ТЕПЛОФІЗИКА ДИСПЕРСНИХ СИСТЕМ

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Elongate coexistence curve and its curvilinear diameter as factors of global fluid asymmetry

Some inconsistencies of the conventional predictive methodologies applied in the region of vapor-liquid VLE-coexistence and its criticality are considered. As a rule, they are related to the semi-empirical concept of "rectilinear diameter" accepted in the temperature-density plane. The often curved, in practice, "rectilinear diameter" of coexistence curve (CXC) is discussable in both alternative descriptions of criticality: 1) by the Ising-based (Ib-) complete scaling phenomenology and 2) by the classical van der Waals-Maxwell-Gibbs-based (Wb-) phenomenology of VLE-transition. The latter has been essentially modified by the model of fluctuational thermodynamics (FT). The new transformation of CXC-representation based on the measurable equilibrium data obtained far away from criticality is proposed in the present work. It leads to the well-established location of critical point (CP) which corresponds to the intersection between the elongate CXC depicted in the compressibility factor-density plane and its strongly curvilinear here diameter. The universality of global fluid asymmetry (GFA)-principle introduced earlier by FT-model becomes apparent in the whole temperature range of VLE-transition. The developed predictive CP-methodology can be especially useful for the set of substances in which the direct experiment on criticality is hardly realizable.

Introduction. Two types of recent works on criticality and their rather contro-versial results make the object of this article to be stimulated and, simultaneously, challenging. The discussion [1]of the complete scaling phenomenology [2,3] per-formed in terms of a discrete continuum (formed by the decorated lattice of a locally-compressible cell-gas-model) poses the important question of the non-universal pecu-liarities arising in the conventional asymptotic Ib-criticality. Since the known Yang-Yang's ratio [4] is incorporated in this methodology, it has been revealed [1] that the certain interrelation between the fluctuating primary and secondary cell-volumes can leads, in principle, to the negative magnitude of above ratio. Its rather unwonted con-sequence is the asymptotic shift of the extrapolated to CP CXC-diameter from the rectilinear extension to the side of higher liquid-like densities of *l*-branch $\rho_l^* = \rho_l(T) / \rho_c$. This trend is opposite to the typical asymptotic behavior of CXC-diameter originated by the revised scaling phenomenology [5].In accordance with it the half-sum of saturated densities must curve up just to lower densities of *g*-branch $\rho_g^* = \rho_g(T) / \rho_c$ due to the dominance of $(1-\alpha)$-singularity [3]. The most unusual feature is here the same trend observable for real fluids. It was revealed that the de-

scribed "asymptotic bifurcation of curvature" in CXC-diameter is also observed [1] in the real, quite similar from the thermodynamic viewpoint [6, 7], even with the equal molecular weight ($M = 44$ g/mol) fluids such as carbon dioxide CO_2 and propane C_3H_8. As a result, it is naturally to suppose that just the non-universal pressure mixing of the complete scaling procedure leads to the so subtle changes in the underlying molecular structure of compounds. The main claimed here consequences are the dominance of 2β-singularity [1-3] over its concurrent $(1-\alpha)$-type (following from the similar decorated lattices [5]) and, at the same time, the invariable symmetric Ib-shape adopted for the heterophase order parameter: $\rho_l^* - \rho_g^* = 2B_0\overline{T}^\beta\left(\overline{T} = 1 - T/T_c\right)$ by all variants of scaling EOS.

The predictive description of an entire CXC-shape in the (T,ρ)-plane and, even, the prediction of its actual topmost part i.e. CP-parameters in terms of the reduced critical Boyle's variables: $\rho_{cB}^* = \rho_c/\rho_B$, $T_{cB}^* = T_c/T_B$; $Z_{cB} = P_c/\left(\rho_B k_B T_B\right) =$ $= Z_c\rho_{cB}^* T_{cB}^*$ are supposedby the widely discussable long ago and recently phenomenology of Zeno-line [6-10]. It is a combination of two conditions. The first is the Boyle's condition adopted at the negligible densities $Z_B = 1$ (where the second virial coefficient tends to zero: $B(T_B) = 0$).It is applied to the original vdW-EOS with only two constant coefficients a_0, b_0 and one T-dependent $B_{vdW}(T)$-coefficient:

$$Z_{vdW} - 1 = \frac{b_0\rho}{1 - b_0\rho} - \frac{a_0\rho}{k_B T} \qquad (1)$$

The second is the Cailletet-Matthias' approximate rule of rectilinear diameter:

$$\rho_d^* - 1 = D\overline{T} \qquad (2)$$

which is fulfilled in the *mf* (mean-field)-CP $\left(T_c^0, \rho_c^0, P_c^0; Z_c^0 = 3/8\right)$ but not, a priori, in the actual $CP(T_c, \rho_c, P_c; Z_c)$.Indeed, the former condition leads to the known Batschinski's rule of a straight *vdW*-line existing in the (T, ρ)-plane:

$$\rho_{Z=1} = \frac{1}{b_0}\left(1 - \frac{b_0 k_B T}{a_0}\right) \equiv \rho_B\left(1 - \frac{T}{T_B}\right) \qquad (3)$$

while the latter condition provides, only presumably, its intersection with the rectilinear diameter $\rho_d(T)$ just at the asymptotic Boyle's point $T_B(\rho_{Z=1} \to 0)$.

The adepts of Zeno-line have assumed additionally [6-10] that the oppositeasymptotic point of "cold" density $\rho_B(T \to 0)$ and its respective excluded vdW-volume: $b_0 = 1/\rho_B$ from Eq.(3) can be also expressed in terms of the virial coefficients. In accordance with [6] they should be calculated at the "hot" Boyle's point:

$$B(T_B) = 0 \quad (a) \qquad \rho_{Z=1} = \frac{T_B}{C(T_B)}\left[\frac{dB(T)}{dT}\right]_{T_B}\left(1 - \frac{T}{T_B}\right) \quad (b) \qquad (4)$$

Such assumption is not in accordance with the *vdW*-EOS (1) and with its direct consequence Eq.(3) where the third virial coefficient C_{vdW} cannot be T-dependent. Besides, Eq.(4b) is apparently unverifiable, in practice, for real fluids. One should

know for this aim the explicit EOS of the virtual Lennard-Jones' (*LJ*-) fluid, for example.Simultaneously, its theoretical virial coefficients $B(T)$, $C(T)$ determined for the infinite-range pair potential $\varphi_{LJ}\left(r \to \infty; \sigma_0, \varepsilon_0\right)$ should be known with the substance-dependent molecular parameters. Authors [8] have used (to construct Zeno-line) the empirical unified *LJ*-EOS [11] developed for the Helmholtz's free energy (so-called, fundamental EOS). It accumulates the massive volume of simulated *LJ*-data including those [12] obtained in the range of VLE-transition. The standard extrapolation treatment of the respective *LJ*-CXC simulated far away from the asymptotic criticality in terms of reduced variables: $\rho_{LJ}^* = \rho \sigma_0^3$; $T_{LJ}^* = k_B T / \varepsilon_0$; $P_{LJ}^* = P \sigma_0^3 / \varepsilon_0$ poses the general task of CP-uncertainty. Thus, one needs the self-consistent determination of the *LJ*-CP's location.

Despite widespread belief of the contrary its solution by the long-range extrapolation (proposed on the ad hoc basis [13] in the framework of empirical "scaling-type" T_{LJ}^*-functions chosen arbitrarily and separatelyfor $\rho_g^*\left(T_{LJ}^*\right)$, $\rho_l^*\left(T_{LJ}^*\right)$ and $P_\sigma^*\left(T_{LJ}^*\right)$ [12]) cannot be considered as the convincing sign, namely, of the universal *Ib*-type of *LJ*-criticality. This widespread but questionable conclusion is contrary to such its typical features of *mf*-behavior as the infinite-range potential $\varphi_{LJ}\left(r; \sigma_0, \varepsilon_0\right)$, its two scales of distance and energy (similarly to those b_0, a_0 used in the simplest *vdW*-phenomenology of PCS (principle of corresponding states) [7]) and, at last, the accepted in [11] methodology of unified (i.e. common for both coexisting phases) *LJ*-EOS. As a result, the "best" estimates of *LJ*-critical parameters $T_{cLJ}^* = 1.31$; $\rho_{cLJ}^* = 0.314$; $P_{cLJ}^* = 0.126$; $Z_{cLJ} = 0.3063$ [12] describe, at best, *the LJ*-model itself but not the real fluids with their individual critical PCS-factors of compressibility $Z_c = P_c / \left(\rho_c k_B T_c\right)$.

It is straightforwardly to demonstrate that the usually postulated"medley" of the *Ib*-type's power law for the order parameter$(\beta \approx 0.326)$ with the *mf*'s-rule of a rectilinear diameter of the type that from Eq.(2):

$$\left(\rho_l^* - \rho_g^*\right)^{1/\beta} = C - D T_{LJ}^* \quad \text{(a)} \qquad \left(\rho_l^* + \rho_g^*\right)/2 = A + B T_{LJ}^* \quad \text{(b)} \qquad (5)$$

leads not only to the sought – after critical LJ-parameters of the most popular now GEMC (Gibbs ensemble Monte-Carlo)-simulated CXC [14]:

$$T_{cLJ}^* = C / D \quad \text{(a)} \qquad \rho_{cLJ}^* = A + B T_{cLJ}^* \quad \text{(b)}. \qquad (6)$$

One obtains also the determination of the standardcritical amplitudes [3, 15]:

$$B_0 = C^\beta / 2\rho_{cLJ}^* \quad \text{(a)} \qquad D_1 = -B \, T_{cLJ}^* / \rho_{cLJ}^* \quad \text{(b)} \qquad (7)$$

expressed in terms of the purely adjustable coefficients (A,B,C,D) and/or CP-parameters (?).

Just the similar, supposedly predictive linear correlations of the type that inEq.6(b) have been proposed in two different "geometric" variants [9,10] of Zeno-line construction:

$$\rho_{cB}^* = S(\beta) - T_{cB}^* \quad \text{(a)} \qquad \rho_{cB}^* = 1/2 - T_{cB}^* / 2 \quad \text{(b)} \qquad (8)$$

where $S_{LJ}(0.326) \approx 0.67$ and $S_{vdW}(1/2) \approx 0.63$. The noticable respectivedistinc-tion in the slopes of suchstraight lines makes the empirical predictive Zeno-procedure to be rather inconclusive from our viewpoint. Another undesirable feature of it(shared by the above-discussed treatment of *LJ*-CXC) is the uncertainty adopted by many authors [6, 7, 9, 10, 14] at the usage either Ib-exponent $(\beta \approx 0.326)$ [15] or the *mf*-one: $\beta_0 = 1/2$ in the description of the heterophase order parameter $\rho_l^* - \rho_g^*$.

The complete scaling leads to the system of asymmetric equations (for the simplicity, considered below without the non-analytic Wegner's correction) for the more appropriate homophase order parameters [3] $\overline{\rho}_{l,g} = \rho_{l,g}^* - 1$:

$$\overline{\rho}_{l,g} = \pm B_0 \overline{T}^{\beta} + \rho_d^* - 1 \quad \text{(a)} \qquad \rho_d^* - 1 = D_0 \overline{T}^{1-\alpha} + D_1 \overline{T} + D_2 \overline{T}^{2\beta} \quad \text{(b)} \qquad (9)$$

CXC-asymmetry corresponds presumably to the supposed divergences of $\rho_d^*(\overline{T})$ [2, 5]. One must conclude, some paradoxically, that no asymptotic divergence of the isochoric heat capacity C_v (revealed commonly for all Ib-systems [4]) can be observable for the real fluids (ethane C_2H_6, for example) with the strictly rectilinear experimental [16] CXC-diameter (see below). Two formal reasons of such inconsistency with the asymptotic experiment performed for $C_v(T, \rho_c)$ of C_2H_6 [17] are obvious. These can be either the coincident compensation of $(1-\alpha)$- and 2β-contributions in the CXC-diameter [3] or, even, the reality of *mf*-exponents: $\alpha_0 = 0$, $\beta_0 = 1/2$. Both are, of course, highly modelistic. The non-classical exponent $\beta \approx 1/3$ leads to the PCS-type of CXC-description developed and tested, mainly, by Guggenheim and Riedel only for *l*-branch:

$$\overline{\rho}_l = B\overline{T}^{1/3} + (B-1)\overline{T}. \qquad (10)$$

It was, then, expanded symmetrically but unfoundedly on the *g*-branch [7]:

$$\overline{\rho}_{l,g} = \pm B\overline{T}^{\beta} + (B-1)\overline{T}. \qquad (11)$$

In other words, two main stimuli (experimental and theoretical) of modern *Ib*-pheno-menology [4] leading to the non-classical exponents $\beta \approx 0.326$ and $\alpha \approx 0.11$ are in the certain disagreement due to the "unendorsed" role of rectilinear CXC-diameter.

FT-model develops the alternative approach to the aforementioned problems [18-21] leading to the concept of curvilinear but not singular CXC-diameter. It is based on the crucial assumption of GFA-principle and the resulting rejection from the conventional usage of any unified *EOS*s at the description and/or prediction of CXC. At the same time, the application of FT-model to the global asymmetric description of real fluids has provided the certain reconciliation between the antagonistic, at first sight, results of the Ib- and Wb-phenomenologies in the region of VLE-coexistence and its criticality.One may consider the FT-model described in full detail in [18-21] as an attempt to develop the mesoscopic molecular-based phenomenology for the measurable (not theoretically-idealized) VLE-transition. The alternative definition of equilibria between two finite-volume inhomogeneous and, even, non-gaussian (i.e. locally-heterophase) hases becomes possible in the region of criticality. So only its

main and relevant to the problem of measurable CXC-diameter results are discussed below (Sec.III). They demonstrate, in particular (see TABLEs I,II), the surprising consistency of some FT-predictions with the Ib-results of complete scaling [2,3]. However, *any nonuniversal distinctions implied in the underlying molecular structures of CO_2 and C_3H_8, for example, discussed in [1] have not been revealed by FT-model*. The obvious reason of such discrepancy between two phenomenologies of criticality is the indeed rectilinear, in practice, diameter obtained by the reliable direct experiment [22] for CO_2 and/or C_2H_6 [16] (the latter substance is very similar on the molecular level just to C_3H_8).

I. Thermodynamic nature and molecular-based reasons of asymptotic singularities in real fluids. It was shown unambiguously by FT-model that the exact parametric WMG-solution [18] proposed by Gibbs for the van der Waals-Maxwell's *mf*-model ofVLE-transition leads to the specific *WMG*-type of critical nonanalyticity, which has not been considered by *Ib*-phenomenology. The most striking feature of it is represented by Fig. 1 and was revealed by introduction of the *mf*-scaled (superscript zero) latent heat $x^0 = \left(s_g - s_l\right)^0 / 2k_B$ instead of the usual temperature-deviation $\bar{T} = 1 - T^*$ from *CP*-position. It was termed [19-21] the heterophase *mf*-disorder parameter determined for entropy per particle. Its usage as the field variable instead of standard temperature leads to the discontinuous change (or "jump") of the asymptotic constant slope $x' = dx / d\rho^*$. For comparison, the slope $d\bar{T} / d\rho^*$ tends to zero in the asymmetric *Ib*-variants of the scaling *EOS*. The real heterophase disorder parameter is changeable from its positive value along $x\left(\rho_g^*\right)$-branch to the symmetric constant negative value along $x\left(\rho_l^*\right)$-branch. Such replacement corroborates but in the quite different $\left(x, \rho^*\right)$-plane (!), the underlying asymptotic symmetry of the lattice gas. The latter is usually discussable only in the (T, ρ)-plane. Its known specific consequence follows from Eq.9(a) as the highly-modelistic vertical $\bar{T}$-independent diameter $\rho_d^* = 1$ namely in the plane $\left(\bar{T}, \rho^*\right)$.

It is important to note that the discussed here asymptotic linearity of both branches $x\left(\rho_g^*\right)$ and $x\left(\rho_l^*\right)$ exists for the actual (i.e. measurable by direct experiment) parameter of disorder $x = \left(s_g - s_l\right) / 2k_B$ too. The constraint of equal chemical potential $\mu_g = \mu_l$ leads to its coupling with the latent heat. This is evident from FIG.1 not only for *mf*-model but also for real fluids. Hence, the introduced here constant $\pm dx / d\rho^*$-slope plays apparently the role similar to that of $\pm B_0$-amplitude from Eq.(9a). Just its elimination was used by Widom long ago for the definition of the original scaling variable. Simultaneously, *GFA*-principle [20, 21] points out the possible discontinuity (see below) in the Riedel's *PCS*-parameter of critical slope: $A_c = \left(T_c / P_c\right)\left(dP_\sigma / dT\right)_c$ revealed unambiguously by *FT*-model. Thusthe normalized entropy disorder parameter may be used, in principle, as an alternative asymmetric
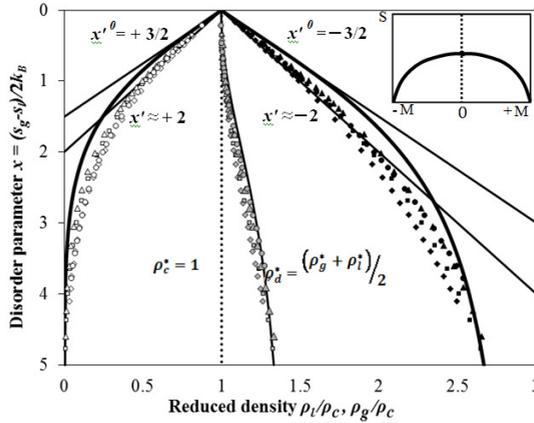
Fig. 1. Asymptotic universal WMG-symmetry [18, 20] of discontinuity in the *mf*-CXC-slopes: $x'^{0} \equiv \rho_c \left(s_g - s_l\right)^{0}/2k_B \rho_{g,l}$ compared with its actual counterpart $x' \equiv \rho_c \left(s_g - s_l\right)/2k_B\rho_{g,l}$ for real fluids: Ar – triangles [23], C_2H_6 – squares [16], CO_2 – diamonds [24], H_2O – circles [26]. The inset illustrates the *principal* Wb-*distinction* from the smooth *CXC*-transition in the *Ib*-models.The latter is observable between two coexisting branches in the plane entropy (S)-magnetization (±M) supposed by the basic Ising (or lattice-gas) model [4] of *Ib*-universality. Curvilinear diameter $\rho_d \left(\rho_l\right)$ is only *asymptotically tangent to the critical isochore* ρ_c from the side of the liquidlike $\left(\rho_l \geq \rho_c\right)$ densities (See also Figs.2-4).

scaling variable instead of original one $\left(\overline{T} / \overline{\rho}^{1/\beta}\right)$ introduced, originally, by *Ib*-phenomenology [4]. One may recognize now that the value of Fig. 1 is, in total and most likely, comparable with the well-known plot of experimental *CXC*-datarepresented long ago by Guggenheim in the $\left(T^{*},\rho^{*}\right)$-plane. It was an obvious sign of non-classical exponent $\beta \approx 1/3$ (needed instead of *mf*-one $\beta_0 = 1/2$) for real fluids [4]. From what has been said above, it follows that *FT*-model [18-21] provides due to its GFA-principle and the respective FT-EOS developed separately for both fluid (*f*)-phases the exactly soluble *Wb*-phenomenological model of *VLE*-transition and of its asymmetric criticality. It goes far beyond the framework of *mf*-model. The non-classical $\beta^{FT} = 1/3$, in particular, can be exactly determined without any appeals to the Ib-models.One of the essential features of *FT*-model is the proposed solution for the long-standing problem on the *explicit hypothetical connection* between the thermodynamic *PCS*-criteria Z_c, A_c of similarity [6,7], from one hand, and their molecular-based effective *PCS*-scales ε_0, σ_0 from another. The latter shave been expressed by *FT*-equations in terms of the reported in Table I new effective *FT/LJ*-parameters ε, σ. These parameters are recommended in the present work for the

common approach to the consistent simulation of the realistic coexisting phases. Indeed, the *FT*-correlation are based exclusively on the respective substance-dependent (i.e. actual) critical data:

$$\varepsilon_{g,l} = k_B T_c \left(1 - Z_c\right) = k_B T_c - P_c / \rho_c, \tag{12}$$

$$\sigma_g^3 = 3\left(A_c - 2\right) / \left[4\pi\left(A_c - 1\right)\rho_c\right] \quad (a) \qquad \sigma_l^3\left(A_c^0 = 4\right) = 1/2\pi\rho_c \quad (b). \tag{13}$$

The some unusual split of the predicted effective diameter σ_f onto the very close but still distinctive values $\sigma_g > \sigma_l$ is related in Eq.(13) to the revealed by FT-model [20, 21] asymptotic difference between the above-mentioned $A_c\left(\rho_g \to \rho_c\right)$- and $A_c^0\left(\rho_l \to \rho_c\right)$-trends of slopes. The recommended *LJ*-parameters for the generalized short-range *FT/LJ*-potential $\varphi_{LJc}\left(r;\varepsilon,\sigma,r_c\right)$ with the third, a priori unspecified para-meter of cutoff radius r_c are represented in Table I, II for the actual *CP*s of several substances.

One may see that the conventional constant values $\varepsilon_o / k_B = 119.8\,\text{K}$, $\sigma_o = 0.3405\,\text{nm}$ of *Ar*, for example, obtained from the second-virial *B(T)*-data atsmall densities [6] seem to be significantly overestimated in comparison with the FT-model's estimates. Besides, in spite of the widespread use of scaling-type Eqs.(5a,b) in the $\left(T^*, \rho^*\right)$-plane [14], another $\left(P^*, T^*\right)$-plane remains purely classical in this extrapolative procedure [13]. The magnitude of critical pressure P_{cLJ}^* and the asymptotic slope of vapor pressure $P_v^*\left(T\right)$ are described, as a rule, by the typical mean-field Eq.(14).One may conclude in this context that the behavior of simulated $P_v^*\left(T_{LJ}^*\right)$- function and its presumable value P_{cLJ}^* could be significantly distorted by the described analysis of the only $\left(T^*, \rho^*\right)$-plane. Indeed, the most usable concomitant form of approximation is here the simplified low-temperature variant of the Clausius-Clapeyron's equation [32]:

$$P_v^* = \exp\left[A - B / \left(T^* + C\right)\right]. \tag{14}$$

Table I. The novel set of LJ-parameters predicted from the CP-data by Eqs.(12,13)

Substances		T_c, K	P_c, MPa	$\rho_c, \textbf{mol/dm}^3$	$\varepsilon_{g,l} / k_B, \textbf{K}$	$\sigma_g, \textbf{nm}$	σ_g / σ_l
Ar	**[23]**	**150.66**	**4.860**	**13.29**	**106.68**	**0.2877**	**1.062**
C₂H₆	**[16]**	**305.33**	**4.872**	**6.870**	**220.04**	**0.3610**	**1.069**
CO₂	**[24]**	**304.14**	**7.373**	**10.62**	**220.65**	**0.3147**	**1.078**
SF₆	**[25]**	**318.71**	**3.718**	**5.155**	**230.98**	**0.4012**	**1.080**
H₂O	**[26]**	**647.14**	**22.06**	**17.89**	**498.80**	**0.2667**	**1.087**
Rb	**[27]**	**2017**	**12.45**	**3.416**	**1578.7**	**0.4715**	**1.106**
Cs	**[27]**	**1924**	**9.25**	**2.852**	**1533.9**	**0.5010**	**1.107**

Table II. The set of reduced *LJ/CP*-parameters recommended at any *MD*- or *MC*-simulations of criticality by the short-range *FT/LJ* [l, *n/m*]-potential. Its advantage is the possibility of iterative calibration determinationof the r_c^*-value just by simulations in the actual *CP*. It becomes the well-established third *PCS*-parameter.

Substances		Z_c	A_c	T_{cLJ}^*	P_{cLJ}^*	ρ_{cLJ}^*	$\rho_0^*\left(\xi_0^+\right)$	
LJ	[12]	0.3073	5.531	1.31	0.1264	0.314		
Ar	[23]	0.2919	5.943	1.412	0.0785	0.1905	0.1775	[33]
C_2H_6	[16]	0.2793	6.400	1.388	0.0754	0.1946	0.2293	[3]
							0.1808	[33]
CO_2	[24]	0.2745	7.044	1.378	0.0753	0.1993	0.1832	[33]
SF_6	[25]	0.2722	7.210	1.370	0.0747	0.2004	0.1576	[3]
							0.1628	[33]
H_2O	[26]	0.2292	7.860	1.297	0.0607	0.2043	0.1861	[3]
Rb	[27]	0.2173	11.27	1.278	0.0598	0.2155		
Cs	[27]	0.2028	11.39	1.254	0.0549	0.2159		

with the adjustable coefficients *A,B,C*. At higher subcritical temperatures the dew non-ideal-gas' density ρ_g^* as well as the respective vapor pressure P_v^* may be alreadywell outside the region of validity supposed by Eq.(14). To our mind, the appearance of many additional constants is the undesirable feature of any approximation. For example, authors [14] have used four additional adjustable constants in Eqs.(5-7) instead of two relevant amplitudes B_0, D_1 to argue that PCS may supposedly fail in the associating fluids and liquid metals [30,34].As a result of such questionable long-range extrapolations, the above value T_{cLJ}^* can be located well below than the expected actual one in the simulated finite *N*-systems. Valleau [28] has supposed that for the popular GEMC-methodology [29] such depression of T_{cLJ}^* is an artificial phenomenon occasioned, in particular, by the very different numbers N_g and N_l in the simulated phases. Another known anomalous consequence of the standard GEMC-approach to simulation of criticality is the three-peaked behavior of the overall reduced density distributions. They are steadily observable by GEMC at the near-critical reduced temperatures. Smit et al. [13] have taken into account that GEMC ignores the surface tension *γ(T)* between *g*- and *l*-phases. This factor explains an appearance of a third peak by thesharp decrease $\gamma_{LJ}\left(T^*\right)$ near T_{cLJ}^*. At the same time, Smit [30], Mon and Binder [31], Johnson et al. [11] have examined the strong influence of the arbitrarily chosen cutoff radius $r_c^* = r_c / \sigma_o$ on the near-critical shape of CXC as well as on the location of T_{cLJ}^* exclusively in the $\left(T^*, \rho^*\right)$-plane. The hypothetical *FT/LJ*-methodology of simulations proposes the alternative choice of reduced r_c^*-parameter by the iterative set of calibrationsimulations performed just at the fixed critical pressure P_{cLJ}^* (taken from Table II). Its possible *f*-dependence is inessential,

of course, in terms of dimensionless LJ-variables due to the coherent change in ρ^*_{cLJ}-density.

The GFA-phenomenology developed in the present work provides, in principle, the possibility of independent test for all above suppositions by thethermodynamic-cally-consistent computer simulations. It is obviously from Table II that two sets of substances with $T^*_{cLJ} > 1.31$ and $T^*_{cLJ} < 1.31$ are revealed by the proposed approach. It is equally interesting to note, that the substances of latter subset (H_2O, Rb, Cs) belong, unquestionably [27] to the type of Ib-systems with the singular CXC-diameter. The careful analysis of this problem performed by Wang and Anisimov in terms of the complete-scaling EOS [3] provides (at the given CP-parameters) the reliable estimate of the non-universal cubic "normalized interaction volume" $(2\xi_o)^3$ for the very different substances:

$$\rho^*_o = (2\xi_o)^3 \rho_c \quad \text{(a)} \qquad \xi = \xi_o \bar{T}^{-\nu} \quad \text{(b)} \qquad (15)$$

were ξ_o is the standard amplitude of a correlation length $\xi(T \geq T_c)$. The promisingcomparison of the ρ^*_o-values taken from [3] (0.2293 for C_2H_6, 0.1861 for H_2O, 0.1576 for SF_6) with the similar ρ^*_c-values of FT-model is represented in Table II. The found trends of their change from substance to substance are, however, opposite ($\rho^*_c = 0.1946$ for C_2H_6, 0.2004 for SF_6, 0.2043 for H_2O) in the FT-model. The close values of ρ^*_o and the similar trend of their change were also independently observed by the two-scale analysis of universality reported in [33].

The discussed relatively small distinction between ρ^*_0 and ρ^*_c becomes, however, noticeable for SF_6 which is the known origin of experimental contradictions. One group of experimentalists [25, 35] have observed the singular CXC-diameter.They estimated the rather low critical density as $\rho_c = 5.012$ mol/dm³ used, then, by authors [3] in Eq.15(a). Another group [36, 37] has not confirmed this observation and found the *rectilinear* diameter for SF_6 with the respective strong shift of critical density to the upper value: $\rho_c = 6.87$ mol/dm³. The compromising combination of critical SF_6-parameters [25] and those (Z_c, A_c) from the PCS-reference [7] is used in Tables I, II. It follows that the further estimate of the cubic volumes' ratio: $\rho^*_o / \rho^*_c = (2\xi_o)^3 / \sigma^3$ may provide the important insight of the short-range near-critical simulated interactions. It is also a serious challenge to model the highly-directional and short-range attractive interactions in H_2O (it belongs to the subset with $T^*_{cLJ} < 1,31$) arising due to the hydrogen bond by the effective short-range spherically-symmetric FT/LJ [$l,n/m$]-potential. It seems promising, for example, to explain also the impressive near-critical dimerization in the gaseous Rb and Cs by the simulation based on the proposed FT/LJ [$l, n/m$]-potential with the given $\varepsilon_{g,l}$, σ_g / σ_l-parameters taken from Table I. Hensel [34] has supposed that the presumable different nature of the net inter-particle interactions in g- and l-phases leads to the strongly asymmetric shape of CXC. From what has been said above, it follows that the same reason may be crucial for the explana-

tion of the observed *CXC*-asymmetry in the whole set of real fluids. However, one must take into account (at the performance of simulations) that in the liquid metals, for example, the universal *[l,n/m]*-part of *LJ*-potential is changeablein the manner of PCS-description. Hoover et al. [38] have simulated long ago at $T^* = 1$ the restricted class of purely repulsive pair potentials $[l = 1; n / (m = 0)]$:

$$\varphi / \varepsilon = r^{*-n} \tag{16}$$

and found the value $n = \infty$ for the singular hard-sphere-system and n ranging from about 6 for metals to about 12 for rare gases including *Ar*.

The preliminary conclusions are here worthwhile. The correlation of complete scaling [3] connecting the amplitude-radius ξ_0 from Eq.15(b) with the thermodynamic amplitude of the isochoric heat capacity $C_v(T \le T_c) A_0^-$: $(2\xi_0)^3 \approx 2.62 k_B / (A_0^- \rho_c)$ can be reliably represented in terms of *FT*-Eqs.13(a, b) due to the above-discussed similarity of cubic volumes: $(2\xi_0)^3 \approx \sigma_g^3 (A_c, \rho_c)$ or $\approx \sigma_l^3 (A_c^0, \rho_c)$. Such usage based also on the FT-model's approximate correspondence: $B_0 \approx A_c^{1/3}$ [19] provides the apparently testable possibility for an additional estimate A_0^+ for $C_v(T \ge T_c)$ by the other accepted correlation in the complete scaling: $A_0^+ \cong 0.523 A_0^-$ [3].

II. Curvilinear diameter cannot be tangent to the elongate cxc in both (*x, ρ*)- and (*z, ρ*)- planes. It was earlier shown [19] that in the physically informative (*x, ρ*)-plane (see Fig. 1) any *Wb*-diameter (*mf*-one or that for real fluids) demonstrates two essential features:

(a) –it is asymptotically tangent to the critical isochore ρ_c;

(b) – it crosses symmetrically at $x = 0$ the both *CXC*-branches discontinuous at *CP*.

The natural question may be now formulated. Are these geometric properties invariant at the transformation of a field-type variable *x* to any other field: ($x \to y$ or $x \to \overline{T}$) while the role of density remains unchangeable? The negative answer to this question follows immediately from the description of singular Ib-diameter implied by Eq.(9b). It becomes asymptotically tangent [39, 40] to the itself CXC (see insertion to FIG.2a) and, hence, cannot cross it at the origin of specific transformation: $x \to \overline{T}$. Obviously, that the experimental and, even, theoretical determination of critical density ρ_c is the hardly realizable procedure in the (*T, ρ*)-plane under the circumstances of a fluctuation CXC-flattening [15,17].

To elucidate the choice of independent variable $Z_\sigma(\rho)$ in the proposed below transformation, one may start from the identity between two scaled by Z_σ – value dimensional pseudo-densities:

$$Z_\sigma \rho = P_\sigma / k_B T \tag{17}$$

determined along the implied *CXC* near its actual *CP*. The isothermal and isobaric derivatives should give the straight linesasymptotically tangent to *CXC* in the $Z(\rho)$-plane.

This feature arises due to the fluctuation divergence of the isothermal critical compressibility $\chi_T = (1/\rho)(\partial\rho/\partial P)_T$ and the isobaric critical expansivity $\alpha_P = -(1/\rho)(\partial\rho/\partial T)_P$:

$$(\partial Z_\sigma / \partial\rho)_{T_c}\rho + Z_c = (\chi_T^0/\chi_T)_c \quad \text{(a)} \quad (\partial Z_\sigma/\partial\rho)_{P_c}\rho + Z_c = (\alpha_P^0/\alpha_P)_c \quad \text{(b)}. \quad (18)$$

The finite pseudo-ideal-gas' quantities at CP itself $(Z_c \neq 1)$ are normalized here by the Z_c-value scaled by the critical fields of pressure and temperature:

$$\chi_T^0 = 1/(\rho_c k_B T_c) = Z_c/P_c \quad \text{(a)} \qquad \alpha_P^0 = Z_c/T_c \quad \text{(b)} \qquad (19)$$

Thus, the asymptotic behavior on approaching CP-position along the critical field-iso-lines P_c and T_c has to be accurately determined by the symmetrical equalities:

$$\chi_T = \frac{1}{P_c}\cdot\frac{Z_\sigma}{Z_\sigma + (\partial Z/\partial\rho)_{T_c}\rho} \quad \text{(a)} \qquad \alpha_P = \frac{1}{T_c}\cdot\frac{Z_\sigma}{Z_\sigma + (\partial Z/\partial\rho)_{P_c}\rho} \quad \text{(b)} \quad (20)$$

Both quantities (Z_σ,ρ) shouldtend to their critical values (Z_c,ρ_c) simultaneously but asymmetrically in accordance to the GFA-principle [19, 20] from the gaslike $(\rho_g \to \rho_c)$ and liquidlike $(\rho_l \to \rho_c)$ ranges of near-critical states.

The accurate experimental CXC-data are represented in Figs. 2-4 for the selected illustrative examples of C_2H_6 (rectilinear diameter), H_2O (curvilinear diameter), $[C_4\text{mim}][BF_4]$ (diameter with the non-specified asymptotic curvature). The elucidative denotations explain in each case the physical and geometric features of the proposed transformation. The above properties (a) and (b) are, in total, fulfilled in the (Z, ρ)-plane though the possible asymptotic discontinuity between $Z_g(\rho_g \leq \rho_c)$- and $Z_l(\rho_l \geq \rho_c)$-branches is here the featurehardly testable by experiment. This restriction is also typical for all measurements directed to determine either ρ_c at the fixed fields P_c, T_c or its consequence Z_c calculated from Eq.(17) written for CP. The similar situation is observable at the prediction of mf-critical point (Z_c^0, ρ_c^0) too if one uses preliminarily the more reliable estimates of actual fields P_c, T_c to calculate the constantcoefficients a_0, b_0. In accordance with PCS-phenomenology [6, 7] one should substitute, on the ad hoc basis, the actual third parameter Z_c instead of univer-sal but unrealistic Z_c^0-value 3/8 to obtain the correct estimate of ρ_c. Such procedure destroys unavoidably the WMG-equality $(\partial^2 P/\partial\rho^2)_{T_c} = 0$ for second derivative at the critical point. The chosen in Figs. 2-4 system of coordinates provides the unique possibility to estimate the both rather elusive critical parameters Z_c, ρ_c in any complicated situation.

The discussion of mf-model arising as a combination of the rectilinear CXC-diameter approximated by Eq.(2) with the oversimplified WMG-concept of binodal:

$$\rho_d^* \approx 3/2 - T^*/2 \quad \text{(a)} \qquad P_\sigma^* \approx \rho_l^* \rho_g^* T^* \quad \text{(b)} \qquad (21)$$
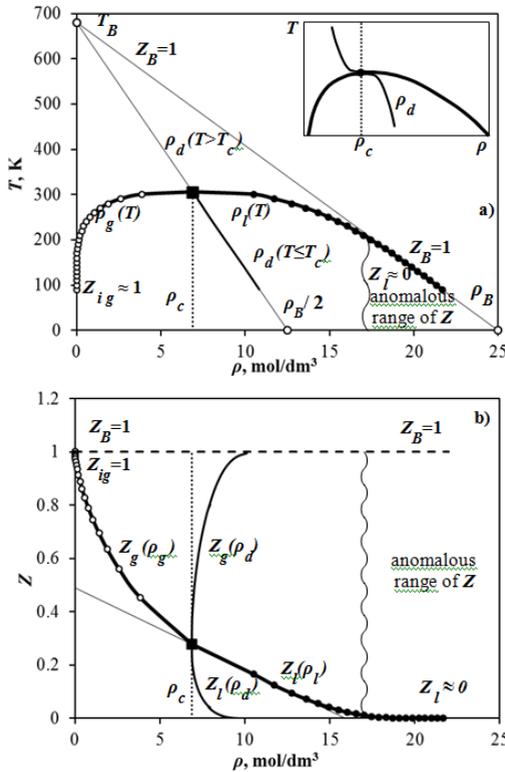
Fig. 2(a) – *CXC of ethane [16] as an example of the (coincidently) rectilinear diameter.* The shown formal application of Zeno-line's methodology leads at low temperatures in the (T, ρ)-projection to the visible anomaly of compressibi-lity factor. Inset demonstrates schematically the singular diameter of *Ib*-phenomenology.

2(b) – The elongate *CXC* and its curvilinear diameter in the (Z, ρ)-projection of *GFA*-transformation as the "inversion" counterparts of *CXC*-diameter and *CXC* itself, respective-ly. The rectilinear part of *l*-branch shown by thin tangent line crosses the curvilinear diame-ter of C_2H_6, practically, in the actual critical point (black square).

has been proposed in [9] "to derive" the purely empirical Timmermans' and Riedel's equations [7]:

$$\rho_{cB}^* \approx Z_c \quad \text{(a)} \qquad \ln P_\sigma^* = A + B/T^* + C \ln T^* + DT^{*6} \quad \text{(b)} \quad (22)$$

Authors of this approach started from the use of Eq.(17) written as the identity be-tween two functionals of vapor pressure $P_\sigma[\rho_g(T)] = P_\sigma[\rho_l(T)]$. They have applied to its analysis the rather inaccurate interpretation of Eq.(21b). Ithas been admitted that all three critical parameters P_c, ρ_c, T_c of reduced variables can be simultaneously taken

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as the actual ones in the description of *mf*-binodal. To revise this obvious incon-
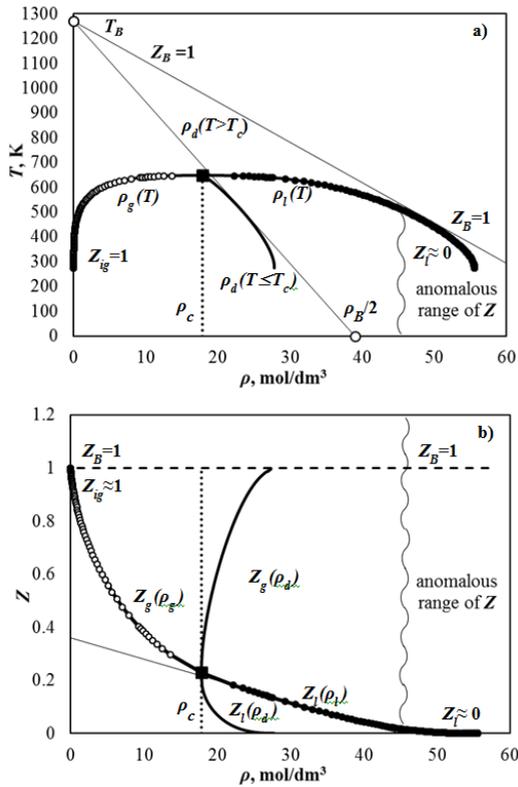
Fig.3(a) – *CXC* of water [26] as an example of the *strongly curvilinear diameter*. The formal application of Zeno-line's methodology may lead, in principle, to the serious errors at the prediction of critical parameters $\rho_c(T_c, P_c)$.

3(b) – The elongate *CXC* and its curvilinear diameter provide the exact location of critical point although the rectilinear part of *l*-branch shown by thin line (see for comparison Fig.2(b)) is located for H_2O significantly lower than the actual critical point (black square).

sistency one should fix ρ_c, T_c -parameters from Eq.(21a), but assume the *mf*-value P_c^0 in the resulting approximate equalities:

$$Z_g \equiv \frac{P_\sigma}{\rho_g k_B T} = \rho_l^* Z_c \frac{P_c^0}{P_c} \quad \text{(a)} \qquad Z_l \equiv \frac{P_\sigma}{\rho_l k_B T} = \rho_g^* Z_c \frac{P_c^0}{P_c} \quad \text{(b)} \qquad (23)$$

Thus, the empirical Timmermans' equation [7] leads in the framework of above assumptions [9] to the *T*-dependent ratios of CXC-parameters. They can be approximated by the constant only as the rather rough assumption:
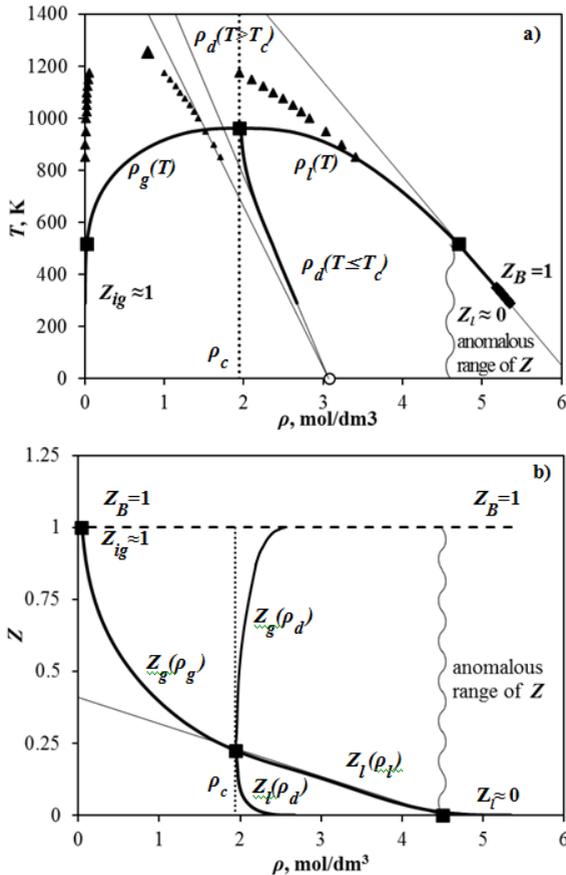
Fig. 4(a). Two variants of *curvilinear (non-divergent) diameter* and *CXC* of ionic liquid $[C_4 mim][BF_4]$ predicted a) in [41] (small and large triangles) by *GEMC*-simulation of the high-temperature region $T > 850$ K with the predicted data from [42] (lines with large squares) obtained by *FT-EOS* in which only the low-temperature input experimental data of liquid at atmospheric pressure $\rho_l(P_0, T)$ [43] (small diamonds) have been used for prediction.
4(b) The elongate CXC and its curvilinear diameter are shown only for *FT-EOS* [42].

$$\rho_{cB}^* = \frac{\rho_l(T)}{Z_g(T)} \cdot \frac{P_c^0}{P_c} = \frac{\rho_g(T)}{Z_l(T)} \cdot \frac{P_c^0}{P_c}. \tag{24}$$

The "derivation" of Riedel's Eq. (22b) based on the same approximate Eq.(21a) and (21b) gives [9] the typical *mf*-result for the reduced slope $A_\sigma(T)$:

$$A_c^0 = 1 + 3/T^* = 4\left(T_c^* = 1\right). \tag{25}$$

The respectiveClapeyron's-type equation similar to that in Eq.(14):

$$\ln P_\sigma^* = \ln T^* + 3\left(1 - 1/T^*\right) \tag{26}$$

is applicable, at best, at low temperatures.

FT-model claims [19-21] that the role of critical slope A_c (Riedel's parameter) is quite essential and different (Sec.II) from that of Z_c in opposite to the conventional *PCS*-viewpoint [6,7]. In particular, two *GFA*-equations for *CXC* can be used for the predictive aims with two *f*-dependent sets of also *T*-dependent *FT*-EOS' coefficients:

$$Z_g\left(T, \rho_g \le \rho_c\right) \equiv P_\sigma / \rho_g k_B T = \left[a(T)\rho_l(T)/k_B T\right]\left[1 - 2b(T)\rho_d(T)\right], \tag{27}$$

$$Z_l\left(T, \rho_l \ge \rho_c\right) \equiv P_\sigma / \rho_l k_B T = \left[a^0(T)\rho_g(T)/k_B T\right]\left[1 - 2b^0(T)\rho_d(T)\right]. \tag{28}$$

The aim is here (see, for comparison Eq.(24)) to take into account the difference of $A_\sigma(T)$- and $A_\sigma^0(T)$-slopes which may represent the same measurable *CXC*-branches separately in terms of the *CXC*-diameter (the locus of midpoints) $\rho_d(T)$ and the density of another coexisting phase $\rho_{l,g}$. At the critical point two different asymptotic slopes A_c and $A_c^0 = 4$ arise due to the described GFA-distinction:

$$a_c = P_c\left(A_c - 1\right)/\rho_c^2, \qquad b_c = \left(A_c - 2\right)/\left[2\rho_c\left(A_c - 1\right)\right], \tag{29}$$

$$c_c = 1 - Z_c A_c^2 / \left[2\left(A_c - 1\right)\right], \tag{30}$$

$$a_c^0 = 3P_c/\rho_c^2, \qquad b_c^0 = 1/3\rho_c, \tag{31}$$

$$c_c^0 = 1 - Z_c/Z_c^0 = 1 - 8Z_c/3. \tag{32}$$

Thus, two universal criteria of the simplest *vdW*-variant of *PCS* [6, 7] Z_c^0, A_c^0 are used here together with the actual (i.e. measured) critical parameters $\rho_c, P_c; Z_c, A_c$. It is remarkable that at the plausible asymptotic assumption $\bar{\rho}_l = 1 - \rho_l^* << B_0^0/2 = 1$ accepted for the critical isobar $\bar{P}_c = 1 - P^* = 0$ (it forms the *l*-branch of CXC in the (T, ρ)-plane), *FT*-model [18-21] predicts accurately the set of non-classical *l*-exponents: $\alpha_{FT} = 1/6, \beta_{FT} = 1/3, \gamma_{FT} = 7/6, \delta_{FT} = 9/2$. Moreover, any *mf*-exponent never appears in *FT*-model (!) due to the *GFA*-principle, which rejects the concept of *CXC*-analyticity and hence the concept of a unified *EOS*.

At low subcritical temperatures, the dew densities $\rho_g(T)$ are about ideal-gas-ones. They tend to zero $\rho_g \to 0$ simultaneously with the vapor pressures $P_\sigma \to 0$ while their ratio becomes about unit $\left(Z_g \to 1\right)$. Simultaneously at low temperatures of *l*-branch the Boyle's-locus $Z_B = 1$ coincides, practically, in the (T, ρ)-plane with the *CXC*-locus $Z_l \approx 0$ (see Figs 2(a)-4(a)) arising due to the respective negligible values $P_\sigma \approx 0$. As a result of such "collapse" the symmetric quadratic functions of Zeno-line for pressure expressed in terms either reduced temperature or reduced density with the same Boyle's constants ρ_B and T_B:

$$P_{Z=1} = k_B \rho_B T\left(1 - \frac{T}{T_B}\right) \quad \text{(a)} \qquad P_{Z=1} = k_B T_B \rho\left(1 - \frac{\rho}{\rho_B}\right) \quad \text{(b)} \tag{33}$$

become inapplicable alongside the isolines ρ_B and T_B of a low-temperature *CXC*. The revealed by *FT*-model asymptotic discontinuities of the disorder parameter $x = (s_g - s_l)/2k_B$ and the reduced slope $A_\sigma = (T/P_\sigma)dP_\sigma/dT$ are also interconnected at each point of *VLE*-transition by the thermodynamic Clausius-Clapeyron's equation:

$$x = A_\sigma(Z_g - Z_l)/2 \tag{34}$$

The asymptotic behavior of compressibility factor $Z_{g,l}$ is presumably (see Figs 2(b)-4(b)) smooth, at least, for its first derivative $(\partial Z/\partial\rho_g)_{T_c} = (\partial Z/\partial\rho_l)_{T_c}$ taken at CP along the critical T_c-isotherm. In this case the critical jump-like discontinuity of x is determined completely by the critical discontinuity of $A_\sigma(\rho)$ changeable from the non-universal value $A_c(\rho_g \to \rho_c)$ to the universal one $A_c^0(\rho_l \to \rho_c) = 4$. The Clausius-Clapeyron's Eq.(35) is reducedat low temperatures to the quite simple approximate form termed theClapeyron'sequation (T_b is the normal boiling point):

$$A_\sigma(T \le T_b) = 2x. \tag{35}$$

Thus thecritical isochore ρ_c is asymptotically tangent to theCXC-diameter. This is similarly to that observable in the (x,ρ)-plane of Fig. 1. Since the critical isotherm T_c is supposedly tangent to *CXC* [39, 40] in both (T,ρ)- and (Z,ρ)-planes one may admit the only crossing between *CXC* and its diameter but not the divergence of latter. However, the role of critical isobar P_c in the (T,ρ)-plane is crucial, in accordance with *FT-EOS* [20, 21], to explain the singular *CP*-nature. Indeed, in the (T,ρ)-plane P_c-curve is asymptotically tangent to *CXC* only at $\rho_g \le \rho_c$ but for the higher densities $\rho_l > \rho_c$ it coincides with the l-branch $\rho_l(T)$ of *CXC*. Analogously, in the (P,ρ)-plane T_c-curve is asymptotically tangent to *CXC* only at $\rho_l \ge \rho_c$ but for the lower densities $\rho_g < \rho_c$ it coincides with the g-branch $\rho_g(P_\sigma)$ of *CXC*.

The existence of a low-temperature anomalous range of compressibility detected by Figs. 2-4 makes the widespread now linear Zeno-methodology of predictions [6-10] to be rather questionablein this region. As a consequence, the supposed direction of the tangent Boyle's $Z_B = 1$-line to the *l*-branch of CXC $\rho_l(T)$ can be determined only visually. This procedure can lead to the similar uncertainties (see Figs 3(a), 4(a)). The curvilinear shape of *CXC* diameter provides also the similar uncertainties in the (*T*, ρ)-plane. The situation can be essentially revised, from our viewpoint, by the long-range linear extrapolation to zero temperature only the reliable experimental data $\rho_0(T \le T_b; P_0)$ measured at atmospheric pressure P_0. The aim of such assumption is, first of all, the reliable estimate of a physically plausible value of the excluded volume b_0 (similar to that from Eq.(3)) without any appeals to the fictive Boyle's density ρ_B introduced by Eq.(4) in the context of Zeno-methodology.

Table 3. GFA-variants of the Boyle's temperature predicted by Eqs.(36a,b).

Fluid	Z_c	A_c	T_c / T_B	T_c / T_B^0	T_c / T_B [7]
Argon	0.2919	5.833	0.281	0.381	0.38
Krypton	0.2911	5.787	0.284	0.382	0.38
Xenon	0.2900	5.818	0.284	0.383	0.38
Methane	0.2895	5.900	0.281	0.384	0.38
Nitrogen	0.2895	6.072	0.273	0.387	0.39
Ethylene	0.2812	6.354	0.270	0.395	0.40
Ethane	0.2793	6.390	0.270	0.398	0.40
Propane	0.2790	6.520	0.266	0.398	0.40
Nitrous Oxide	0.2760	6.590	0.266	0.403	
Acetylene	0.2750	6.810	0.259	0.404	
Carbon Dioxide	0.2745	6.838	0.259	0.405	0.41
Sulfur Hexafluoride	0.2739	6.960	0.255	0.406	
Ammonia	0.2433	7.269	0.276	0.457	
Water	0.2292	7.860	0.272	0.485	
Methanol	0.2209	8.438	0.263	0.503	
Ethanol	0.2411	8.295	0.245	0.461	

It is interesting to note that the restrictions of the basic lattice-gas model implied by the Ib-scaling *EOS* at the description of real fluids in any range of subcritical temperatures become understandable for some adepts of Zeno-line's methodology too. In particular, authors [44] have concluded that the accuracy of empirical projective map proposed in [10] for the transformation of actual *CXC* into the lattice-gas' symmetric (T,ρ)-locus may be significantly improved "by using as input, in place of the lattice gas, the original *vdW EOS* or (it is our cursive) simulation results for the *LJ*-potential" (see, however, Sec. I).Such alternative possibility is emphasized in [44] by the illustrative drawing of two combinations of Zeno-line with rectilinear diameterfor the *vdW*- and *LJ*-fluids in the (T,ρ)-plane (see also [6]. For both straight lines, the intersection at the supposed Boyle's point can be realized (in opposite to Zeno-methodology [8-10]) only at the meaningless negative densities. Such discrepancy was also discussed [45] in terms of the alternative empirical straight line described by Eq.(8a). The presumable resulting correlation Z_c (ω – the Pitzer's acentric factor) [10, 41] is, of course, the known and typical *PCS*-property [6, 7].

FT-model provides two independent GFA-variants of analytic prediction for the ratio $T_{cB}^* = T_c / T_B$ by the exact equations:

$$\frac{T_c}{T_B} = \frac{A_c - 2}{2Z_c (A_c - 1)^2} \quad \text{(a)} \qquad \frac{T_c}{T_B^0} = \frac{A_c^0 - 2}{2Z_c (A_c^0 - 1)^2} = \frac{1}{9Z_c} \quad \text{(b)} \quad (36)$$

This result obtained without any geometric constructions is reported in Table 3. The excellent predictive ability of *FT*-model (see the last column) corresponds just to the asymptotic universal $A_c^0 = 4$ slope measurable along *l*-branch. Namely it provides also the *FT*-model's prediction of non-classical critical exponents for liquid:
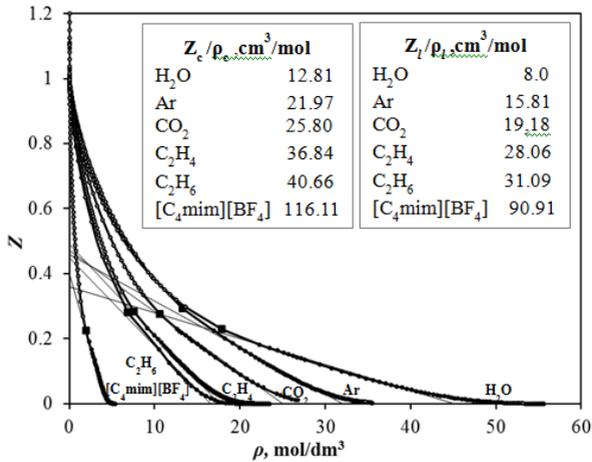
Fig. 5. Elongate forms of CXC for the different molecular compounds represented: a) – to confirm the universal and, simultaneously, quite distinct shapes of g-branch $Z_{g,}(\rho)$ and l-branch $Z_l(\rho)$ in accordance to GFA-concept [20]; b) – to demonstrate the existence of *impressively rectilinear segment of l-branch* located between the near-critical and low-temperature regions; c) – to emphasize the presence of singular (marginal) segments of $Z_{g,l}(\rho)$-behavior belonging to both axes of (Z,ρ)-plane (see text); d) – to point out the approximate lower boundary Z_l/ρ_l of anomalous liquid state (see insertion).

$\alpha_{FT} = 1/6$, $\beta_{FT} = 1/3$, $\gamma_{FT} = 7/6$, $\delta_{FT} = 9/2$ following from the exact *WMG*-model. The average accuracy of graphic predictive Zeno-methodology in Fig. 2(a) for C_2H_6 and Fig. 3(a) for H_2O can be now estimated by comparison with the analytic *FT/PCS*-prediction of Table 3: $\delta_{C_2H_6} = 11.4\%$, $\delta_{H_2O} = 4.8\%$. The second predicted by Eq. (36a) value T_c / T_B based on two actual nonuniversal PCS-criteria Z_c, A_c for an asymptotic g-phase determines the upper boundary of predicted T_B-value which indicates the overall uncertainty $T_B - T_B^0 > 0$ of its thermodynamic definition (see the recent work [46].

III. Conclusion. The "Procrustean bed" of binodal (with its restrictive *mf criticality*) and the *em-pirical rectilinear (only coincidentally) CXC-diameter* are main obstacles to wake to the understanding *GFA*-concept and to the respective discussed here *FT/LJ*-simula-tion. The measurable *CXC* of real fluids and its curvilinear (slightly or strongly) locus of midpoints can be very approximately represented in terms of *mf*-concepts (binodal and rectilinear diameter). They are, most likely, the thermodynamically more complex objects in comparison with the discrete models of ordinary or even decorated lattices. Nevertheless, the additional involvement of the universal *GFA*-behavior accepted for the vapor pressure is desirable. It reveals the fundamental interrelation between the *Ib*-phenomenology of local criticality and the *Wb*-

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phenomenology of an entire (or global) *VLE*-transition. To our mind, this revision is the necessary step to reconcile the traditional *PCS*-methodology with the different variants of the scaling universality without the crossover concept [15]. Fig. 5 and its illustrative meaning can be considered as the striking confirmation of *GFA*-principle formulated as the modified *FT*-model's variant for *Wb*-phenomenology. The universal and similar shapes of the elongate *g*- and *l*-branches are evident as well as a further necessity to investigate the *GFA*-concept and *Wb*-phenomenology modified by FT-model.Recently, the set of discussed here results and observations has been used to formulate the novel predictive *GFA*-methodology termed the *congruent vapor-liquid* (*CVL*) *diagram* [46]. It is applicable to the real fluids in the whole *f*-range of temperatures $(0, T_B]$. Hence, the traditional *VLE*-diagram corresponds only to the certain fragment of a more general *CVL*-diagram. The performed numerical estimates of *CP*- and *CXC*-prediction are quite promising for the hardly measurable in the region of criticality fluids.

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Роганков О. В. мл., Мазур В. А., Калинчак В. В., Сергеева А. Е., Левченко В. И., Швец М. В., Роганков В. Б.

Вытянутая кривая сосуществования и её криволинейный диаметр как факторы глобальной флюидной асимметрии

АННОТАЦИЯ

Рассмотрены ряд несогласованностей в принятых методологиях предсказания, используемых в районе пар-жидкостного сосуществования и критической точки. Как правило, они возникают в связи с разными толкованиями концепции «прямолинейного диаметра» в плоскости температура-плотность. Он часто искривлен на практике и может расходиться в двух альтернативных описаниях критичности: 1) основанной на модели Изинга феноменологии полного скейлинга и 2) классической феноменологии перехода пар-жидкость, разработанной ван-дер-Ваальсом-Максвеллом-Гиббсом. Вторая из них существенно модифицирована в модели флуктуационной термодинамики. Новое преобразование для полной кривой сосуществования основано на измеряемых равновесных данных, полученных вдали от критической области. Предложенное в настоящей работе, оно позволяет с приемлемой точностью определить положение критической точки, которое соответствует пересечению между вытянутой кривой сосуществования в плоскости фактор сжимаемости-плотность и её выраженно-криволинейным здесь диаметром. Универсальность принципа глобальной флюидной асимметрии, сформулированного ранее в модели флуктуационной термодинамики, доказана для всего температурного интервала перехода пар-жидкость. Развитая предсказательная методология определения критической точки может быть особенно полезной для ряда веществ, в которых её прямое измерение крайне затруднено или невозможно.

Роганков О. В. мол., Мазур В. О., Калінчак В. В., Сергєєва О. Є., Левченко В. І., Швець М. В., Роганков В. Б.

Витягнута крива співіснування і її криволінійний діаметр як фактори глобальної флюїдної асиметрії

Анотація

Розглянуто ряд неузгодженостей в прийнятих методологіях передбачення, використовуваних в районі пара-рідинного співіснування і критичної точки. Як правило, вони виникають у зв'язку з різними тлумаченнями концепції «прямолінійного діаметра» в площині температура-густина. Він часто викривлений на практиці і може розходитись в двох альтернативних описах критичності: 1) заснованої на моделі Ізінга феноменології повного скейлінга і 2) класичної феноменології переходу пара-рідина, розробленої ван-дер-Ваальсом-Максвеллом-Гіббсом. Друга з них суттєво модифікована в моделі флуктуаційної термодинаміки. Нове перетворення для повної кривої співіснування засноване на вимірюваних рівноважних даних, одержаних вдалині від критичної області. Запропоноване в цій роботі, воно дозволяє з прийнятною точністю визначити положення критичної точки, яке відповідає перетину між витягнутою кривою співіснування в площині фактор стисливості-густина і її виражено-криволінійним тут діаметром. Універсальність принципу глобальної флюїдної асиметрії, сформульованого раніше в моделі флуктуаційної термодинаміки, доведена для всього температурного інтервалу переходу пара-рідина. Розвинута передбачувальна методологія визначення критичної точки може бути особливо корисною для ряду речовин, в яких її пряму вимірювання вкрай утруднене або неможливе.