP} = 0$

No anomalous density fluctuations typical for standard critical point **!**

Non-congruent phase transitions in general

Any phase transition in system of two or more chemical elements must be non-congruent !

Congruent phase transition in such system is exception only !

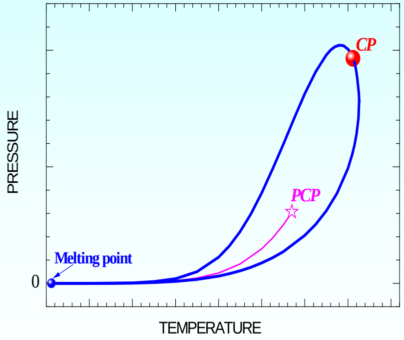
arXiv:1005.4181 / arXiv:1005.4186 /

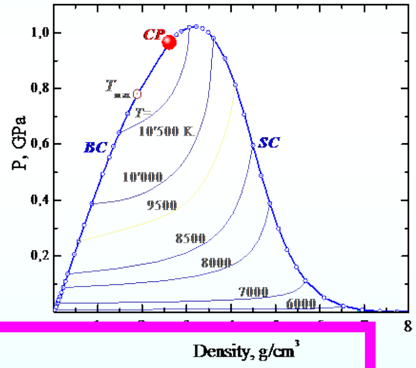
Hypothetical non-congruent phase transitions

(*short list*)

Terrestrial applications:

- ***Uranium*** *- and* ***Plutonium*** *-bearing compounds:*
  - *UO_2, PuO_2 , UC, UN, … ets.,*
- ***Metallic alloys:*** *(Li-K-Na,…etc.)*
- ***Oxides:*** *(SiO_2, MgO, Al_2O_3…etc.)*
- ***Hydrides*** *of metals (LiH,… etc.)*
- ***Ionic liquids*** *and* ***molten salts:***
  - *alkali halides (NaCl, CsF… etc.)*
- ***"Dusty"*** *and* ***Colloid plasmas:***
  (Coulomb system of macro-ions +Z and micro-ions: +1, –1)





Non-Congruence *in* Planets *and* Cosmic Matter:

- ***Phase Transitions*** *in mixture:* **H_2/ He /H_20 / NH_3 / CH_4 .. SiO_2, MgO, Al_2O_3…**
  in the ***Earth, Giant Planets, Brown Dwarfs*** *and* ***Extra-Solar Planets,***
- ***Phase Transitions*** *in* ***White Dwarfs,***
- ***Phase Transitions*** *in* ***Neutron Stars,***
- ***Phase Transitions*** *in* ***Hibrid "Strange" Stars*** *(quark-hadron transition … ets.)*

Iosilevskiy I. / Int. Congress on Plasma Physics / Fukuoka, Japan, 2008 (*J. of Plasma and Fusion Research*, 2009)

The Moon: - **18 May 2013**, 07:21 (Msc.) // 40 kg // 30 cm // **30** km/sec // ~ 5 tons TNT eq.
The Moon: (**LunarCROSS**) - **9 Oct 2009** // ~ **2’300** kg // ~1 m // **3 km/sec** // **2** tons TNT eq.
The Moon: (**赫映姫 Kaguya**) - **10** June **2009** // ~ **3’000** kg // ~1 m //~ **3 km/sec** // **2** tons TNT eq.
The Earth: - 15 Feb **2013** (*Chelyabinsk*) // **10’000** kg // **17 m** // **18** km/sec // ~ **0.5-1.5** Mtons TNT eq.
The Earth: - 17 June **1908** (***Tunguska** meteorite, Siberia*) // **$5_{10}9$** kg // **200 m** // **50** Mtons TNT eq.

The question is:

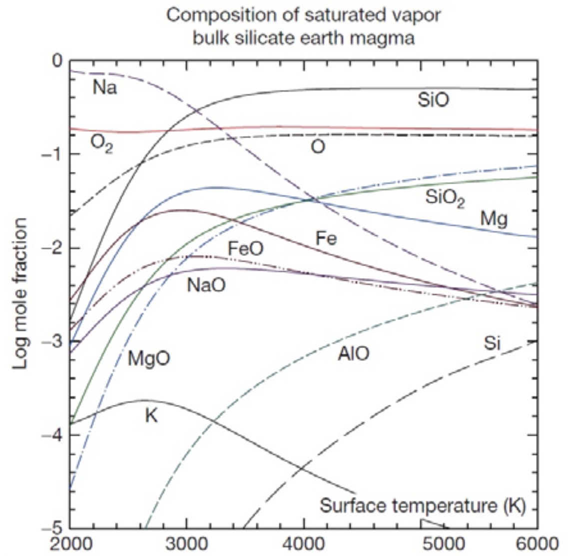
What kind of phase transition one can expect in high-*T*_high-*P* complex plasma ?

The Earth
bulk silicate

$$SiO_2 + FeO + Al_2O_3 + CaO + \ldots$$

Oxide	%
SiO_2	45.86
MgO	37.12
FeO	8.18
Al_2O_3	4.55
CaO	3.69
Na_2O	0.353
TiO_2	0.215
K_2O	0.031

EMMI : *Cosmic Matter in the Laboratory*



Fegley B.Jr., Schaefer L.K., *Treatise on Geochemistry*, (2013)
Chemistry of Earth’s Earliest Atmosphere // arXiv:1210.0270

Launch – June 18, 2009 // Impact – 9 October 2009
Impact velocity ~ 9’000 km/h ⇔ Impact plume ~ 50 km high

What kind of phase transition one can expect in high-*T*_high-*P* complex plasma?

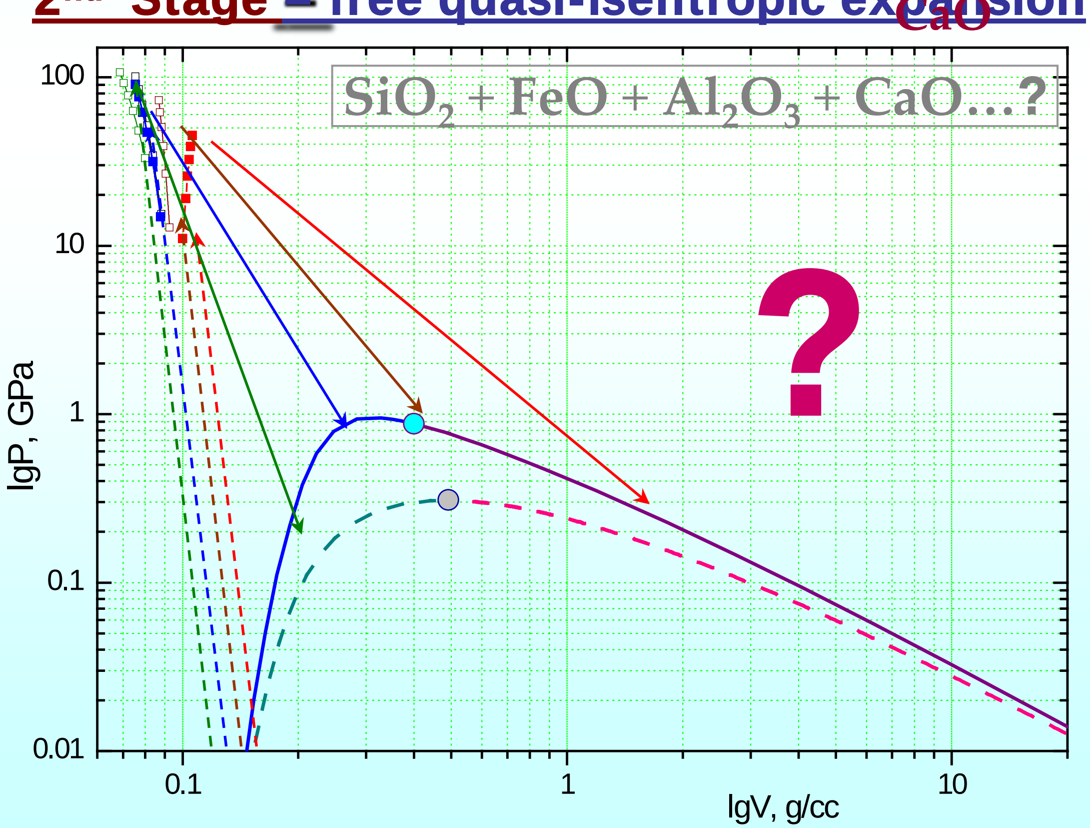
$SiO_2 + FeO + Al_2O_3 + CaO$

T ~ eV & P ~ GPa

The question is open

1st Stage – strong shock compression

2nd Stage – free quasi-isentropic expansion



9 // Impact – 9 October 2009 12:30 a.m. !

00 km/h ⇔ Impact plume ~ 50 km high

What kind of phase transition one can expect in high-T_high-P complex plasma?

$SiO_2 + FeO + Al_2O_3 + CaO$

$T \sim eV$ & $P \sim GPa$

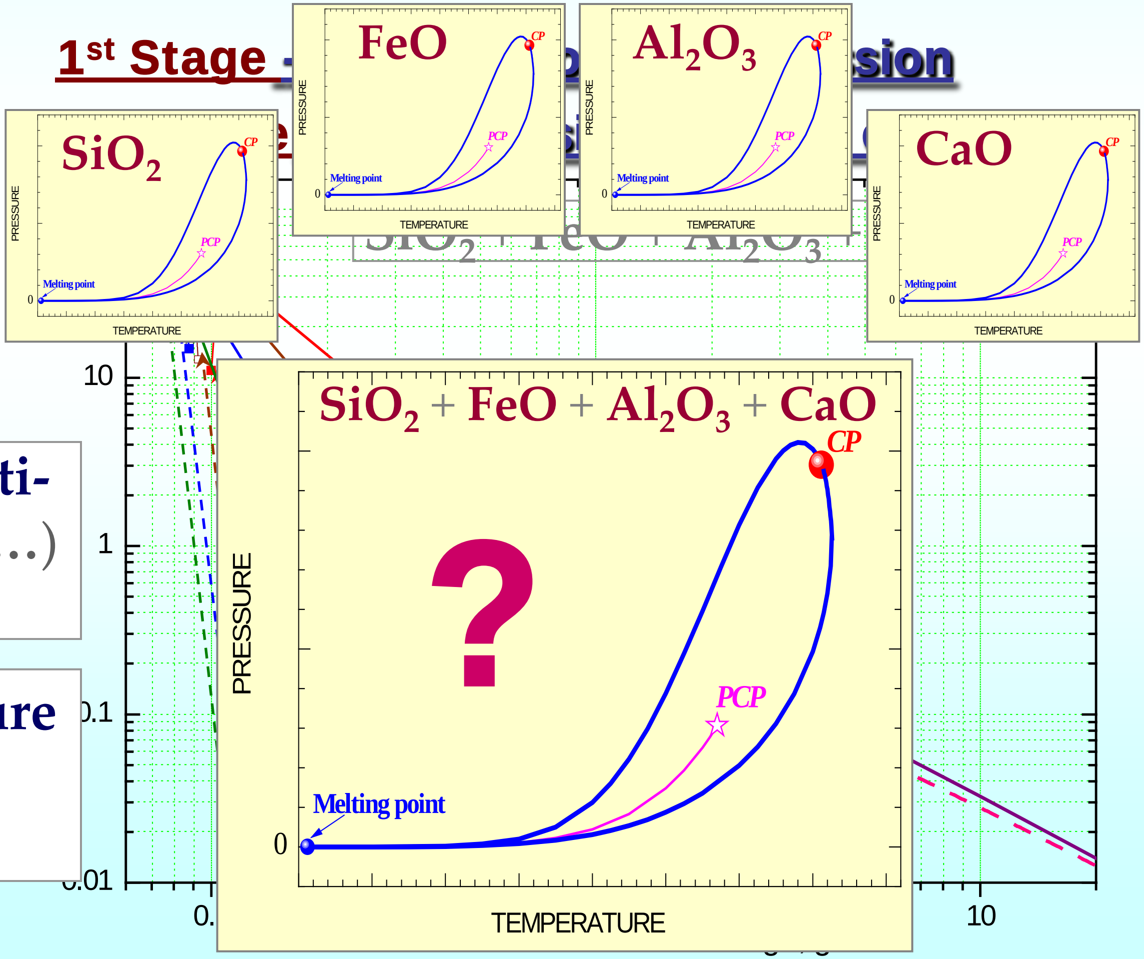
The question is open

NB !

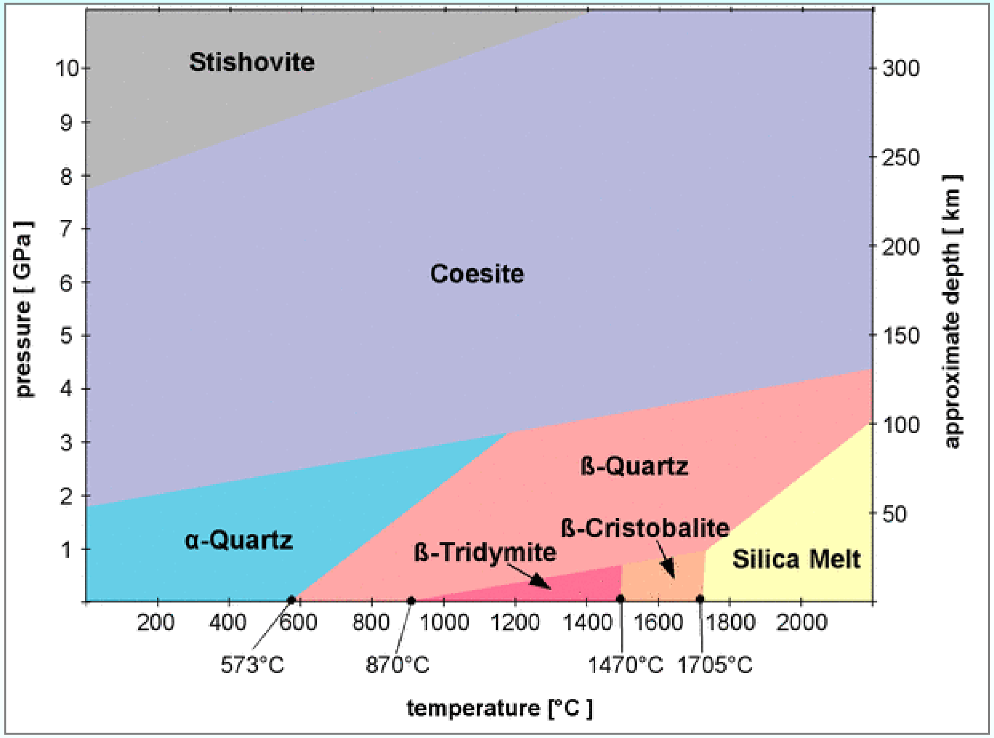
Phase transition in each constituent (SiO_2, FeO, Al_2O_3, CaO…) must be *non-congruent* !

Phase transitions in the mixture must be *non-congruent* moreover !

1st Stage

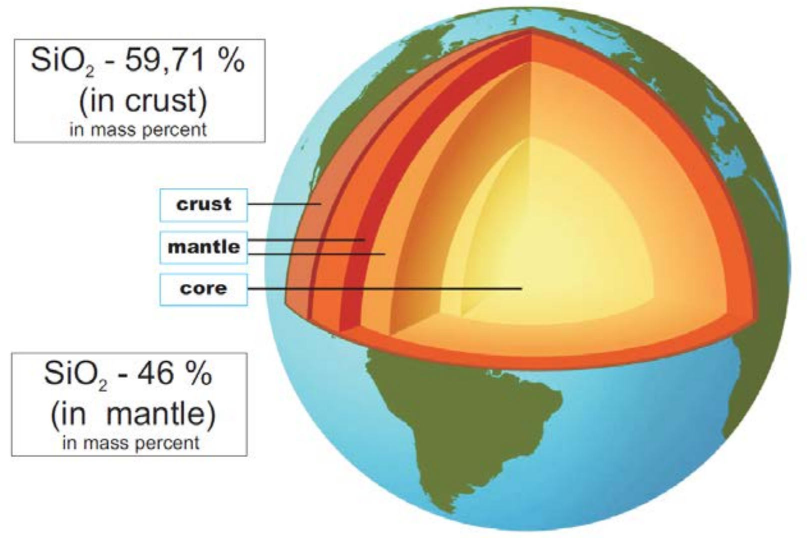


Phase diagram of SiO_2



The phases of SiO_2 in the temperature and pressure regions in which they are favored

(http://www.quartzpage.de/gen_mod.html)

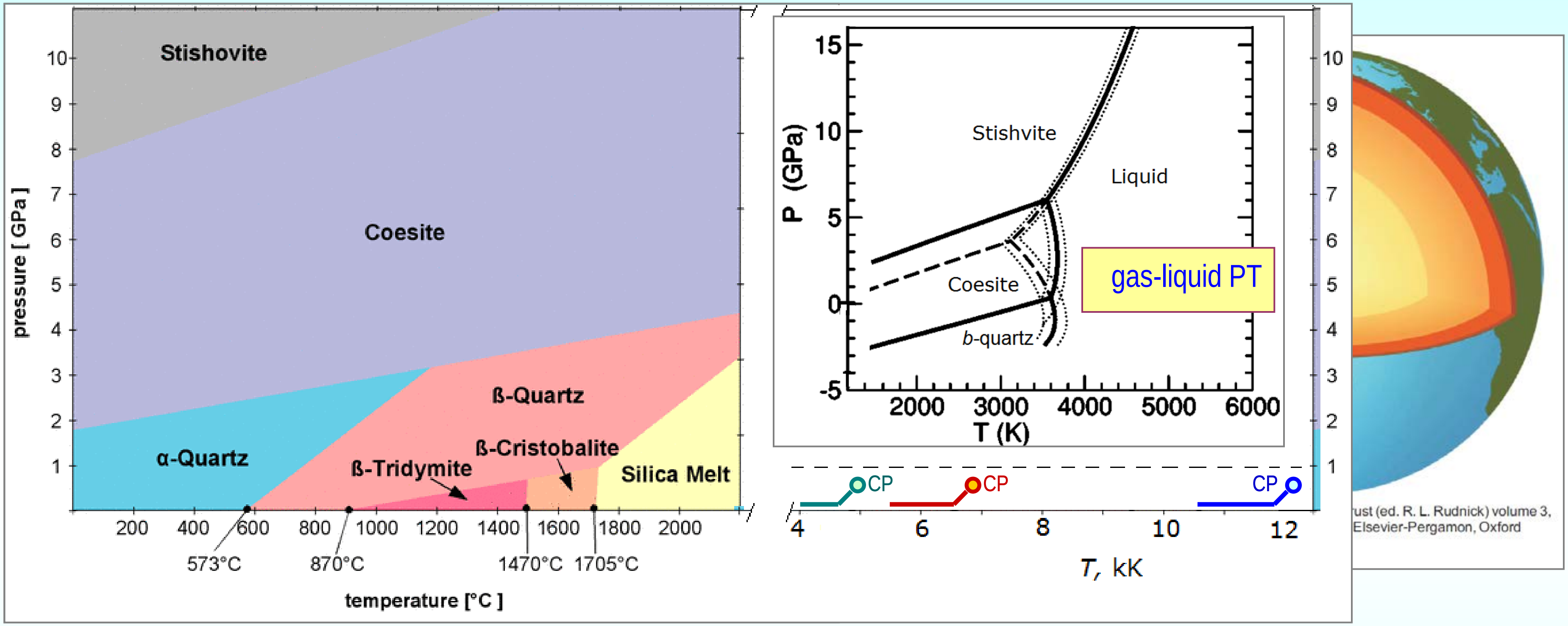


R. L. Rudnick and S. Gao, 2003, Composition of the Continental Crust. In The Crust (ed. R. L. Rudnick) volume 3, pages 1-64 of Treatise on Geochemistry (eds. H. D. Holland and K. K. Turekian), Elsevier-Pergamon, Oxford

Tectonics (1995), Moores & Twiss, W.H. Freeman & Co.

Ordinary field of interest –
– polymorphic phase transformations

Phase diagram of SiO_2



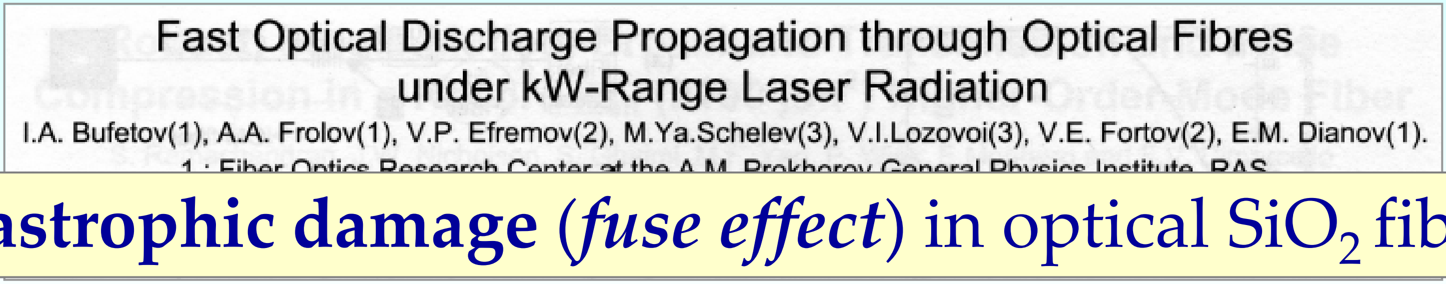
The phases of SiO_2 in the temperature and pressure regions in which they are favored

(http://www.quartzpage.de/gen_mod.html)

Our field of interest – non-congruent gas-liquid phase transition in SiO_2

Iosilevskiy I., Gryaznov V., Solov'ev A., *High Temp.-High Pressure,* **43,** 227 (2014) // arXiv:1312.7592

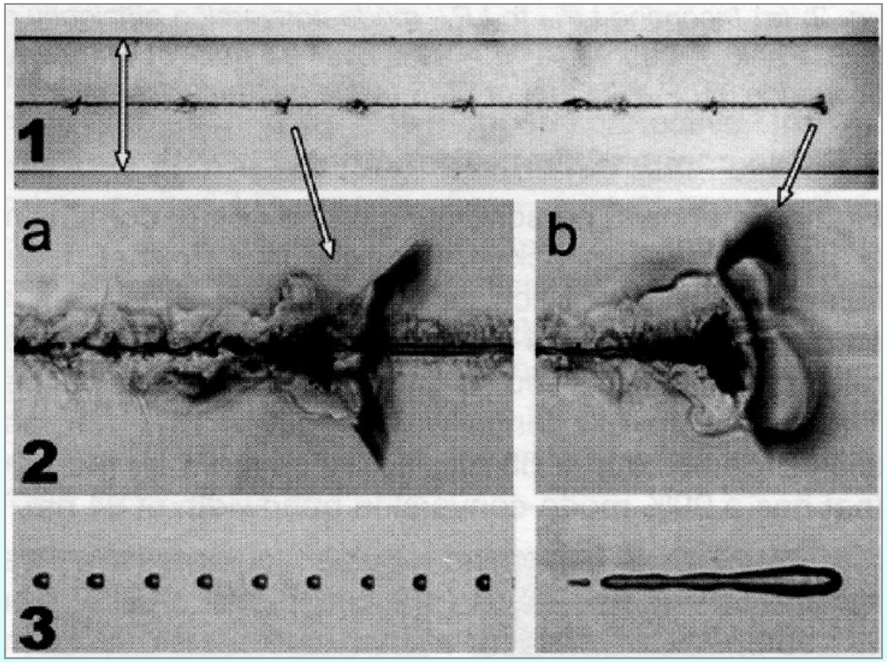
High-temperature evaporation in SiO_2 - is it congruent or not ?



Fast Optical Discharge Propagation through Optical Fibres
under kW-Range Laser Radiation

I.A. Bufetov(1), A.A. Frolov(1), V.P. Efremov(2), M.Ya.Schelev(3), V.I.Lozovoi(3), V.E. Fortov(2), E.M. Dianov(1).

Catastrophic damage (*fuse effect*) in optical SiO_2 fibers



D ~ 100 mkm

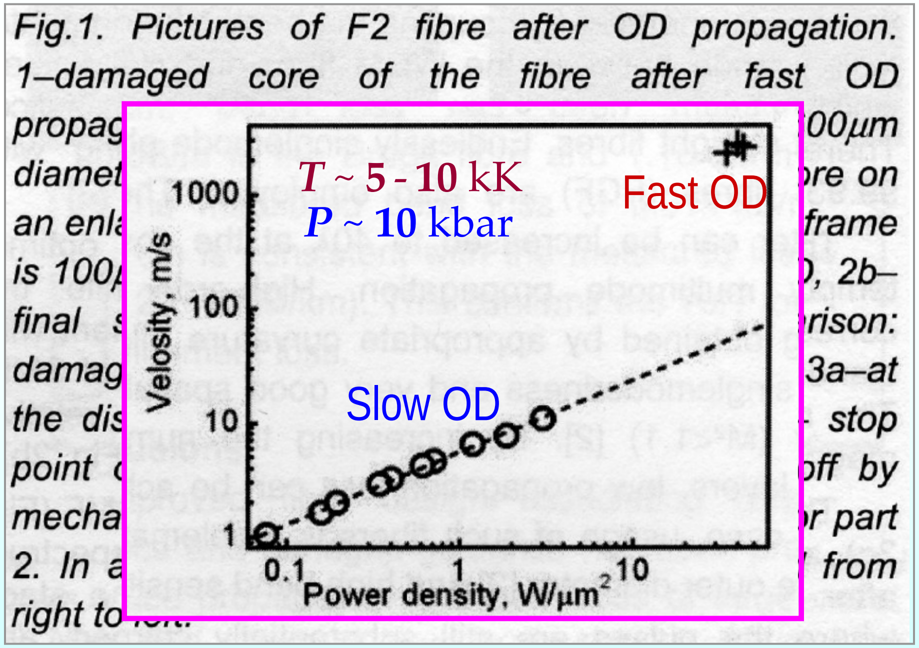
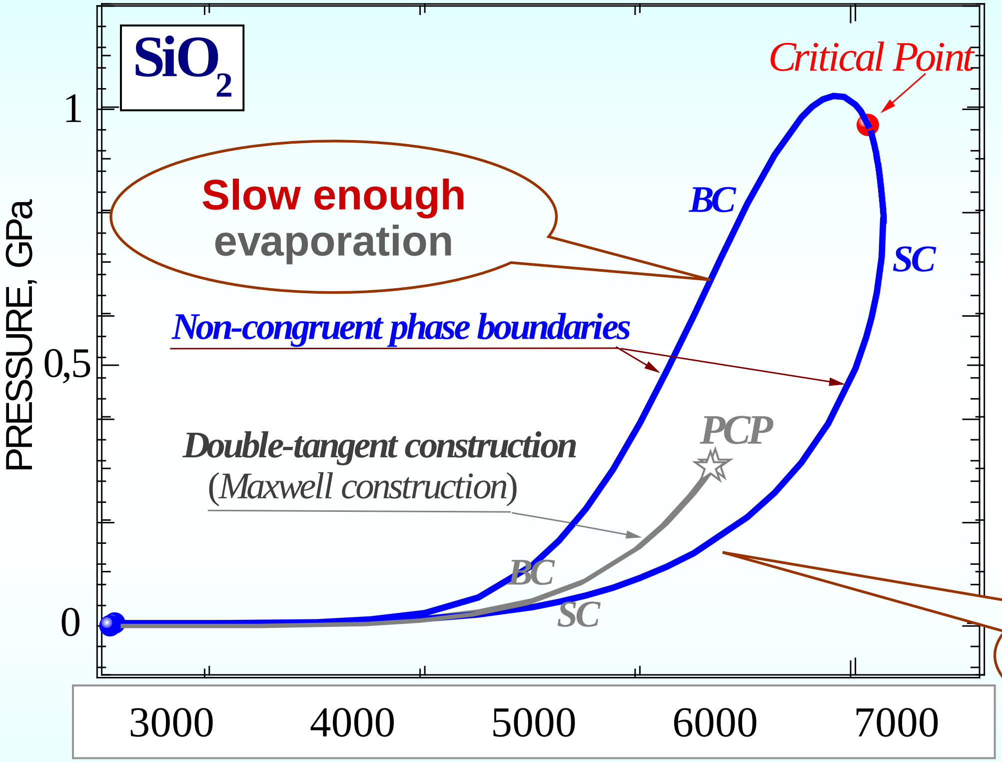


Fig.1. Pictures of F2 fibre after OD propagation. 1–damaged core of the fibre after fast OD
propag … 00μm
diamet … ore on
an enla … frame
is 100 …), 2b–
final … rison:
damag … 3a–at
the dis … stop
point … off by
mecha … r part
2. In a … from
right to left.

Bufetov I.A. & Dianov E.M. *Phys. Uspekhi.* **48,** 91 (2005); *Optical discharge in optical fibers*

High-Temperature evaporation in SiO$_2$
- is it congruent or not ?



Expected qualitative
phase diagram for SiO$_2$
*(non-congruent gas-liquid
phase transition)*

Parameters of non-congruent evaporation in SiO$_2$
strongly depend **on the** ***rapidity*** **of phase transformation !**

Comparison of theoretical EOS models

Iosilevskiy I., Gryaznov V., Solov'ev A., *High Temp.-High Pressure,* **43,** 227 (2014) // arXiv:1312.7592

Theoretical EOS models that were used for comparison of predicted high-*T* phase diagram and critical point in SiO_2

Gas-liquid phase transition in SiO_2

EOS SAHA – Quasi-chemical model *(Non-ideal multi-component mixture)*

MPQ-EoS – Modified **semi-empirical** EOS (*wide-range EOS*)
(*"MPQeos-JWGU" – S.Faik et al*. based on EOS-model of R.Moore and D.Young*)*

Ionic-MD – Direct numerical **MD** simulations for **Ionic Model** of SiO_2 $(Si^{+4} + 2O^{-2})$

Liquid SiO_2

DFT / MD – *Ab initio* quantum **MD** simulations for **Liquid** SiO_2 { Si + O (MD) + e (DFT) }

Theoretical EOS models that were used for comparison of predicted high-*T* phase diagram and critical point in SiO_2

Gas-liquid phase transition in SiO_2

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- Gryaznov V., Iosilevskiy I., Krasnikov Yu., Kuznetsova N., Kucherenko V., Lappo G., Lomakin B., Pavlov G., Son E., Fortov V. // *Thermophysics of Gas-Core Nuclear Engine* / Ed. by V.M. Ievlev, (ATOMIZDAT, Moscow, 1980)
- Iosilevskiy I., Gryaznov V., Yakub E., Semenov A., Hyland G., Ronchi C., Fortov V. // *Bull. of Russ. Atomic Agency* , Moscow (2003) // *Int. Journal of Thermophysics* **22**, 1253 **(**2001**)** // *Contrib. Plasma Phys.* **43**, 316 (2003) //

MPQ-EoS – Modified **semi-empirical** EOS (*wide-range EOS*)
(*"MPQeos-JWGU" – S.Faik et al*. based on EOS-model of R.Moore and D.Young)

- R. More, K. Warren, D. Young, G. Zimmerman; *Phys. Fluids* **31** (1988) 3059; // D. Young, E.M. Corey; J. Appl. Phys. **6** (1995) 3748;
- Faik S., Tauschwitz A., Maruhn J., Iosilevskiy I. // "Dynamics of metastable states in ion-beam irradiated foils", EMMI workshop "Particle dynamics under extreme matter conditions" Speyer, Germany, 26-29 September 2010
- Faik S., Tauschwitz An., Maruhn J., Iosilevskiy I., // *MPQeos-JWGU: A new equation-of-state package for warm/hot dense matter,* GSI Annual Report, 2011 //
- Faik S., Basko M., Tauschwitz An., Iosilevskiy I., Maruhn J., *High Energy Density Physics*, **8**, 349 (2012) *Dynamics of volumetrically heated matter passing through the liquid-vapor metastable states* // arXiv:1205.2579

Ionic-MD – Direct numerical **MD** simulations for **Ionic Model** of SiO_2 ($Si^{+4} + 2O^{-2}$)

Y. Guissani & B. Guillot, *J. Chem. Phys*. **104** (1996) *Numerical investigation of the liquid–vapor coexistence of silica*

Liquid SiO_2

DFT / MD – *Ab initio* quantum **MD** simulations for **Liquid** SiO_2 { Si + O (MD) + e (DFT) }

B. Karki, D. Bhattarai, L. Stixrude, *Phys. Rev.* B **76** (2007) *First-principles simulations of liquid silica*

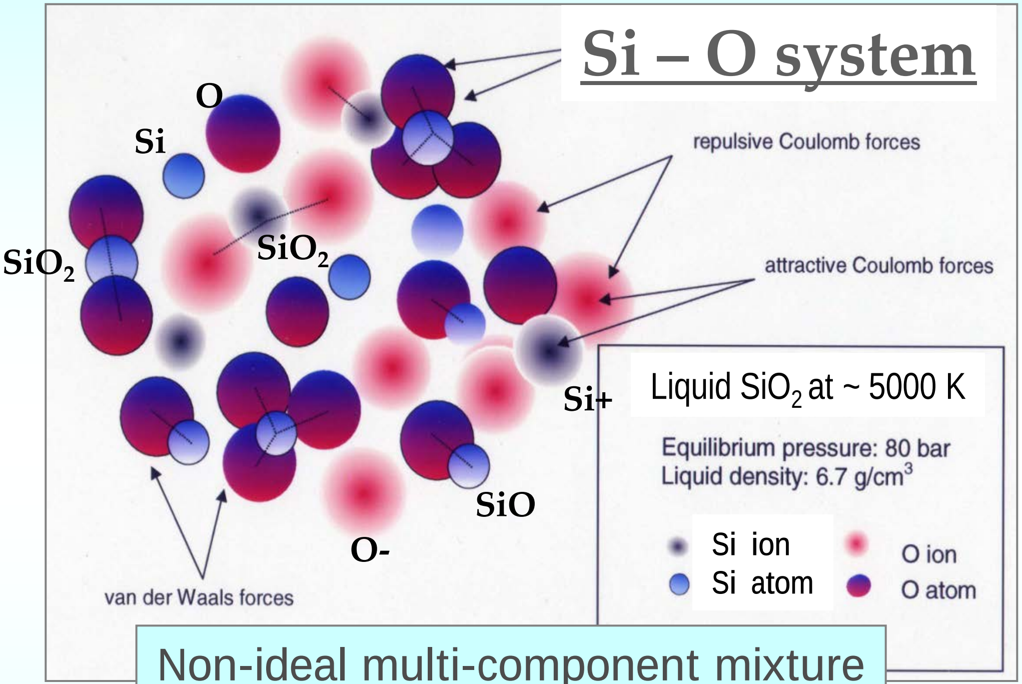
EOS SAHA – Quasi-chemical model *(Non-ideal multi-component mixture)*

Free energy minimization method

$\mathbf{N} = \{N_1, N_2, N_3 \ldots N_k\}$

$$F = min\{F^{\mathrm{id.gas}} + \Delta F^{\mathrm{Coul.}}(T,\{N_i\}) + \Delta F^{\mathrm{Rep.}}(T,\{N_i\}) + \Delta F^{\mathrm{Attr.}}(T,\{N_i\})\}$$

- Ionization
- Chemical reactions
- Electroneutrality
- Coulomb non-ideality
  Modified Debye corrections
- Short-range repulsion
  Model of soft-sphere mixture
- Short-range attraction
  Van der Waals-like corrections



EOS calibration (*T* = 0):
ϱ – *normal density*
$\Delta_s H^0$ – *vaporization heat*

EOS validation (*T* >> 0):
P(*T*) – *saturation vapor*
H(*T*) – *enthalpy diagram*

Non-ideal multi-component mixture
(*Liquid & Gas*)
Neutrals: SiO // SiO$_2$ // O$_2$ // O // Si // Si$_2$
Charged species: e // O(+) // Si(+)

$\mathrm{Si} + 2\mathrm{O} \Leftrightarrow \mathrm{SiO_2}$

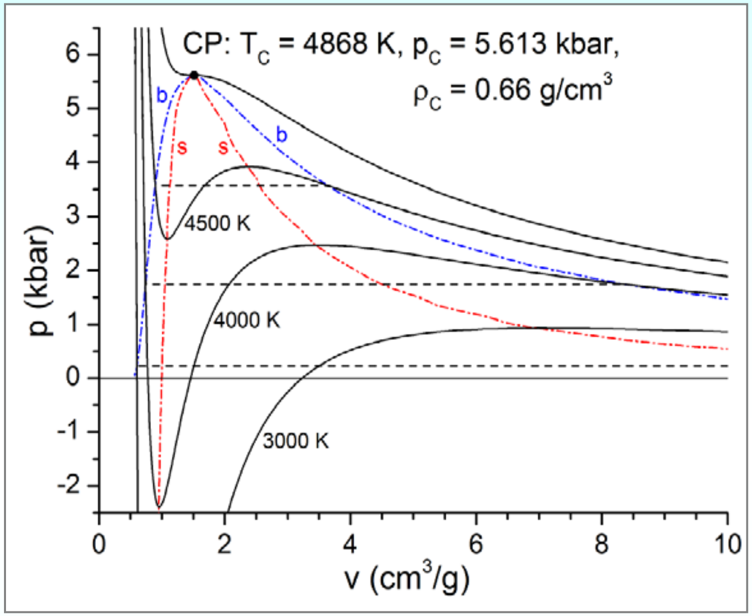
$\mu_{\mathrm{Si}} + 2\mu_{\mathrm{O}} = \mu_{\mathrm{SiO2}}$

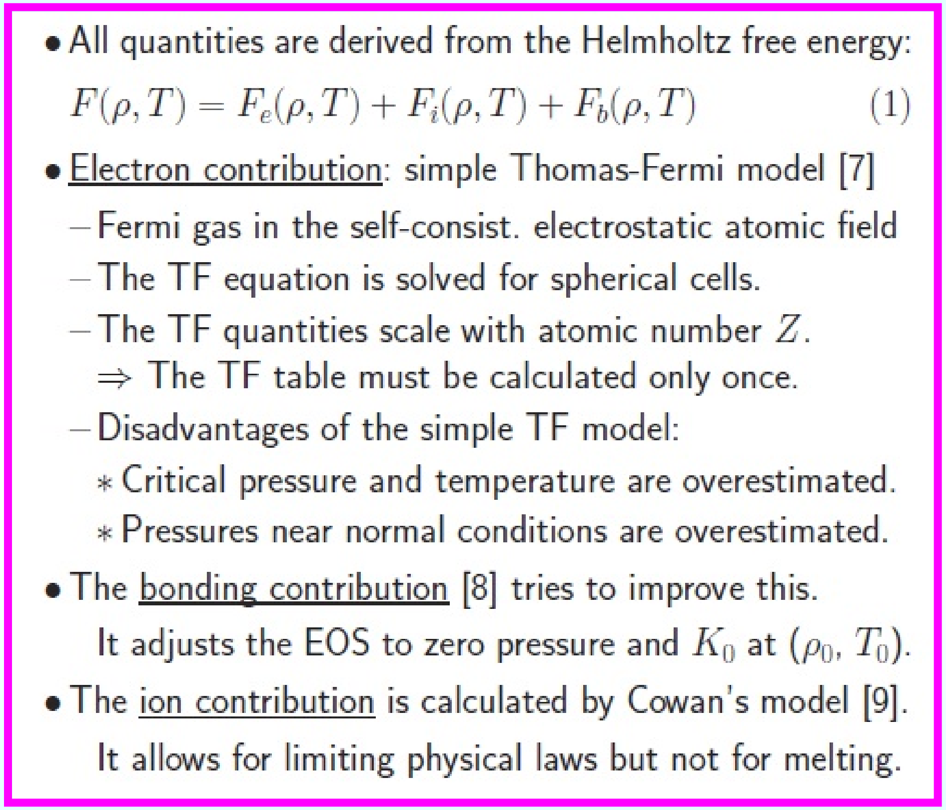
Phase coexistence:
Gibbs-Guggenheim conditions + *Forced-congruent equilibrium* [(O/Si) = *const*]

- Gryaznov V., Iosilevskiy I.,…. Son E., Fortov V. *et al* // *Thermophysics of Gas-Core Nuclear Engine* / Ed. by V.M. Ievlev, (ATOMIZDAT, Moscow, 1980)
- Iosilevskiy I., Gryaznov V., Yakub E., Semenov A., Hyland G., Ronchi C., Fortov V. *Bull. of Russ. Atomic Agency* , Moscow (2003) // *Int. Journal of Thermophysics* **22**, 1253 (2001)

MPQ-EoS – Modified semi-empirical EOS (*wide-range EOS*)

EOS - algebraic form with free “calibrated” parameters,
– far improvement of simple generic Van-der-Waals formula





- All quantities are derived from the Helmholtz free energy:

$$F(\rho,T) = F_e(\rho,T) + F_i(\rho,T) + F_b(\rho,T) \qquad (1)$$

- Electron contribution: simple Thomas-Fermi model [7]
  - Fermi gas in the self-consist. electrostatic atomic field
  - The TF equation is solved for spherical cells.
  - The TF quantities scale with atomic number Z.
    ⇒ The TF table must be calculated only once.
  - Disadvantages of the simple TF model:
    - Critical pressure and temperature are overestimated.
    - Pressures near normal conditions are overestimated.
- The bonding contribution [8] tries to improve this.
  It adjusts the EOS to zero pressure and K_0 at (ρ_0, T_0).
- The ion contribution is calculated by Cowan's model [9].
  It allows for limiting physical laws but not for melting.

EOS calibration ($T = 0$):
ϱ – *normal density*
$\Delta_s H^0$ – *vaporization heat*

EOS validation ($T \gg 0$):
P(T) – saturation vapor
H(T) – enthalpy diagram

Phase coexistence:
Maxwell *“Equal Square” or Double-Tangent construction*

- Faik S., Tauschwitz An., Maruhn J., Iosilevskiy I., *MPQeos-JWGU: A new equation-of-state package for warm/hot dense matter*, GSI Annual Report, 2011
- Faik S., Basko M., Tauschwitz An., Iosilevskiy I., Maruhn J., *High Energy Density Physics*, **8**, 349 (2012)
Dynamics of volumetrically heated matter passing through the liquid-vapor metastable states // arXiv:1205.2579

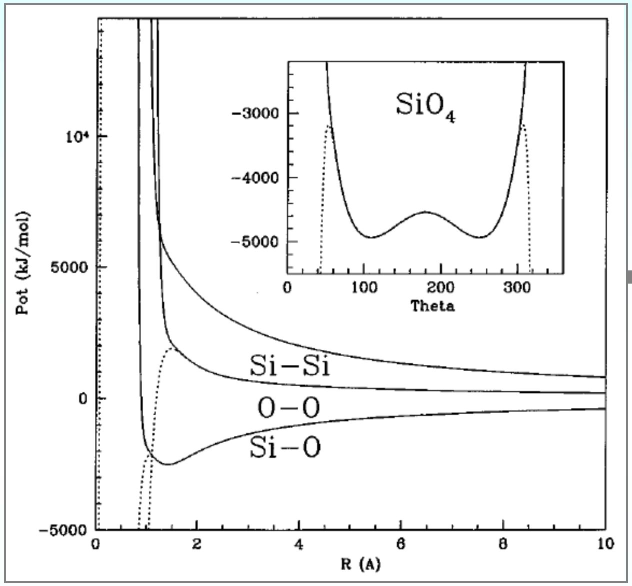
Ionic-MD – Direct numerical **MD** simulations for **Ionic Model** of SiO_2 ($Si^{+4} + 2O^{-2}$)

Born–Huggins–Mayer TTAM pair potential

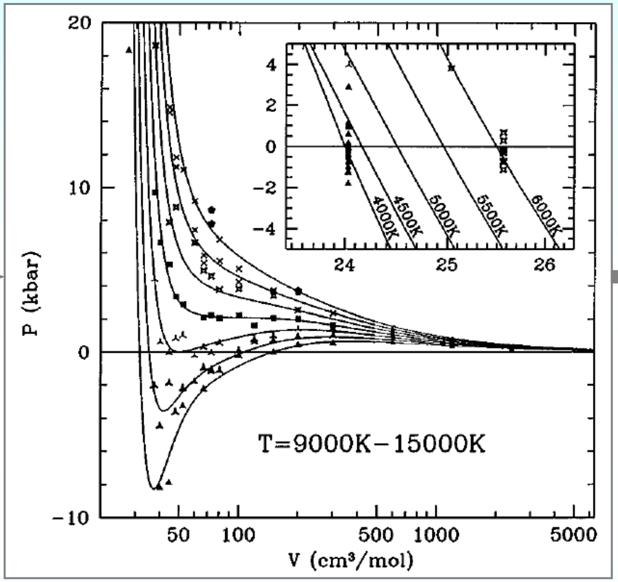
$$\phi_{ij}^{\mathrm{TTAM}} = q_i q_j / r_{ij} + a_{ij}\ \exp(-b_{ij} r_{ij}) - c_{ij} / r_{ij}^{6},$$

EOS polynomial for $Z(T,\rho) \equiv PV/RT$

$$Z = 1 + z_0\rho^{1/2} + z_1\rho + z_2\rho^2 + z_3\rho^3 + z_4\rho^4 + z_5\rho^5,$$



Interionic pair potential



Isotherms with VdW loops

$$z_0 = x_0 . 10^3 / T^{3/2},$$

$$z_1 = x_1 + \frac{x_2 . 10^6}{T^2}\left(1 + \frac{x_3 . 10^{12}}{T^4}\right),$$

$$z_2 = x_4 + \frac{x_5 . 10^6}{T^2}\left(1 + \frac{x_6 . 10^{12}}{T^4}\right),$$

$$z_3 = x_7 + \frac{x_8 . 10^6}{T^2}\left(1 + \frac{x_9 . 10^{12}}{T^4}\right),$$

$$z_4 = x_{10} + \frac{x_{11} . 10^6}{T^2}\left(1 + \frac{x_{12} . 10^{12}}{T^4}\right),$$

$$z_5 = x_{13} + \frac{x_{14} . 10^6}{T^2}\left(1 + \frac{x_{15} . 10^{12}}{T^4}\right),$$

Thermal EOS $P(\rho,T)$

Phase coexistence:

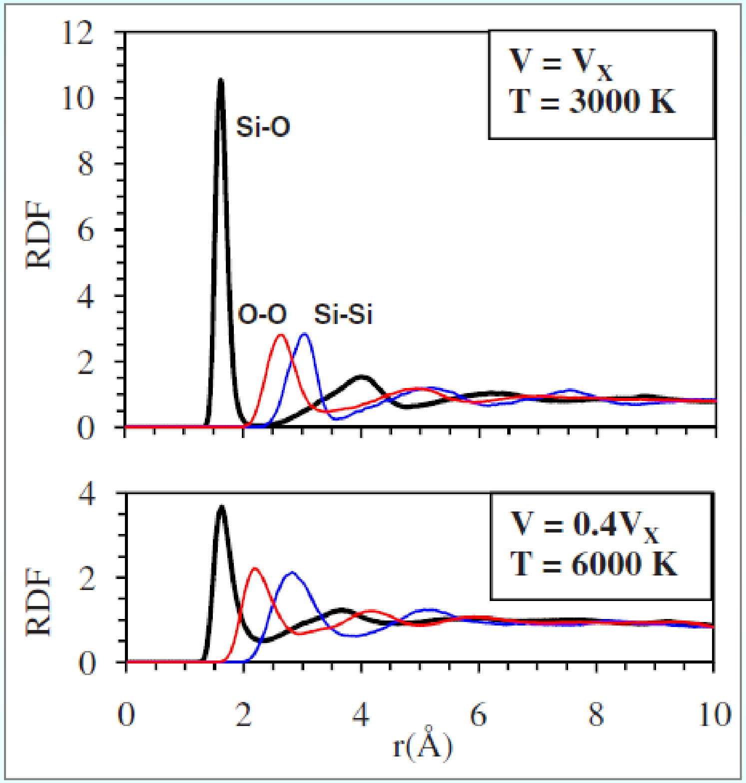
Maxwell *"Equal Square" or Double-Tangent construction*

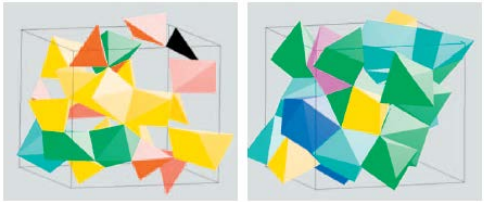
Forced-congruent phase coexistence { $(Si/O)_{liquid} = (Si/O)_{vapor}$ }

Y. Guissani & B. Guillot, *J. Chem. Phys.* **104** (1996) *Numerical investigation of the liquid–vapor coexistence of silica*

DFT / MD – *Ab initio* quantum **MD** simulations for liquid SiO_2 {(Si + O)/**MD**/ + e /**DFT**/}

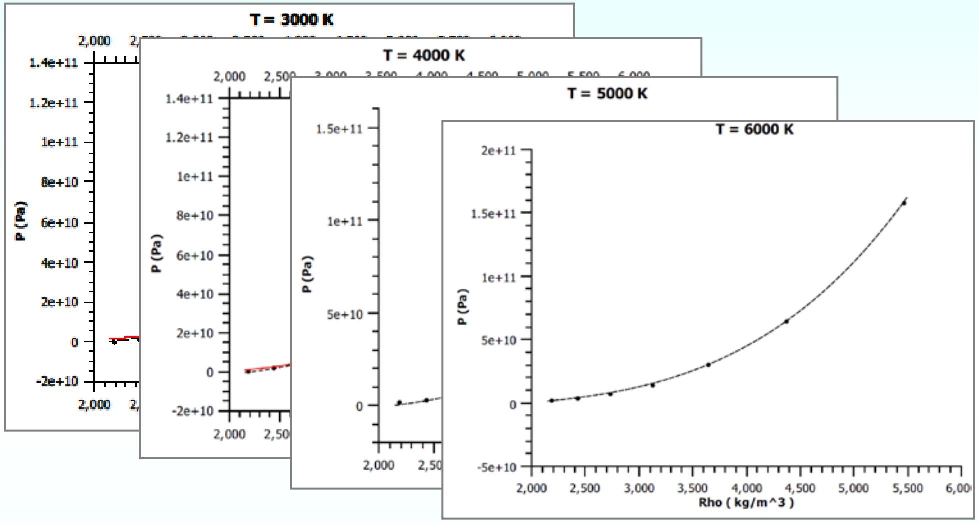
Liquid SiO_2





Visualization of the Si-O coordination

Pressure on isotherms *T* = 3 - 6 kK



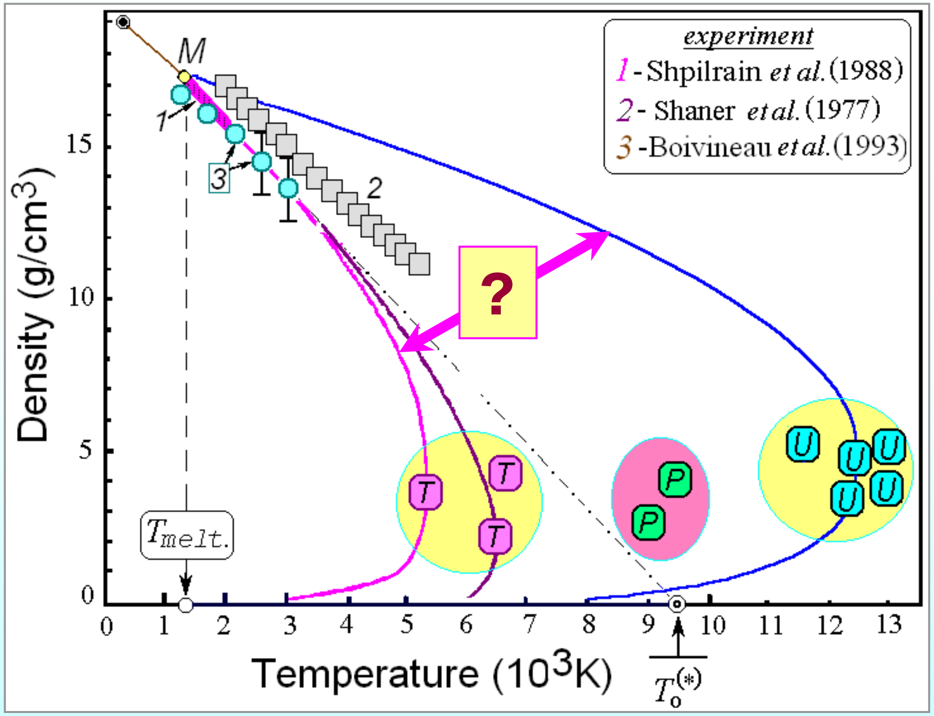
Pressure on isotherms *T* = 3 - 4 kK

Belonoshko A. (1994)
{ MD+ modeling potential }
P(V,T)-data
Geochim. et Cosmochimica Acta. 58 (1994)

B. Karki, D. Bhattarai, L. Stixrude, *Phys. Rev.* B **76** (2007) *First-principles simulations of liquid silica*

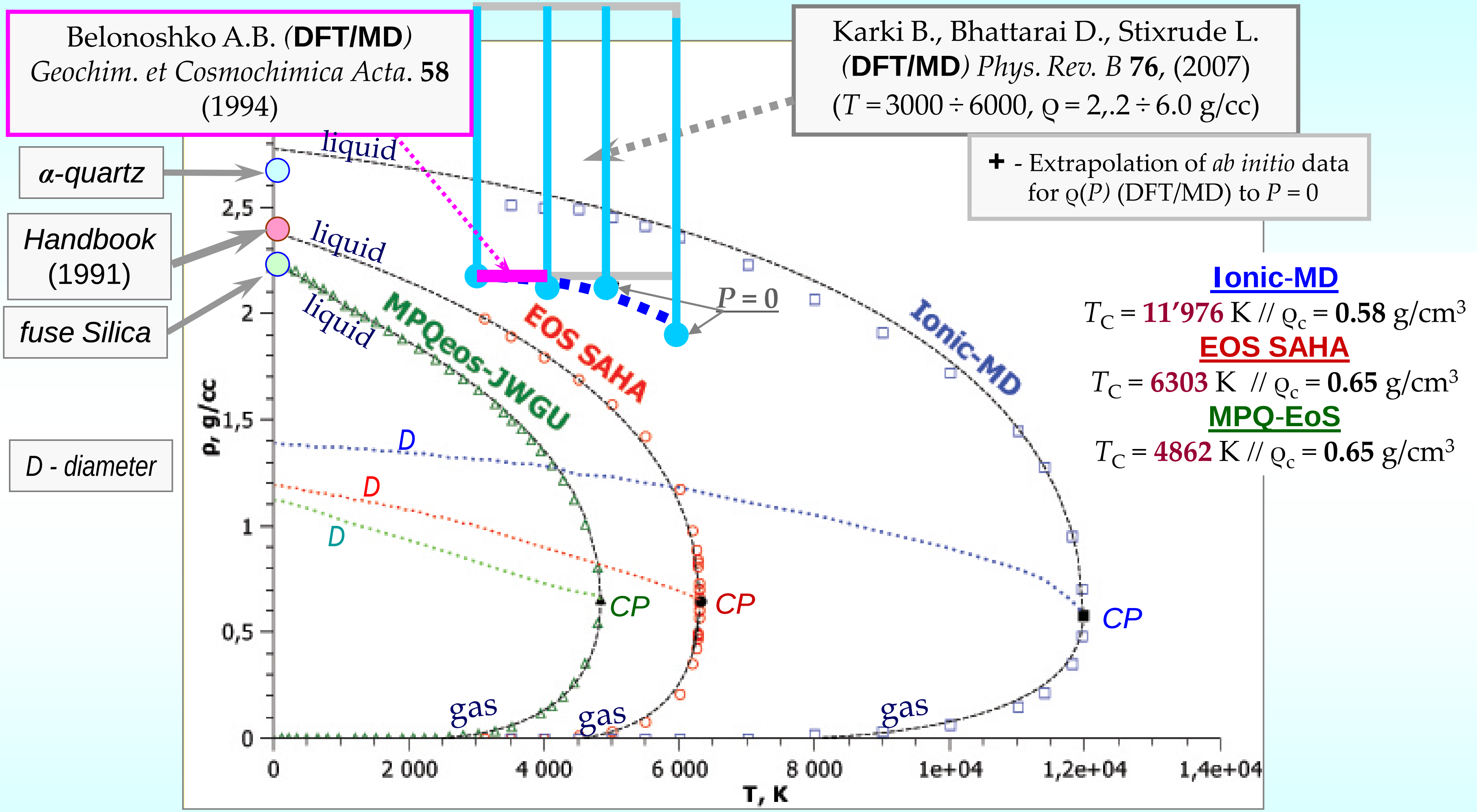
Comparison *of* theoretical predictions

(keeping in mind glaring contradiction in predicted high-*T* uranium phase diagram)



Iosilevskiy I., Gryaznov V., Solov'ev A., *High Temp.-High Pressure*, **43,** 227 (2014) // arXiv:1312.7592

Density–temperature phase diagram *for* **silica** (SiO_2)



Belonoshko A.B. (**DFT/MD**)
Geochim. et Cosmochimica Acta. **58**
(1994)

Karki B., Bhattarai D., Stixrude L.
(**DFT/MD**) *Phys. Rev. B* **76**, (2007)
($T = 3000 \div 6000$, $\varrho = 2{,}.2 \div 6.0$ g/cc)

+ - Extrapolation of *ab initio* data
for $\varrho(P)$ (DFT/MD) to $P = 0$

α-quartz

Handbook
(1991)

fuse Silica

D - diameter

Ionic-MD
T_C = **11'976** K // ϱ_c = **0.58** g/cm^3

EOS SAHA
T_C = **6303** K // ϱ_c = **0.65** g/cm^3

MPQ-EoS
T_C = **4862** K // ϱ_c = **0.65** g/cm^3

● *Handbook on Physics* // Eds. I. Grigoriev et al.
ATOMIZDAT, Moscow, 1991

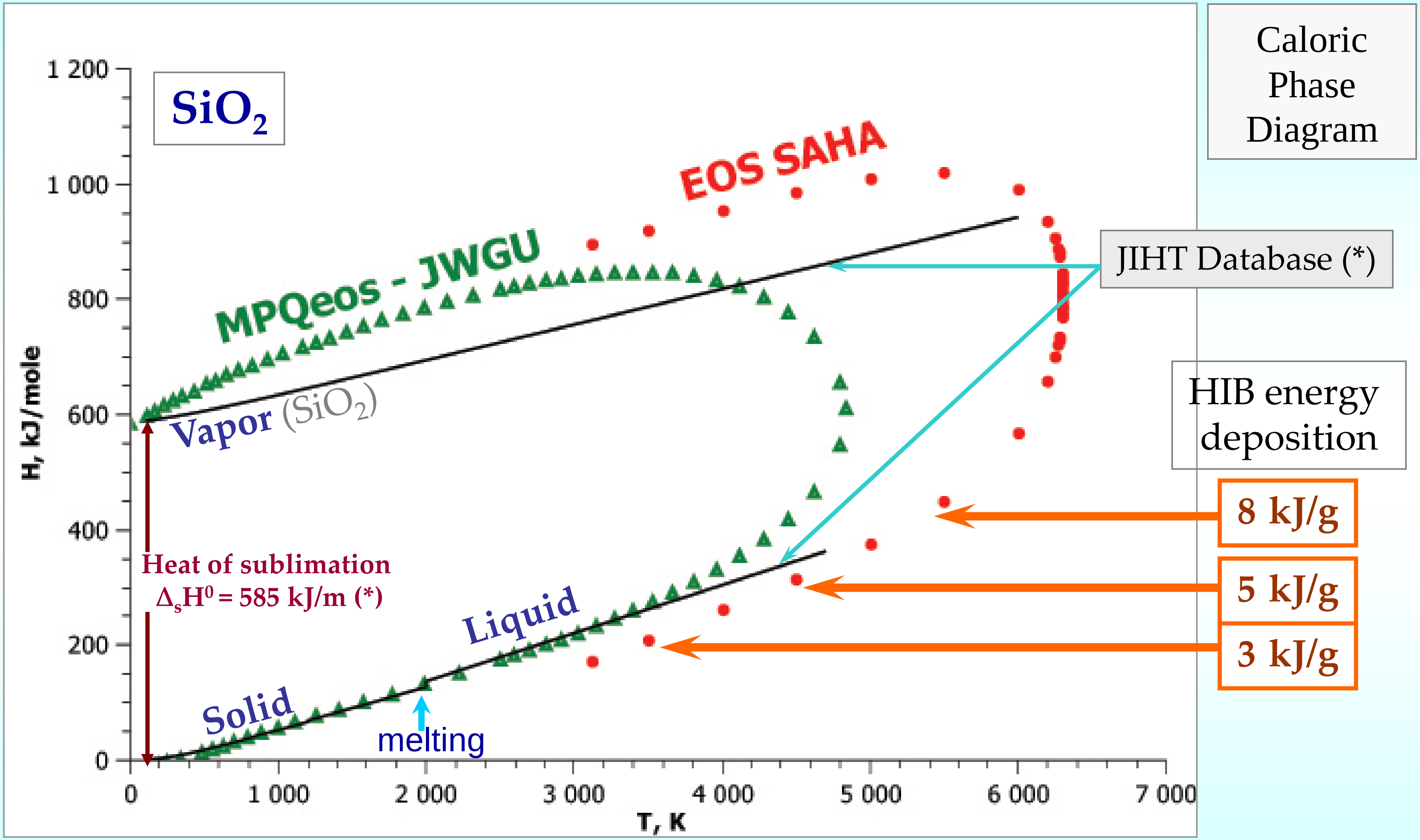
Ionic-MD – MD simulations for Ionic Model of SiO_2 ($Si^{+4} + 2O^{-2}$)

MPQ-EoS – Modified Semi-empirical EOS (*wide-range*) (*S.Faik et al.*)

EOS SAHA – Quasi-chemical model (*Non-ideal multi-component mixture)*

Enthalpy–Temperature phase diagram *for* silica

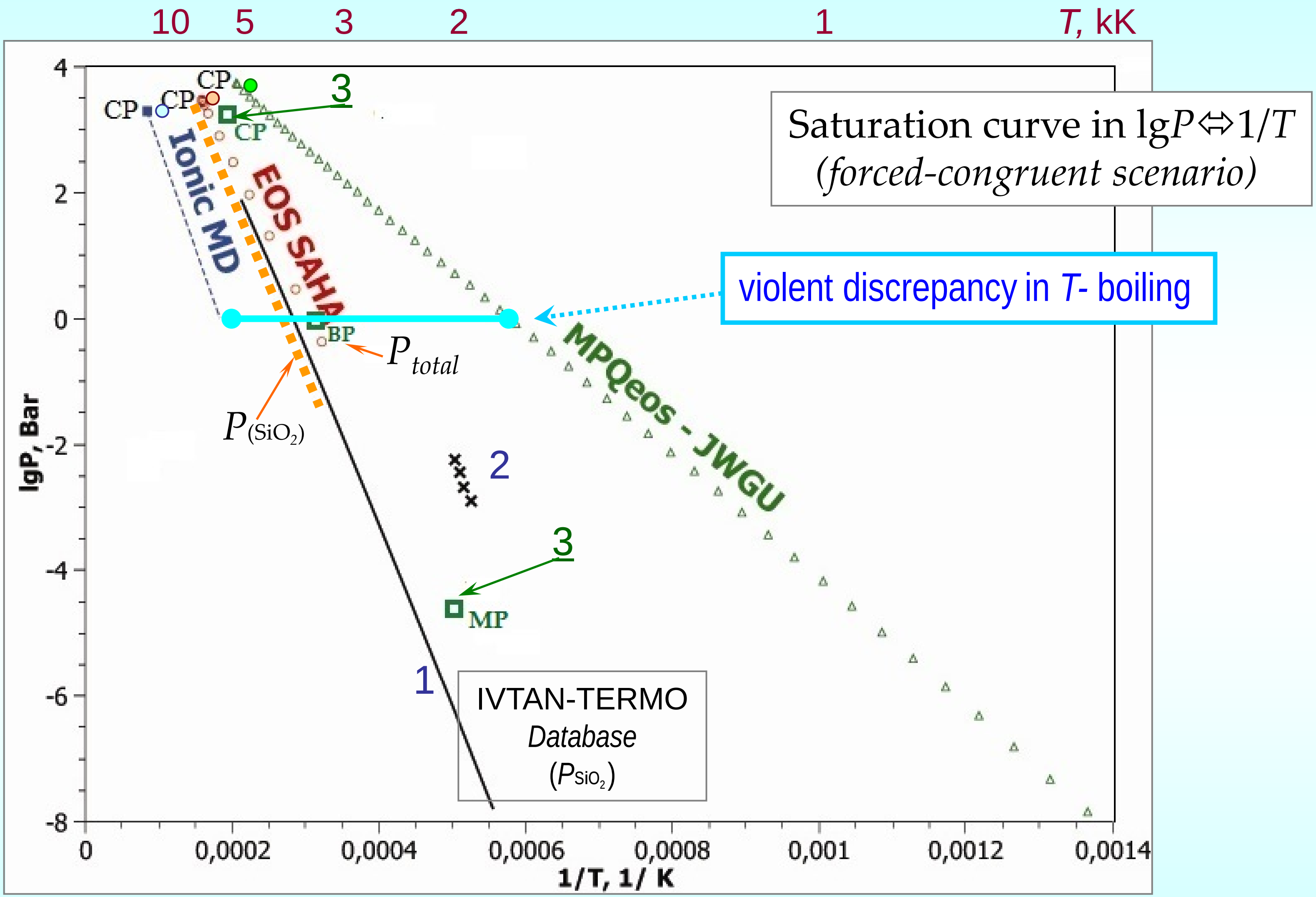
Caloric Phase Diagram



(*) Gurvich L., Veits I., Medvedev V., "*Thermodynamic properties of individual substances*" M.: Nauka 1982

Iosilevskiy I., Gryaznov V., Solov'ev A., *High Temp.-High Pressure*, **43,** 227 (2014) // arXiv:1312.7592

Pressure–temperature phase diagram *for* silica (SiO_2)



Saturation curve in lg*P*⇔1/*T*
(*forced-congruent scenario*)

violent discrepancy in *T*- boiling

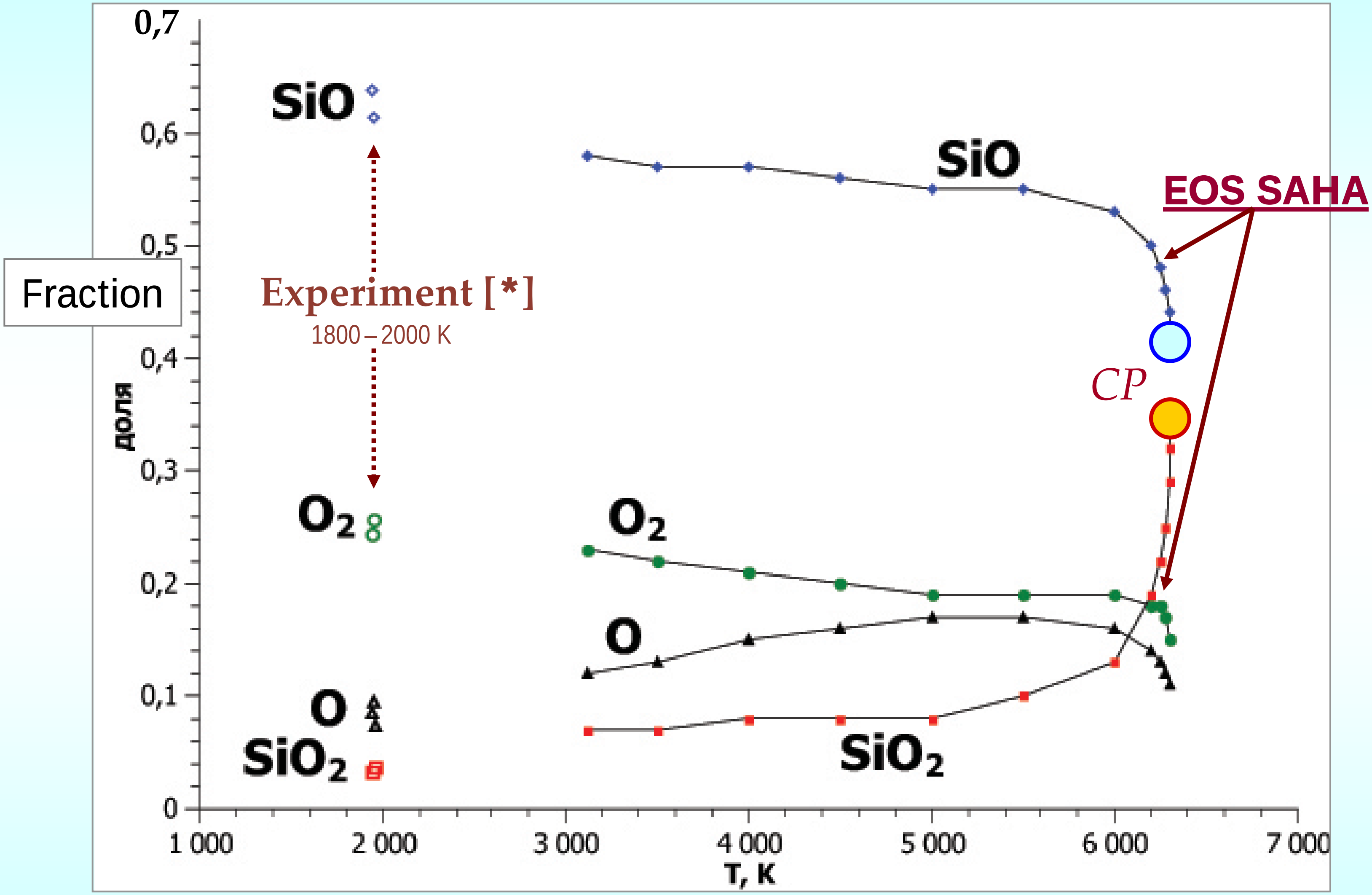
1. Gurvich L.V., Veits I.V., Medvedev V.A. "*Thermodynamic properties of individual substances*", M.: Nauka 1982

2. Kazenas E.K. , Tsvetkov Yu.V., *Thermodynamics of evaporation for oxides*, M.: LKI, (2008) pp 474. (*in Russian*)

3. **MP, BP, CP**: - Melosh H.J., *Meteoritics & Planetary Science* **42**, (2007) // *A hydrocode Equation of State for* SiO_2

Equilibrium vapor composition over the boiling SiO_2

(comparison of theoretical predictions with experimental data)



[*] Experiment

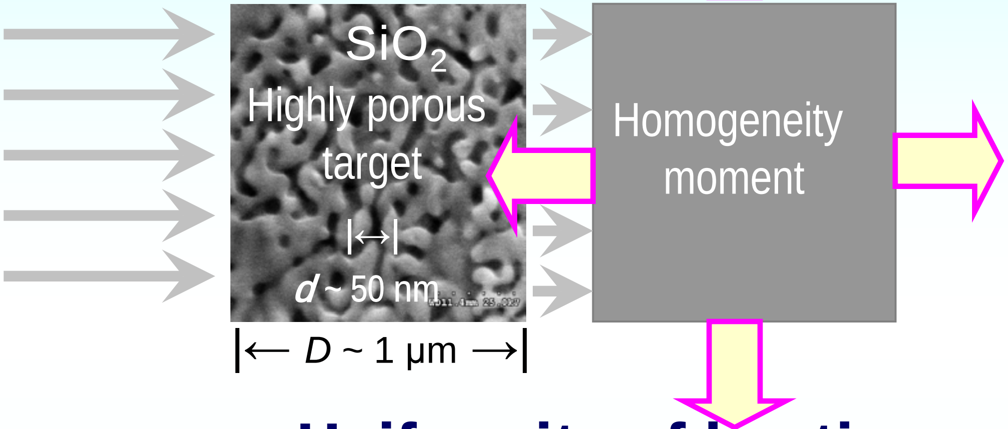
Kazenas E.K. & Tsvetkov Yu.V., *Thermodynamics of evaporation for oxides*, M.: LKI, 2008, PP 474 (*in Rus.*)

Calculations of eq. composition via SAHA-EOS: (*molecular data - JIHT Database IVTANTERMO)*

Measurements of **thermal expansion** for **liquid SiO_2** (FAIR-GSI)

HIB volumetric heating of porous sample

Acoustic time (*single grain*) $\tau_d \equiv \quad c_s$ << τ_{HIB} << $\tau_D \equiv D/c_s$ (*whole sample*)



Real Experiment in GSI (2006)

d ~ 50 nm, D ~ 1 mm, τ_{HIB} ~ 100 ns

a_{sound} ~ 2 km/sec

$\tau_d \equiv d/a_s$ ~ **25** ps (!), $\tau_D \equiv D/a_s$ ~ **1** μs

τ_d <<< τ_{HIB} < τ_D

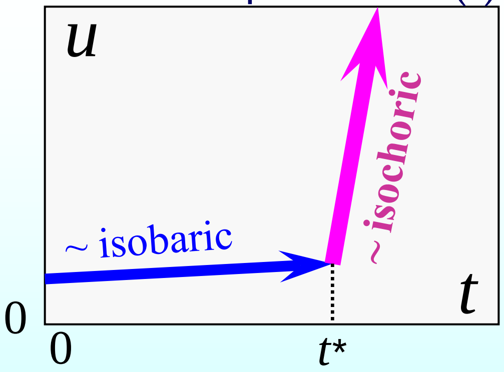
Uniformity of heating

Porous sample: – Grain expansion is quasi-free (*isobaric*)

No surface movement up to **homogeneity moment !**

Fast surface expansion after homogeneity moment **!**

Surface expansion: $u(t)$



HIB heating of highly dispersed porous samples: *Why should we do it ?*

(Iosilevskiy // First HED experiments in FAIR APPA-cave)

Porous SiO_2 under HIB volumetric heating

	1	2
ΔU (kJ/g) [*]	**5 kJ/g**	**8 kJ/g**
ΔU (kJ/mole)	300 kJ/mole	480 kJ/mole
Δt	**100 ns**	**100 ns**
$q = \Delta U/\Delta t$	50 J/g·ns	80 J/g·ns
$t_{melting}$	40 ns	20 ns
T_{final} (K) (code SAHA [1])	≈ **4000** K	≈ **5700** K
ρ_{melt}/ρ_0 [1] \\ (ρ_0/ρ_{melt})	≈ 0.9 \\ ≈ 1.12	=”=
ρ_{fin}/ρ_0 [1] \\ (ρ_0/ρ_{fin})	≈ 0.75 \\ ≈ 1.33	≈ 0.5 \\ ≈ 2
m_{target} (porocity) Homogeneity moment t_{hmg} = **70 ns**	**1.2** 3.5 kJ/g \\ T_{hmg} ≈ **3000 K** $\rho_{hmg} \approx 2$ g/cc	**1.5** 5.6 kJ/g \\ T_{hmg} ≈ **5000 K** $\rho_{hmg} \approx 1.62$ g/cc
$T_{melt} \approx 2000$ K	$\Delta H \approx 127$ kJ/mole ≈ 2 kJ/g	$Q_{melt} = \Delta H_{melt} \approx 10$ kJ/mole ≈ 0.17 kJ/g

[*] O.Rosmej – private communication (

[1] Iosilevskiy I., Gryaznov V., Solov’ev A., *High Temp.-High Pressure,* **43,** 227 (2014)
Properties of high-temperature phase diagram and critical point parameters in silica // arXiv:1312.7592

Fundamental physical problems

- Problem of high-*T* phase diagram and critical point of Uranium and some „bad“ metals, e.g. W, Mo,Ta,Ca (*but not Pb, Al, Cu etc. which were irradiated by HIB in GSI during last ~ 15 years* **!**)

- Problem of high-*T* phase diagram and critical point parameters of SiO_2 (even forced-congruent) – there is no still decisive experiments and *ab initio* calculations (I.I.-2014)

- Problem of high-*T* *polymerization* of *nitrogen*. New non-standard type of „pressure ionization“ not from atomic and/or molecular state, but from *polymeric* state **!** (I.I. EMMI – 2011)

- Problem of *non-congruent phase transitions* in high-*T* mixtures (e.g. H_2 + He *etc*) // in alloys (e.g. K+Na, Pb+Bi *etc*) // in chemical compounds, e.g. UO_2, UC, UN *etc* // in planetary materials: H_2O, NH_3, CH_4, SiO_2, MgO/ molten salts e.g. NaCl, CsF... *etc*)

- Problem of anomalous features of “*entropic*” phase transitions. In contrast to the ordinary enthalpic (VdW-like) phase transitions (I.I. / Hirschegg-2013)

- Long-living problem of hypothetical “*plasma*” and “*dissociative*” *phase transitions* in isentropically compressed hydrogen (deuterium) in Megabar pressure range

- Hydrodynamic anomalies due to thermodynamic anomalies (e.g. phase transitions, regions of negative Gruneizen coefficient etc.) – „*binodal layers*“, *rarefaction shock*, *reverberation* compression regime *etc*. (I.I. / Hirschegg-2014)

(discussion)

Conclusions *and* Perspectives

- Our knowledge of high-*T* parameters for **SiO_2 gas-liquid phase transition** in (partially equilibrium) *forced-congruent* scenario is **very poor**

- We **know almost nothing** about totally equilibrium (**non-congruent**) version of this phase transition

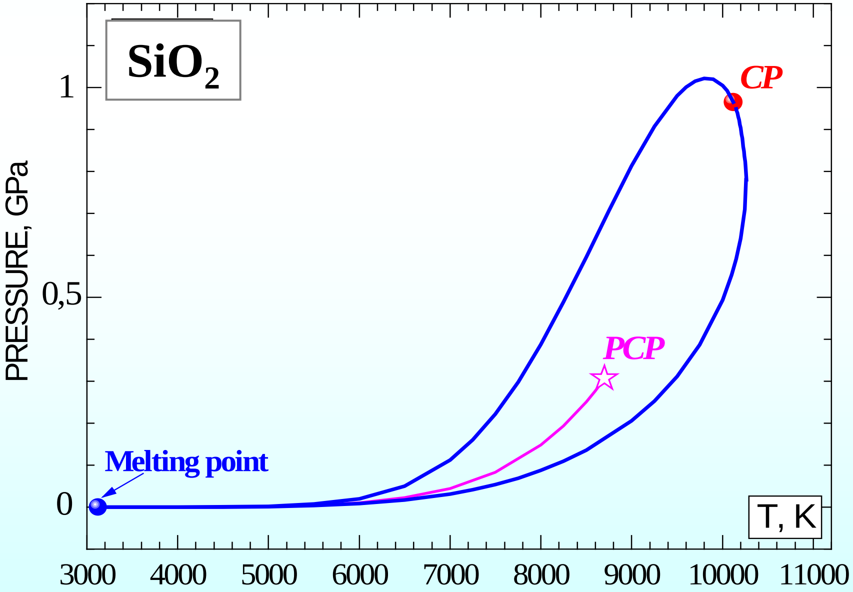
- We have enough reasons to expect **anomalous phase behavior** due to **non-congruence** for silica at high temperature and pressure

- It is promising to study phase transition in silica (SiO_2) with **subsecond experimental approaches** (*Laser and Heavy-Ion-Beam heating, shock comp. & iso-S release..etc.*)

- *Ab initio* approaches are very promising for **direct numerical simulation** for **gas-liquid phase transition** in silica (SiO_2): (*Density Functional Theory -* **DFT**// *Quantum Monte Carlo –* **QMC**, *and Quantum Molecular Dynamic -* **QMD** *simulations etc.*)

- If one takes into account hypothetical **non-congruence** of **phase transitions** in **silica** he should **revise** ordinay **scenario** for **phase transformations** in silica in many cosmic and terrestrial applications

Thank you!



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