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The critical parameters and congruent vapor-liquid diagram of ten metallic alkali and alkaline earth fluids and one H-bond organic (methanol)

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ABSTRACT

We report the first reliable prediction of the critical point (CP) $(T_c,\ P_c,\ \rho_c)$ and two separate branches of the *coexistence curve* (CXC) for 10 alkali and alkaline earth fluids metals as well as for methanol. It is based on the recently proposed methodology of the *congruent vapor-liquid* (CVL) – diagram following from the developed earlier model of the fluctuational thermodynamics (FT). Both CXC-branches are predicted by the quite different (i.e. asymmetric and non-“symmetrized” artificially) FT-correlations. They are completely conformed in the asymptotic CP-region not only to the non-classical (with the exponent $\beta \approx 1/3$) projection of CXC on the (T,ρ)-plane but also to the well-known classical Clausius-Clapeyron approximation of the vapor-pressure curve in the (P,T)-plane. The respective interrelations between two *phase-dependent* factors of thermodynamic similarity introduced, originally, by Riedel (Ri) and Trouton (Tr) in the classical principle of corresponding states (PCS) are estimated without any fitting. We show that neither any analytic expansion (it fails near CP) nor the known non-analytic Wegner's expansion (it diverges far from CP) are necessary *to predict* with the reasonable accuracy the entire range of CXC including its CP. The only input data for this aim are the standard low-temperature measurements of one-phase liquid performed at atmospheric pressure. The reasons of violation of the classical PCS for the metallic and ionic fluids have been analyzed. Despite the widespread belief on the contrary, FT-methodology *predicts* the striking similarity of all studied fluid metals revealed by their CVL-diagrams.

1. Introduction

At the search for actual CP (critical point)-location one should take into account three factors:

1) the thermodynamic definition and/or experimental identification [1];
2) the possible experimental discrepancies in its estimate (going far beyond the claimed uncertainties of different measurements);
3) the unavoidable specific feature of any extrapolation scheme or theoretical CP-model is the necessity to conform its *predicted* position to the measurements of supercritical and/or subcritical data obtained away from CP.

The comprehensive analysis of first factor represented, for example, in Ref. [1] leads to the conclusion that the classical Andrews – van der Waals' CP-definition by two zero-derivatives accepted by the van der Waals, Maxwell and Gibbs (WMG)-model is the sign of mean-field (*mf*) criticality. Nevertheless, many authors still use it in the framework of a *unified* EOS (common for both fluid *f*-phases (vapor or gas (*g*) and liquid (*l*)). The alternative fluctuation flattening of the coexistence curve (CXC) in the (T,ρ)-plane has been introduced in terms of the non-classical scaling theory and its main irrational exponent $\beta \approx 0.326$ [2]. The reason of such discrepancy is recognizable because the Ising-based *Ib*-model in opposite to the *mf*-model does not predict the CP-location itself. More exactly, the scaling phenomenology exploits the precise measurements of CP-parameters $(P_c,\ T_c,\ \rho_c)$ as *input data* to study the peculiarities of asymptotic criticality by power laws.

FT (fluctuational thermodynamics) model used in the present work and its GFA (global fluid asymmetry) principle [3–6] *rejects a concept of unified EOS at least in the region of criticality*. This *mf*-concept has been realized by the classical notions of *binodal*,

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spinodal and by the *common set of coefficients* fitted simultaneously to the one-phase properties of both fluid *f*-phases (hence *f* denotes below *g* or *l*). It was shown earlier [3,4] that the reasonable for a variety of practical tasks *predictive accuracy* of the one-phase thermophysical properties can be achieved by the cubic FT-EOS with the well-established set of *T*-dependent coefficients constructed separately for both *f*-phases. It is necessary for this aim to know (from experiment or theory) only the entire CXC-information. Its input segment for CVL-diagram is presumably located between the melting temperature T_m and the normal boiling temperature $T_b(P_0)$. Let us note that the experimental determination of latter at atmospheric pressure P_0 is not a trivial task at very high temperatures.

GFA-principle distinguishes [5,6] between the onsets of *condensation* $P_l(T)$ in a saturated vapor and *vaporization* $P_v(T)$ in a saturated liquid. This (*v,l*)-*hysteresis* should be, strictly speaking, observable by experimenter at the same temperature of (*v,l*)-transition *in the real finite-volume f-phases*. Respectively, the distinction between two measurable *bubble* $T_v(P)$ and *dew* $T_l(P)$ temperatures at the same subcritical pressure can be also observable. The described *f*-distinctions (resembling those in a dew-bubble curve for binary mixture) have to disappear, in accordance with FT-model, only in the implied by WMG-model *thermodynamic limit of* two *infinite* and *homogeneous Gibbsian*, coexistent *f*-phases. The GFA-principle based on the FT-model's notion of *disorder parameter* $(s_g - s_l)/2k$ leads just to the thermodynamic (*v,l*)-hysteresis as it is illustrated by Fig. 1. One may note that the fundamental thermodynamic distinction between the classical WMG- and non-classical Ib-models exists in both variants of the (*s,ρ*)-projection.

The adepts of more traditional viewpoint on the phenomena of a first-order (*v,l*)-transition may recognize the effectually used below special $T_b^{FT}(P_0)$ -point introduced by FT-model only as a subsidiary one. It was revealed by FT-model in addition to the standard experimental (reported usually in Handbooks) $T_b^{\exp}(P_0)$ -point as the important auxiliary "tool" of FT-predictive procedure. However, it should be emphasized that the demonstrated recently [7] *excellent and universal for any compounds* accuracy of CP-predictions cannot be achieved without this key component of FT-methodology [5,6]. Besides, the revealed below steady distinction between the *neutral* (including a variety of polar ones) and *ionic* (molten salts, liquid metals) fluids consists *in the change of sign for the difference*: $T_b^{\exp} - T_b^{FT}$. It is positive for formers and negative for latters (studied mainly in the present work). The universal predictive capability of FT-methodology was described in full detail earlier [3–7]. Section 2 contains only its main steps for the convenience of reader. We will use below the specific term of the *congruent vapor-liquid (CVL -) diagram* to distinct it from a variety of PCS (principle of corresponding states)-methodologies [8,9] developed to describe the standard VLE-diagram. As a rule, any predictive PCS-strategy is developed only for a single CP-parameter (i.e., T_c and/or P_c, etc.) but not for their thermodynamic CP-complex at the top of CXC.

We have applied here (Section 3) the discussed FT-methodology to the set of 5 alkali metals (Li, Na, K, Rb, Cs), 5 alkaline earth metals (Be, Mg, Ca, Sr, Ba) and 1 H-bond organic (CH_3OH) chosen for comparison. Indeed, it was interesting (Sections 3,4) to confront our FT-results with a number of recent works (see Refs. [10–12] and references therein) in which the same fluids have been studied by the so-called ZL (Zeno-line) methodology. As a matter of fact, the known concept of the pseudo-ideal-gas ($Z = 1$) geometric regularities was applied by ZL-methodology [10–12] together with the postulated singularity of CXC-diameter developed in the complete scaling Ib-phenomenology [13,14]. Such compiled ZL/Ib-approach realizes just the concept of unified EOS to obtain CXC-description as a "symmetrized" (symbolized by ± signs) combination of the binodal's *f*-branches.

The comparison of FT- and ZL-methodologies seems to be informative in the general context of CP-predictions. Another reason for it is the revealed recently [7] close location of the predictive *FT-hyperbolae* in the $(T_c/T_B,\ \rho_c/\rho_B)$ -plane with the certain

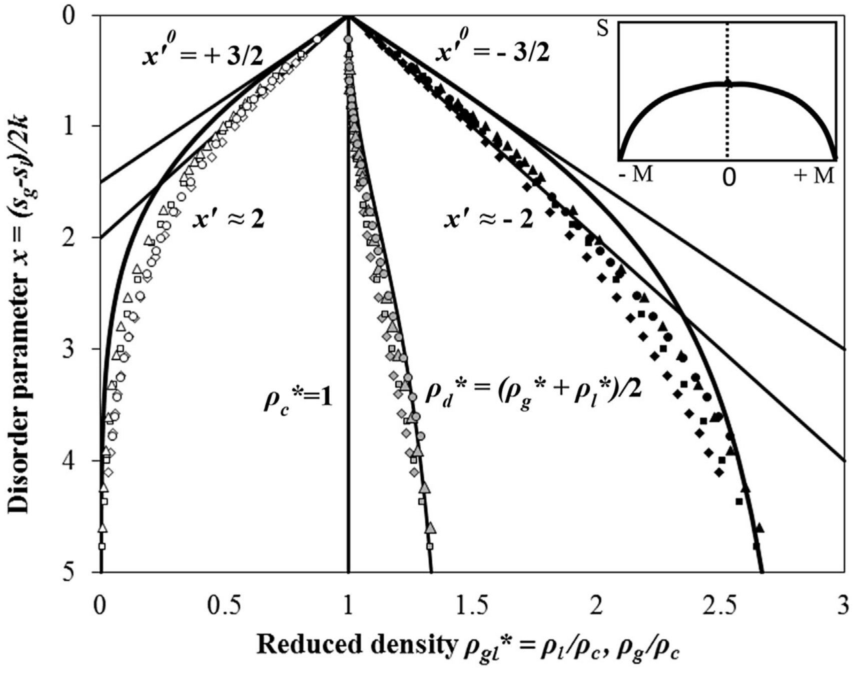

Fig. 1. Asymptotic universal WMG-symmetry [3–5] of the entropy discontinuities (termed the FT-*disorder parameters*) in classical CXC-slopes: $x'^0 \equiv \rho_c (s_g - s_l)^{\ 0} / 2k\ \rho_{g,l}$ (*mf*-model); and non-classical CXC-slopes $x' \equiv \rho_c (s_g - s_l)/2k\rho_{g,l}$ (real fluids: Ar – triangles, C_2H_6 – squares, CO_2 – diamonds, H_2O – circles). The underlying failure of the asymptotic isomorphism between real fluids and lattice-gas model postulated by the scaling theory [2] becomes evident from the comparison with the Inset where two CXC-branches of Ib-universality are represented in the plane entropy (S)-magnetization (±*M*).