

Non-Congruent Phase Coexistence in Strongly Coupled Chemically Reactive Plasmas

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Received 8 May 2003, revised 7 July 2003.

Key words Non-congruent phase transitions, chemically reactive plasmas, ionic liquid.

PACS 51.30.+i; 52.25.Ub; 52.25.Kn; 82.60; 82.60.Fa; 82.60.Lf; 82.60.Hc; 96.30.-t; 96.30.Kf; 96.30.Mh; 96.35.Mz

1 Introduction

Phase equilibrium in chemically reactive non-ideal plasmas of two or more chemical elements differs fundamentally from the case of “ordinary” substances with fixed stoichiometry. Phase transitions in high-temperature chemically reactive mixtures, including those in uranium-bearing compounds are typical for many nuclear energy devices both contemporary [1] and perspective [2, 3]. The basic feature of such two-phase systems is their non-congruency i.e. their ability to vary stoichiometries of coexisting phases without violation of the bulk stoichiometry. The non-congruency changes significantly the properties of all phase transitions in such systems, namely: (A) - The significant impact of the *phase transformation dynamics*, i.e. of the strong dependence of the phase transition parameters on the rapidity of the transition emerge. This dependence is of primary importance in the interpretation of experiments with surface evaporation of condensed samples under the conditions of heating by powerful laser or by the electron-beam energy deposition. The strong competition between diffusion and thermal conductivity processes determines the parameters of such non-congruent evaporation; (B) - The *phase transition thermodynamics* becomes more complicated, the essential changes include the topology of all two-phase boundaries (in the space of individual phases), as well as properties and even nature of the singular points (gas-liquid critical and triple points first of all). One of the most remarkable consequences of the non-congruency is the change of the general form of two-phase boundary in the pressure-temperature plane (see Fig.1 below). It should be stressed also essentially non-monotonic behavior with temperature and significant increase (up to several times) of the entropy change in true non-congruent evaporation in UO_2 [1, 4, 5, 7] in contrast to the widely accepted recommendations [8] and our calculation results in mono-molecular approach.

2 Non-congruent phase transitions in the uranium-oxygen system

The development of a new high-temperature equation of state (EOS) of the uranium-oxygen system (U–O system) was the main point of our multi-annual theoretical study [1, 4, 5]. It is known as a system where the large-scale non-congruency effects are experimentally observed. From the technological viewpoint, the physics of phase transformations of uranium oxides ($\text{UO}_{2\pm x}$) is of primary importance in calculations of the behavior of nuclear reactors during hypothetical severe accidents [1], where temperatures of thousands of Kelvins and pressure peaks of several kilobars may be expected, conditions under which the molten reactor core undergoes the rapid disassembly.

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Despite the practice importance of U-bearing systems and multi-annual theoretical efforts, including sophisticated approaches based on “significant structure theory” [6], the true non-congruent nature of their evaporation has had no adequate thermodynamic description during a long time. In this work we present a new model of non-congruent evaporation in U–O system. The basic point of the model is the attempt to describe both coexisting fluid phases (liquid and vapor) in a uniform manner, as equilibrium multi-component strongly interacting (non-ideal) mixtures of atoms, molecules, molecular and atomic ions, and electrons as well. This formalism is commonly referred to as a “chemical picture” (see e.g. [3]). Chemical reactions including ionization and the parameters of phase equilibrium have been calculated self-consistently by taking into account all non-ideality corrections which are significant. Essential Coulomb corrections have been described within modified “mean spherical approximation” (MSA). Intensive short-range repulsion and attraction were taken into account using a modified version of thermodynamic perturbation theory (TPT). Details of the non-ideality corrections adopted are described elsewhere [1, 4, 5, 7].

3 Calibration of the model using new computational algorithms

As a first step the whole set of inter-particle interaction parameters has been estimated theoretically [1, 4]. Then the EOS was additionally ‘calibrated’ using known thermodynamic properties of liquid UO_2 at the melting point, $T_m = 3120$ K. Finally the fluid model (common for liquid and vapor phases) has been applied for self-consistent calculations of non-congruent phase coexistence within the range of temperature and pressure ($T \leq 10 \div 20$ kK, $P \leq 1 \div 2$ GPa) including the vicinity of the new critical point [1, 4, 5]. We applied directly the adequate conditions of non-congruent phase coexistence: the exact equality of chemical potentials of *all neutral species* in both phases, the conditions, which have been actually violated in all previous studies [6].

The adequate numerical algorithms and an effective numerical code “SAHA-VI” (based on the “SAHA” code-line, which was successfully applied during a long time for thermodynamic support to many investigations of perspective nuclear devices [2, 3]) have been developed to implement this calculation scheme for strongly non-ideal multi-component mixture with simultaneous chemical, ionization and non-congruent phase equilibrium. The pressure-temperature relation for non-congruent evaporation in U–O system is shown in Figure 1 as a typical result of these calculations (see also [1, 4, 5]). The present calculations give the following parameters of non-congruent critical point (NCP) (note that $(\partial P / \partial V)_T \neq 0$ in NCP (!)):

$$T_C \approx 10013 \text{ K}, \quad P_C \approx 878 \text{ MPa}, \quad \rho_C \approx 2.51 \text{ gcm}^{-3}, \quad S_C \approx 1.84 \text{ J/g}\cdot\text{K}, \quad \Gamma_D \equiv e^2/kTr_D \approx 12, \\ C_P \approx 1.85 \text{ J/g}\cdot\text{K}, \quad (\beta_T)_C \equiv [\rho^{-1}(\partial \rho / \partial P)_T]_C \approx 1.2\text{e-}04 \text{ bar}^{-1}, \quad (\alpha_P)_C \equiv (\rho^{-1}(\partial \rho / \partial T)_P)_C \approx 5.8\text{e-}04 \text{ K}^{-1}$$

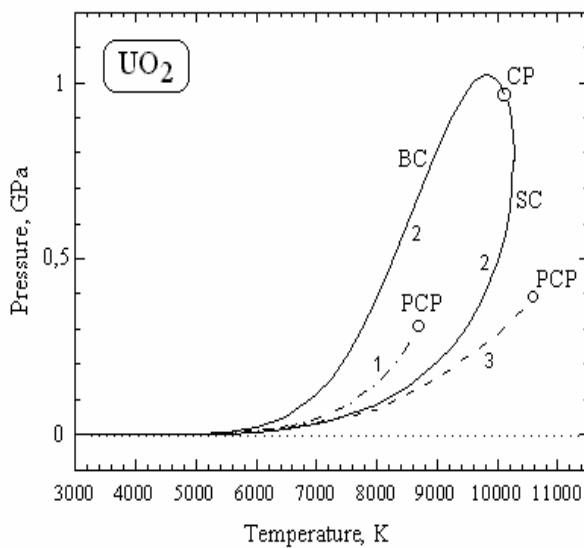


Fig.1. Pressure-temperature diagram for non-congruent evaporation in U–O system at $\text{O/U} = 2.0$ [1, 5]. *Notations:* 1,2 – Results of present theory: 1 – Forcedly congruent phase equilibrium (standard “double tangent” construction) with its pseudo-critical point (PCP) $\{(\partial P / \partial V)_T = 0; (\partial^2 P / \partial V^2)_T = 0\}$; 2-2 – Boundaries of two-phase region of non-congruent evaporation in U–O system with two regimes of phase coexistence corresponding to the *boiling* (BC) and *saturation* (SC) conditions; CP – True critical point of predicted non-congruent evaporation; 3 – Gas-liquid coexistence curve with its pseudo-critical point (PCP) calculated within the “best case” EOS of UO_{2+x} (Fischer-1992 [6]).

4 Plasma aspects of the phase transitions problem in U–O system

The non-congruent phase transitions in chemically reactive U–O system have many features typical for Coulomb systems. Stoichiometric solid $\text{UO}_{2.0}$ is known as predominantly ionic ($\text{U}^{4+} + \text{O}^{2-}$) crystal. In this work we have applied a new version of the ionic model for the non-stoichiometric $\text{UO}_{2\pm x}$ solid [9]. As for the structure of non-stoichiometric liquid $\text{UO}_{2\pm x}$, it seems more complicated and is actually unknown. The relatively small volume change at melting ($< 10\%$) suggests that the ionic bonding is at least partially preserved when UO_2 melts [10]. In this view two extended versions of ionic model have been investigated as candidates for possible representation of liquid $\text{UO}_{(2\pm x)}$. Within the first one [I] the liquid urania has been described [7] as a highly ionic mixture of U and O ions (U^{5+} , U^{4+} , U^{3+} etc; O^{2-} , O^-). The second one [M] considers the liquid $\text{UO}_{2\pm x}$ [5] as a mixture, containing both charged and neutral *molecules* where the UO_n and $\text{UO}_n^{(+,-)}$ ($n=1,2,3$ etc) are dominating species. The ionization equilibrium in ionic model [I] was provided by electronic exchange between species. In the molecular-ionic model [M] the liquid urania was considered as an equilibrium mixture of uranium-bearing *clusters* with the free electronic and oxygen exchange. In both the cases the liquid urania was treated as a strongly coupled Coulomb system (SCCS). At the same time the degree of Coulomb non-ideality is significantly different in both the models of boiling UO_2 . In ionic model [I] the formal Debye non-ideality parameter $\Gamma_D \equiv e^2/kT r_D$ is very high. It decreases from $\Gamma_D \approx 10^3$ at melting point ($T = 3120$ K) to $\Gamma_D \approx 200$ at $T = 7000$ K [7]. The strong Coulomb corrections dominate in the non-ideality effects under these conditions. In molecular model [M] non-ideality parameter decreases from $\Gamma_D \approx 60$ at melting point (3120 K) to $\Gamma_D \approx 10$ at critical point ($T = 10013$ K) [1, 5].

It should be noted that both types of ionic models produce *strikingly similar* results on macroscopic thermodynamic level if both models are ‘calibrated’ at the $T_m = 3120$ K and then extrapolated to higher temperatures. Moreover, besides the description of liquid $\text{UO}_{2\pm x}$ itself, both the ionic models (I and M) have been successfully used for calculation of the non-congruent gas-liquid coexistence. It should be noted that such calculation could be realized even in the case of highly ionic representation of liquid $\text{UO}_{2\pm x}$ (model I) when liquid and vapor compositions have *no common species*: (U^{5+} , U^{4+} , U^{3+} , O^{2-} , O^- in liquid vs. UO_n and $\text{UO}_n^{(+,-)}$ ($n=1,2,3$ etc) in vapor). The point is in adequate definition of chemical potentials $\{\mu_i\}$ for all species, leading to the implicit definition of the chemical potential of electron, μ_e . The latter is the key value for definition of basic pair of chemical potentials (say: μ_U and μ_O) in both coexisting phases. In turn, the equations for these basic chemical potentials are the key points in the non-congruent equilibrium calculations.

It should be emphasized also that the values of chemical potentials of charged species are not the values to be equated in both coexisting phases [11]. It should be done for *electrochemical* potentials. The inter-phase difference in (local) chemical potentials, μ_i , referred to the charge number of *i*-specie, Z_i , is the same for all charged species. This reduced deviation introduces a new important thermo-electrophysical parameter of the inter-phase boundary in Coulomb systems – its electrostatic potential drop, $\Delta\phi(T)$ [11]

$$e\Delta\phi(T) = \{\mu_e^* - \mu_e^{**}\} = \{\mu_{\text{U}(+)}^{**} - \mu_{\text{U}(+)}^*\} = \{\mu_{\text{O}(-)}^* - \mu_{\text{O}(-)}^{**}\} = \{\mu_{\text{UO3}(-)}^* - \mu_{\text{UO3}(-)}^{**}\} = (1/4)\{\mu_{\text{U}(4+)}^{**} - \mu_{\text{U}(4+)}^*\}$$

The value of this electrostatic potential drop, $\Delta\phi(T)$, at non-congruent vaporization in U–O system correlates with other thermodynamic parameters of coexisting phases. The measured value of $\Delta\phi(T)$ could provide important additional information about non-congruency features in U–O system, as well as in all other plasma-like systems with phase transitions (see below). In both presently investigated ionic models (I and M) electrostatic potential of non-congruent liquid-gas phase boundary of boiling UO_2 is *positive*. It proved to be almost constant in highly ionic model (I): $\Delta\phi_{\text{L-G}}(T) \equiv \phi_{\text{L}} - \phi_{\text{G}} \approx 0.3$ V ($T = 3120 \div 7000$ K), whilst it is slowly decreasing function of temperature in calculation of complete phase boundary within the molecular model (M): $\Delta\phi_{\text{L-G}}(T) \approx 0.77$ V ($T = 3120$ K); ≈ 0.54 V (7000 K); ≈ 0.34 V (9000 K). In accordance with the prediction [11] $\Delta\phi_{\text{G-L}}(T) \rightarrow 0$ when $T \rightarrow T_{cr} \approx 10^4$ K.

5 Non-congruency in U-O system – is it an exclusion or a general rule?

The present study of non-congruent phase equilibrium in U–O system indicates that this feature is not as infrequent at high temperatures as it was seen before. The expected examples of non-congruent phase transitions are inter alia [12]:

- Hypothetical plasma phase transition (PPT) in H/He mixture in interiors of Jupiter, Saturn and brown dwarfs.
- Evaporation in alkali-halides (NaCl etc.)
- Evaporation in alkali alloys (K + Na etc.)

The conclusion drawn from above results could be formulated as the following statement:

- In plasmas containing two or more chemical species the non-congruency of phase coexistence is a general rule. Congruent phase transitions arise as exclusions only.

If the non-congruent phase equilibrium appears, the widely used approximations like of “additive” specific volumes and enthalpies can not, in principle, describe the phase coexistence correctly because this approximation does not change the conventional topology of phase boundaries in mixtures as compared with the “single substance”. Within such approach P – T saturation curve is still the conventional one-parametric relation and the critical point (CP) is still the CP of standard type, where the conditions: $(\partial P/\partial V)_T = 0$, $(\partial^2 P/\partial V^2)_T = 0$, $(\partial^3 P/\partial V^3)_T \leq 0$ are satisfied;

On the contrary, in non-congruent PPT in H/He mixture it could be expected (see Figure 2):

- (1) P – T saturation curve must circumscribe a non-conventional two-dimensional domain;
- (2) CP of non-congruent PPT should be a non-standard type critical point, where the conditions: $(\partial P/\partial V)_T \neq 0$, $(\partial^2 P/\partial V^2)_T \neq 0$, $(\text{He}/\text{H})_{1\text{st phase}} = (\text{He}/\text{H})_{2\text{nd phase}}$, and $\|\partial n_i/\partial \mu_k\| = 0$ are fulfilled.

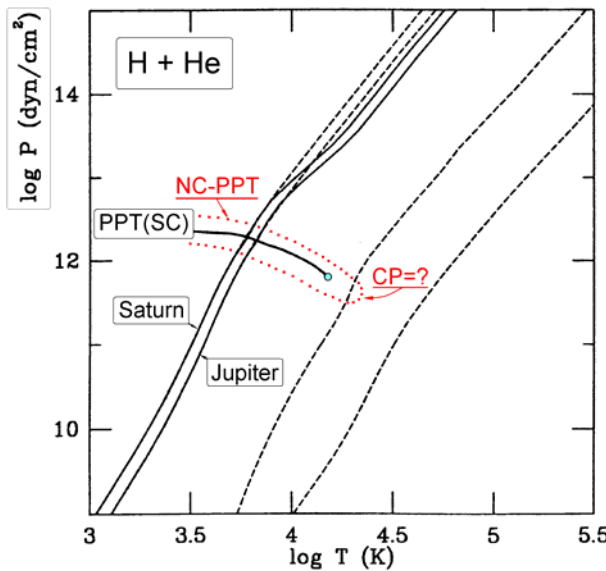


Fig.2 Presently predicted (dotted line) qualitative form of hypothetical two-phase boundary of non-congruent plasma phase transition (NC-PPT) in {H/He} mixture corresponding to the interiors of Jupiter and Saturn (position of true critical point of NC-PPT is unknown). Predicted form is compared with original P – T coexistence curve of PPT in hydrogen predicted by Saumon & Chabrier (*heavy solid line*) and its conventional critical point (open circle). *Solid lines* – adiabats computed in [13] from EOS of Saumon & Chabrier with PPT, *dashed lines* – the same from their interpolated hydrogen EOS. (Figure from [13] with presently added dotted line).

It should be emphasized that present prediction, strictly speaking, corresponds to simplified situation, i.e. to the form of boundary of the two-phase region in H/He mixture of fixed stoichiometry. The problem, how this hypothetical non-congruency of plasma phase transition could manifest itself in real situations, i.e. the problem of influence of the PPT on the evolution of Jupiter, Saturn and brown dwarfs [14], is more complicated one and should be re-examined separately. Two points could be important in such re-examination. First, more extensive parameters of expected region of hypothetical non-congruent phase decomposition, and therefore, more earlier age of brown dwarfs when they reach the phase decomposition boundary (see for example, Fig. 1(above) and Fig. 34 in [15]). Second, noticeably higher value of expected entropy change in non-congruent phase decomposition in comparison with the entropy change in ordinary, forcedly congruent transition.

Acknowledgements.

Present work was supported by Grants: INTAS-93-66, “Universities of Russia” № 2550, RFBR-96-02-18832a, CRDF № MO-0110, and by RAS Scientific Program “Physics and chemistry of matter under extreme conditions”.

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