FEATURES OF GAS-LIQUID PHASE TRANSITION IN SILICA SiO$_2$

Solovyev, A.M.[1]*, Iosilevskiy, I.L.[2,3,5], Gryaznov, V.K.[3], Faik, S.[4], Tauschwitz, An.[4,5]

[1]MIPT, Dolgoprudny, Russia, [2]JIHT RAS, Moscow, Russia, [3]IPCP RAS, Chernogolovka, Russia,
[4]UFTP, Frankfurt am Main, Germany, [5]EMMI, Darmstadt, Germany

МФТИ
SAPERE AUDE

Properties of silica, such as: first of all, parameters of its critical point and equation of state - are poorly known theoretically nowadays.
At the same time experimental investigation of all these properties of silica are very difficult and are poorly known also.
That's why it is important to compare different theoretical predictions for high-temperature behavior of all EOS for silica and especially existing predictions for critical point locations and properties, which are predicted by different theoretical models and semi-empirical rules and compare these theoretical predictions with recommendations of handbooks and scarce experimental data from literature.

THEORETICAL MODELS SELECTED FOR COMPARISON

SAHA-model

It is traditional approach in frames of so-called **quasi-chemical representation** ("chemical plasma picture")[1,2].
In this approach high-temperature product of SiO$_2$ heating are described as multi-component partially ionized mixture of many components, which are strongly interacting with each other via **Coulomb, short-range attractive and repulsive interactions** (i.e. strongly non-ideal plasmas).

Small number of unavoidably used free parameters in the SAHA theory (in addition to the great amount of meaningful physical parameters and constants) are calibrated so that reproduce correctly several basic empirical properties of silica, i.e. normal density and heat of sublimation of low-temperature condensed silica. As a result, calculation via SAHA-code gives all the variety of thermodynamical functions and in addition equilibrium chemical and ionization composition.

In present paper SAHA-code was improved and modified for description of gas-liquid phase transition in SiO$_2$, but presently only in more simple forced-congruenf variant. With the use of this SAHA-code some of features of gas-liquid phase transition in silica (SiO$_2$) have been calculated. It leads to following thermodynamic parameters of (standard) critical point [2]:

$$T_c = 6303 \text{ K}; \quad P_c = 3.052 \text{ kbar}; \quad \rho_c = 0.65 \text{ g/cm}^3$$
$$PV/RT = 0.180; \quad S/R = 14.26; \quad \text{Mol.weight} = 44.87 \text{ g/Mol};$$

and typical equilibrium composition (in 1/cm^3):

e = 4.054+16;   O = 8.676 +20;   O(+) = 3.409 +14;
O$_2$ = 1.330+21;   Si = 4.344+18;   Si(+) = 4.020+16;
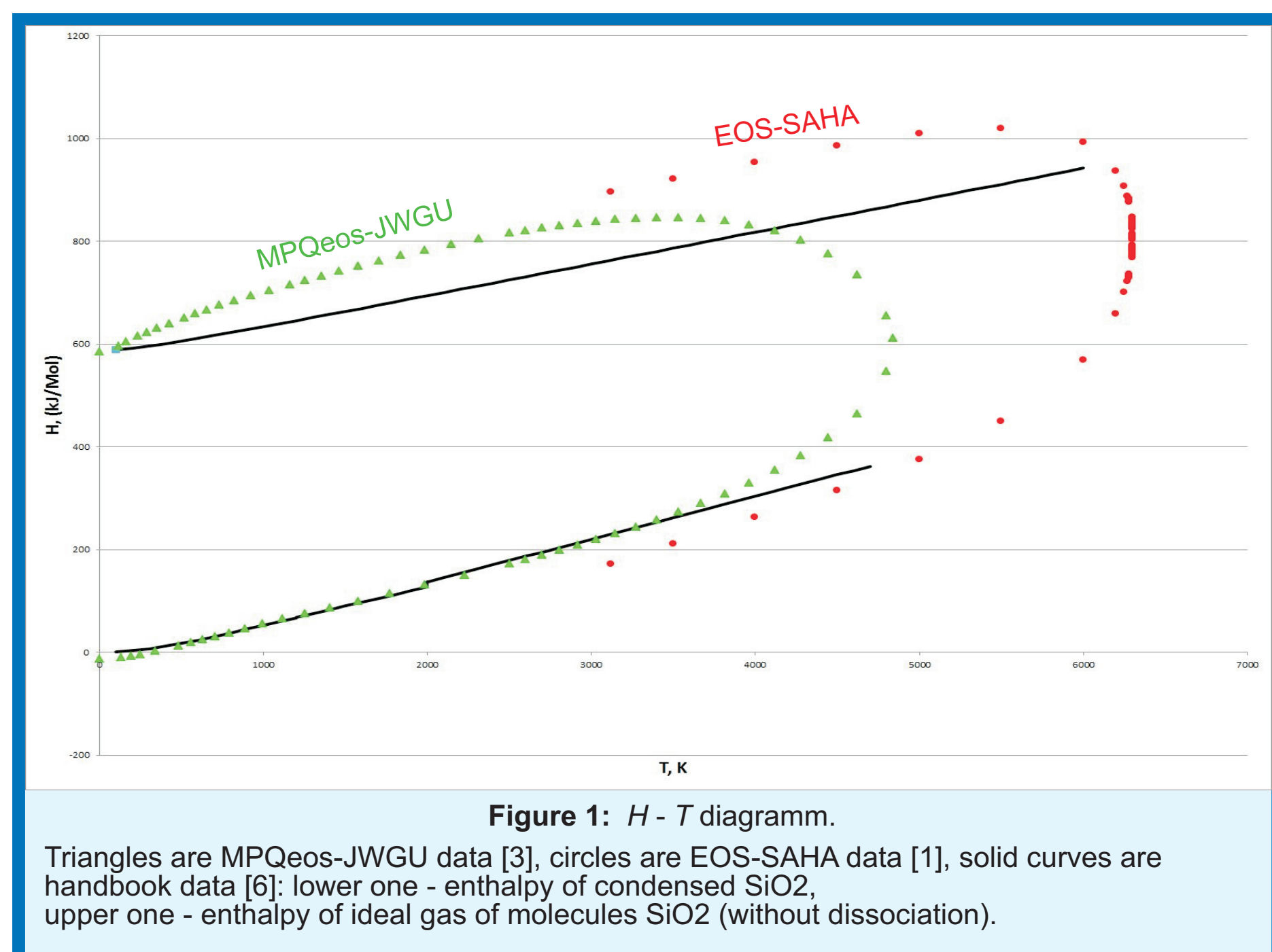Si$_2$ = 3.681+14;   SiO = 3.519+21;   SiO$_2$ = 2.960+21.

Figure 1: H - T diagramm.
Triangles are MPQeos-JWGU data [3], circles are EOS-SAHA data [1], solid curves are handbook data [6]: lower one - enthalpy of condensed SiO2, upper one - enthalpy of ideal gas of molecules SiO2 (without dissociation).

MPQeos-JWGU

It is typical **semi-empirical** so-called "wide-range" **EOS (WD-EOS)** developed by M.Ross and D.Young and titled as "MPQEOS".

Electronic contribution is described via *Thomas-Fermi approximation* combined with approximation of average atomic cell (*Wigner-Zeits cell model*). Special additional "cold term" was added to the EOS to provide realistic EOS behavior at low temperature and relatively low density.
This EOS was improved significantly by Stefan Faik and colleagues [3] (see also presentation on this conference by S.Faik *et al*).
As well as SAHA-EOS this WD EOS was calibrated on to basic parameters: normal density and heat of evaporation in room conditions. This leads finally to rather realistic values for predicted critical point parameters [3] :

$$T_c = 4862 \text{ K}; \quad P_c = 5.506 \text{ kbar}; \quad \rho_c = 0.65 \text{ g/cm}^3.$$

It should be note that all *WD-EOS gives no,* as a rule, *information about equilibrium chemical and ionic composition*.

Classical ionic model with MD simulation

It is typical approach for description of phase transitions in compounds like NaCl, SiO$_2$, H$_2$O etc. as classical binary ionic mixture of positive and negative ions, say Si(+4) and O(-2) [5] with classical semi-empirical pairwise-additive Coulomb-like interaction, corrected at close distances (see [5] for details).
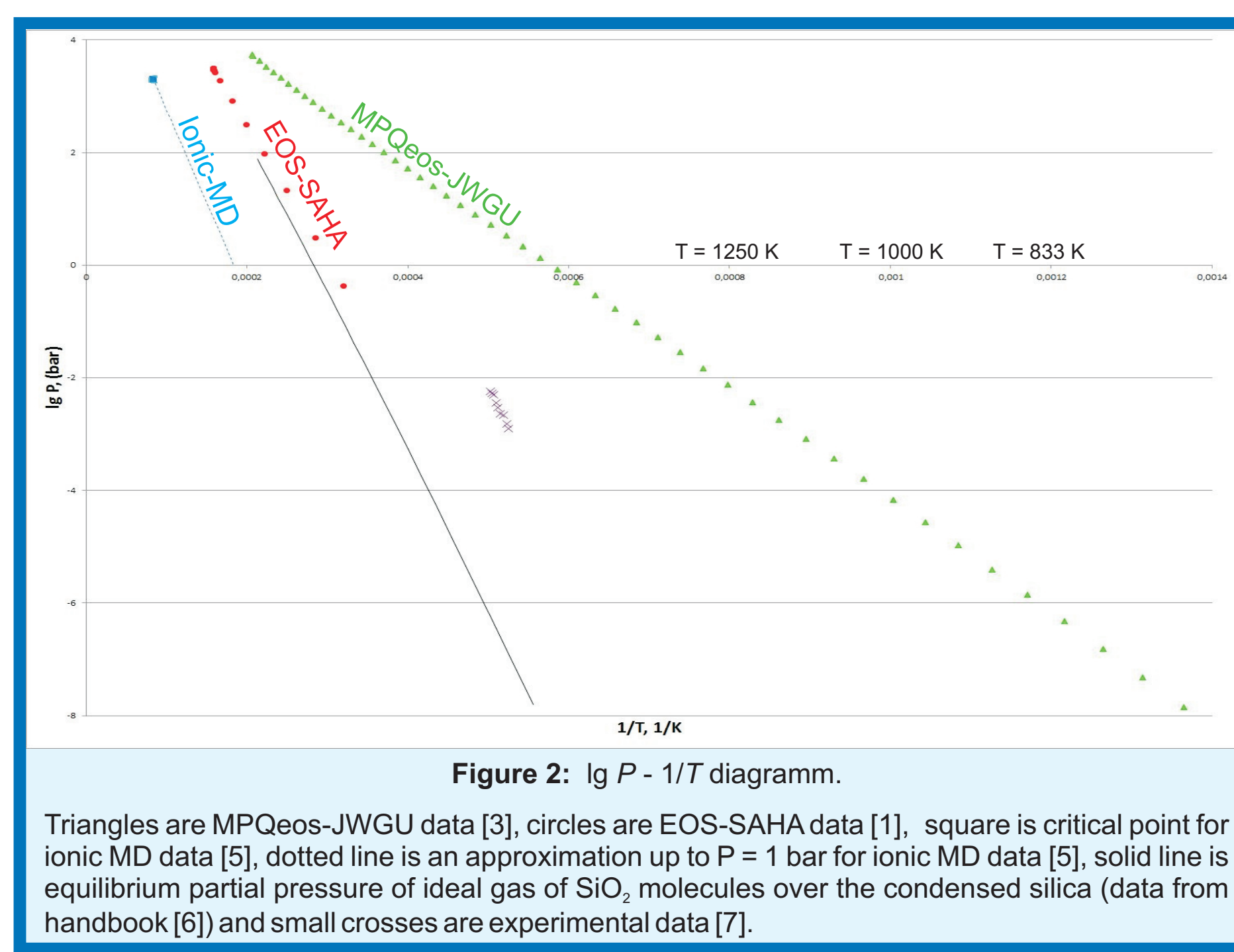

Figure 2: lg P - 1/T diagramm.
Triangles are MPQeos-JWGU data [3], circles are EOS-SAHA data [1], square is critical point for ionic MD data [5], dotted line is an approximation up to P = 1 bar for ionic MD data [5], solid line is equilibrium partial pressure of ideal gas of SiO$_2$ molecules over the condensed silica (data from handbook [6]) and small crosses are experimental data [7].

Thermodynamics of such equilibrium system have been calculated in frames of Direct Molecular Dynamic Simulations. The calculation results were approximated consequently by algebraic EOS-envelope as pressure on density expansion with coefficients depending on temperature.
Such analytic fit have been used for standard calculation of critical point and high-temperature part of coexistence boundaries (binodals) of gas-liquid phase transition. As a result next parameters have been obtained for critical point [5]:

$$T_c = 11976 \text{ K}; \quad P_c = 2.0 \text{ kbar}; \quad \rho_c = 0.58 \text{ g/cm}^3 .$$

DFT/MD

It considered high-T - high-P products of SiO$_2$ heating as quantum mixture of nuclei (or highly ionized ions) Si and O in equilibrium with quantum electronic subsystem.
Electronic contribution is described via density functional theory, while ionic degrees of freedom are describe in frames of Molecular Dynamics procedure (DFT/MD) (see [4] and references therein).
Results of simulation for liquid phase only are available in temperature range 3000 K - 6000 K, and density ρ > 2.2 g/cm.
These simulation give us pressure-density isotherms close to the liquid binodal and without gas-liquid phase boundaries. It should be stressed that this *ab initio* don't use any calibration to empirical properties of silica.
In present work we used the DFT/MD data [4] for close extrapolation of the data on $P(\rho)$ dependence to the zero-pressure isobar. For doing this we use interpolation of initial $\rho(T)$ dependence from [4] by analytical fit: $P = A + B\rho^c$ (see **Fig.4**). It is known that far from critical point zero-pressure isobar practically coincides with liquid binodal of liquid-gas coexistence.

COMPARISON FOR THEORETICALLY PREDICTED PHASE DIAGRAMS AND CRITICAL POINT

CALORIC PHASE DIAGRAM

First comparison is exposed for enthalpy - temperature plane (H - T) (**Fig.1**). Predictions of two EOS-s, described above, SAHA and MPQeos-JWGU, are compared with recommendations of handbook [6] for enthalpy of liquid SiO$_2$ (low branch - T<4500 K) and enthalpy of hypothetical ideal monomolecular gas of SiO$_2$-molecules (top branch 0<T<6000 K).

Calculations via SAHA-code were provided for temperature T >3120 K, while calculations via MPQeos were provided for T >0. It is seen that both comparting EOS are in satisfactory agreement with the handbook recommendations.
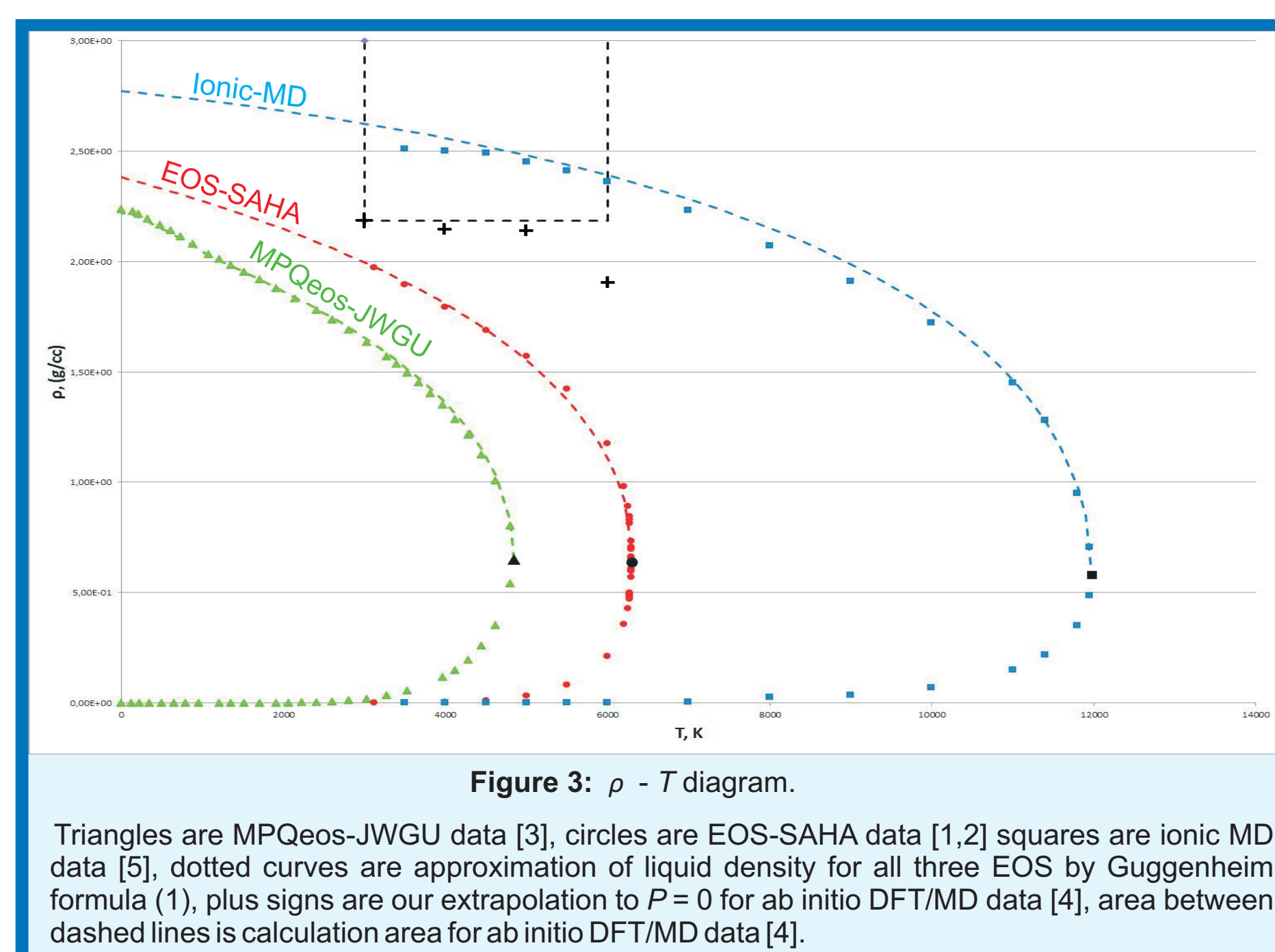

Figure 3: ρ - T diagram.
Triangles are MPQeos-JWGU data [3], circles are EOS-SAHA data [1,2] squares are ionic MD data [5], dotted curves are approximation of liquid density for all three EOS by Guggenheim formula (1), plus signs are our extrapolation to P = 0 for ab initio DFT/MD data [4], area between dashed lines is calculation area for ab initio DFT/MD data [4].

At the same time it should be noted that true enthalpy of equilibrium vapors over the boiling SiO$_2$ can not coincide with the handbook recommendation for vapors because the latter do not take into account equilibrium dissociation of SiO$_2$ in vapor phase (SiO$_2$ = SiO +½ O).
NB! According to calculation via SAHA-EOS degree of dissociations in equilibrium vapors over the boiling, *even when it boils congruently* is of order **90 %** (!)(**Fig. 5**). It is evident that the problem of equilibrium chemical and ionization composition is very important and should be studied carefully.

PRESSURE - TEMPERATURE PHASE DIAGRAM

It is well known that pressure-temperature dependence for very many materials well obeys to old semiempirical rule - quasi-linear behavior of saturation curve in Arrhenius coordinates: lg(P) - 1/T.
It is known that this rule is strictly valid for low temperature when vapors obey to ideal gas law. At the same time this Arrhenius rule works surprisingly good even for high temperature close to the critical one. All these comments are valid for all compared EOS in present paper.
All the saturation curves are exposed at **Fig.2**. All EOS-s expose linear behavior but with different slope and different end-points, i.e. critical points.

It should be stressed that only **SAHA-code** reproduces saturation curve (in forced-congruent regime) in satisfactory agreement with predictions of IVTAN Handbook [6]
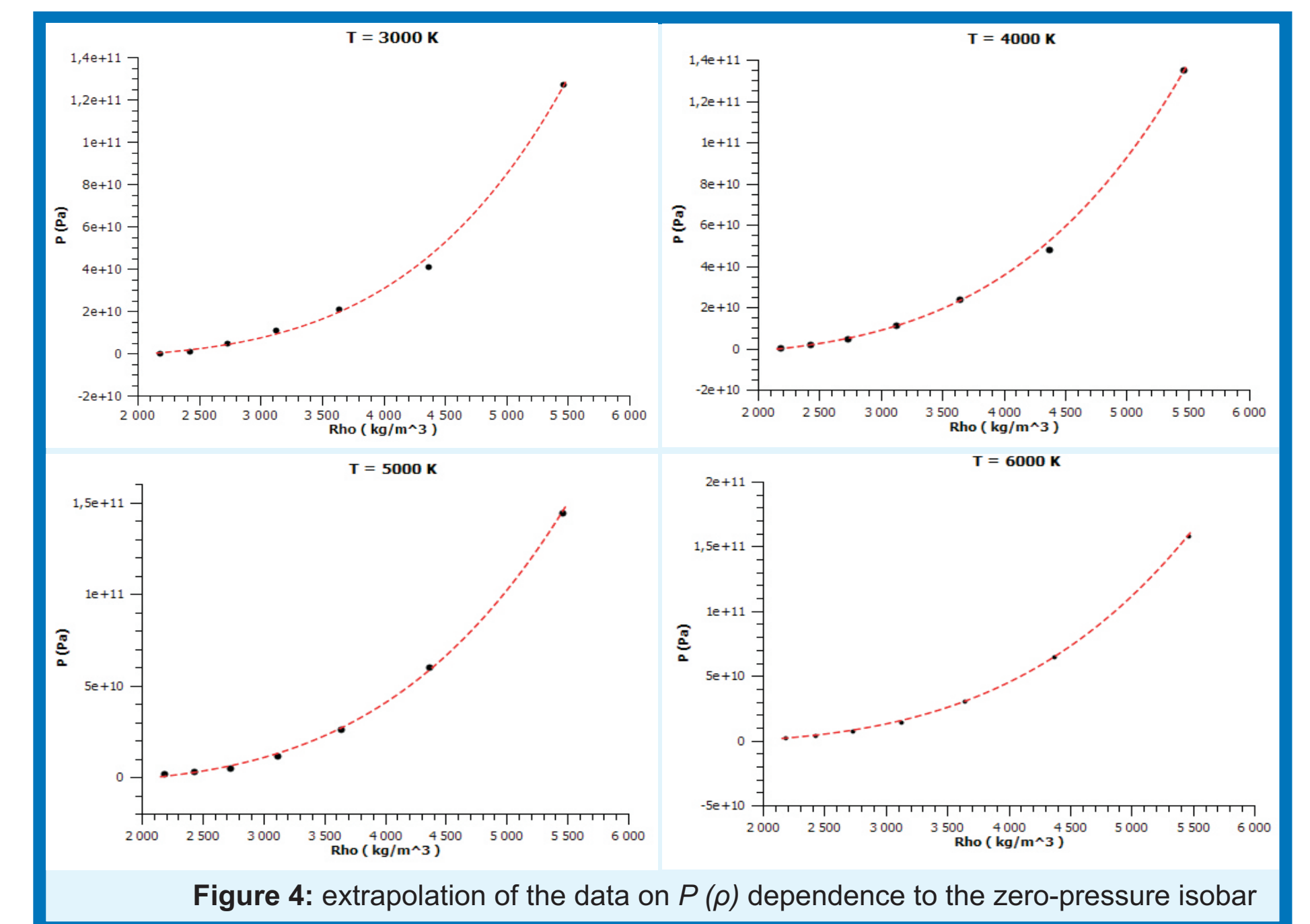

Figure 4: extrapolation of the data on $P(\rho)$ dependence to the zero-pressure isobar

TEMPERATURE - DENSITY PHASE DIAGRAM

It is well known that density-temperature boundaries of two-phase region for very many materials well obeys to two semiempirical rules:

- **this boundary is always strongly convex figure which is totally confined within typical triangle (see for details [9])**

- **It obeys so-called semiempirical "rule of rectilinear diameter" of Calliete-Matthias.**

Three theoretically predicted phase boundaries are compared at ρ - T plane (**Fig.3**).
All three EOS expose significant discrepancy in their predictions. It is necessary to discriminate all these very different predictions. In our opinion the zero-pressure isobar, extrapolated in present paper, just can make such discrimination. It exposed at **Fig.3**. One can conclude that all three EOS should be improved significantly to reach agreement with this DFT/MD [4] P=0 curve.
It is known [8] that typical ρ - T diagrams for gas-liquid phase boundary surprisingly well obey to very simple analytical fit - so-called Guggenheim formula (1). This approximation have been made in this paper for all three ρ - T diagram exposed at **Fig.3**. Agreement proved to be surprisingly good for all three tested theoretical EOS (**Fig.3**).

$$\omega \equiv \frac{\rho - \rho_c}{\rho_c} \approx \pm B\theta^\beta + C\theta \; \left(\theta \equiv \frac{T_c - T}{T_c}\right) \; (1)$$
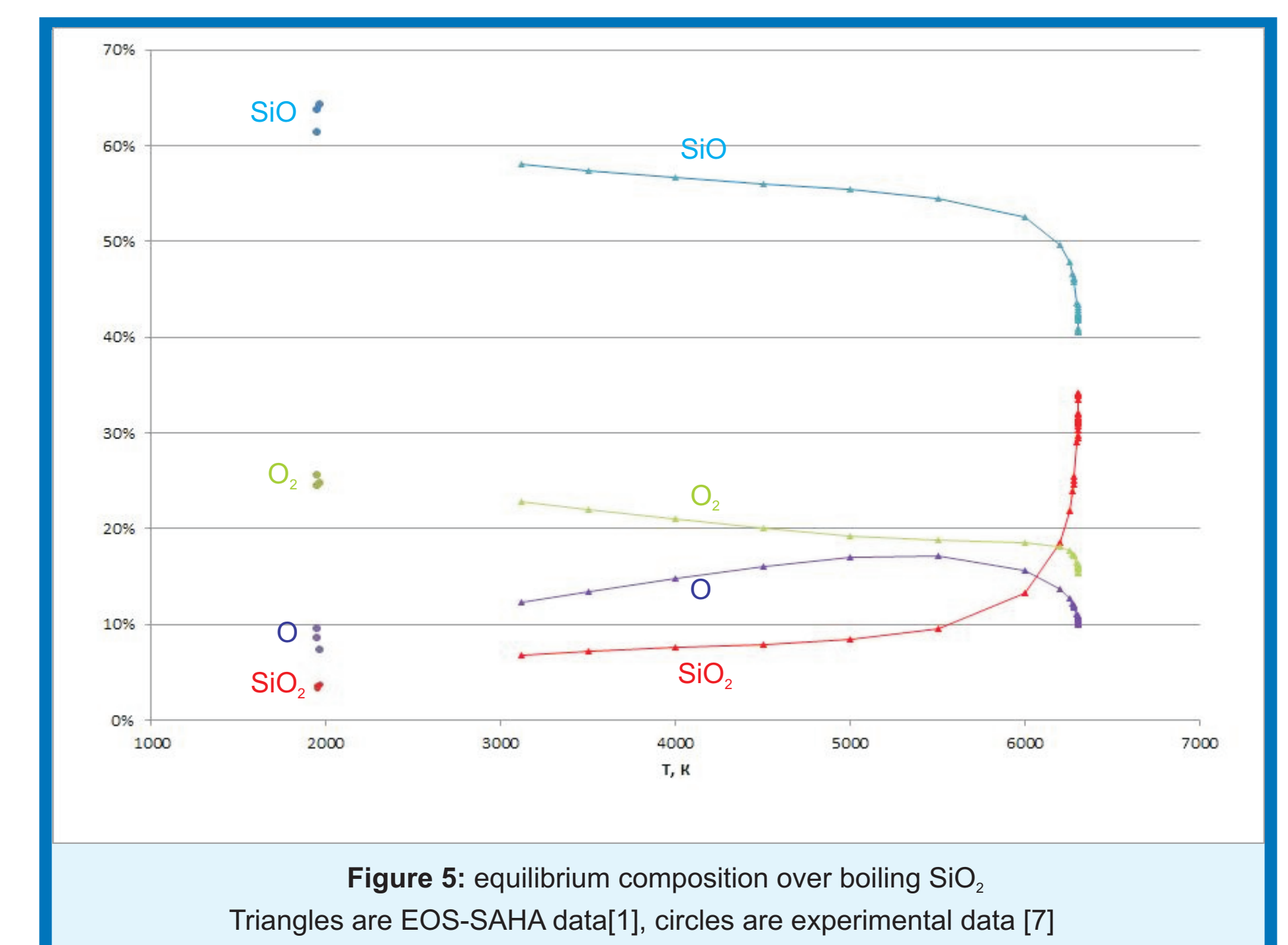

Figure 5: equilibrium composition over boiling SiO$_2$
Triangles are EOS-SAHA data[1], circles are experimental data [7]

The 4th EMMI workshop on plasma Physics with Intense Heavy Ion and Laser Beams.

1. Iosilevskiy I., Gryaznov V., Yakub E., Ronchi C., Fortov V. Contrib. Plasma Phys. V.43, 316 (2003)
2. Ronchi C., Iosilevskiy I., Yakub E., "Equation of State of Uranium Dioxide" / Springer, Berlin, 2004, 366 pp.
9. Iosilevskiy I., Gryaznov V., J. Nuclear Materials, V.344, 30, (2005), Uranium Critical Point Location Problem

3. Faik S., Tauschwitz An., Maruhn J., Iosilevskiy I., "Dynamics of metastable states in ion-beam irradiated foils", EMMI workshop "Particle dynamics under extreme matter conditions" Speyer, Germany, September 2010; see also: Faik S. et al. contribution at this conference.
4. Karki B., Bhattarai D., Stixrude L., Phys. Rev.B V.76, 104205 (2007)
5. Guissani Y. and Guillot B,. J. Chem. Phys.V.104, 7633(1996)

6. Gurvich L.V., Veits I.V., Medvedev V.A. "Thermodynamic properties of individual substances",M.: Nauka 1982
7. Kazenas E.K., Tsvetkov Yu.V. "Thermodynamics of evaporation of oxides", M.: LKI Pub. 2008 (in Russ.)
8. Filippov L., High Temp. (TVT), V. 22, 679 (1984); ibid, V. 25, 1087 (1987)

EMMI
FAIR