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 controversial results make the object of this article to be stimulated and, simultaneously, challenging. The discussion [1] of the complete scaling phenomenology [2,3] performed 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 peculiarities 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 consequence 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 \((M = 44 \text{ g/mol})\) fluids such as carbon dioxide \(\text{CO}_2\) and propane \(\text{C}_3\text{H}_8\). 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 \(2\beta\)-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:

\[
\rho_i^* - \rho_g^* = 2B_0 T_B^{\alpha}(T = 1-T/T_c)
\]

by all variants of scaling EOS.

The predictive description of an entire CXC-shape in the \((T, \rho)\)-plane and, even, the prediction of its actual topmost part i.e. CP-parameters in terms of the reduced critical Boyle's variables: 

\[
\rho_{cB}^* = \rho_c/\rho_B, \quad T_{cB}^* = T_c/T_B; \quad Z_{cB} = P_c/(\rho_B k_B T_B) = Z_{cB}\rho_{cB} T_{cB}^*
\]

are supposed by 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:

\[
Z_{vdW} - 1 = \frac{b_0 \rho}{1 - b_0 \rho} - \frac{a_0 \rho}{k_B T}
\]  

(1)

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

\[
\rho_d^* - 1 = D \bar{T}
\]  

(2)

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

\[
\rho_{Z=1} = \frac{1}{b_0} \left( 1 - \frac{b_0 k_B T}{a_0} \right) = \rho_B \left( 1 - \frac{T}{T_B} \right)
\]  

(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 opposite asymptotic point of "cold" density \(\rho_g(T \to 0)\) 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:

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

(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 \(\varphi_{LJ}(r \to \infty; \sigma_0, \epsilon_0)\) 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: \(\rho_{LJ}^* = \rho \sigma_0^3; T_{LJ}^* = k_B T / \epsilon_0; P_{LJ}^* = P \sigma_0^3 / \epsilon_0\) 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 separately for \(\rho_g^*(T_{LJ}^*), \rho_l^*(T_{LJ}^*), P_o^*(T_{LJ}^*)\) [12]) cannot be considered as the convincing sign, namely, of the universal \(LJ\)-criticality. This widespread but questionable conclusion is contrary to such its typical features of \(mf\)-behavior as the infinite-range potential \(\varphi_{LJ}(r; \sigma_0, \epsilon_0)\), 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 \(Z_c = P_c / (\rho_c k_B T_c)\).

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):

\[
\left(\rho_l^* - \rho_g^*\right)^{1/\beta} = C - DT_{LJ}^* \quad (a) \quad \left(\rho_l^* + \rho_g^*\right) / 2 = A + BT_{LJ}^* \quad (b)
\]

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

\[
T_{cLJ}^* = C / D \quad (a) \quad \rho_{cLJ}^* = A + B T_{cLJ}^* \quad (b).
\]

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

\[
B_0 = C^\beta / 2 \rho_{cLJ}^* \quad (a) \quad D_1 = -B T_{cLJ}^* / \rho_{cLJ}^* \quad (b)
\]

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 in Eq.6(b) have been proposed in two different "geometric" variants [9,10] of Zeno-line construction:

\[
\rho_{cB}^* = S(\beta) - T_{cB}^* \quad (a) \quad \rho_{cB}^* = 1 / 2 - T_{cB}^* / 2 \quad (b)
\]
where \( S_{\text{LJ}}(0.326) \approx 0.67 \) and \( S_{\text{vdW}}(1/2) \approx 0.63 \). The noticable respective distinction in the slopes of such straight 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 \( \text{LJ-CXC} \)) 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] \( \bar{\rho}_{l,g} = \rho_{l,g}^* - 1 \):

\[
\bar{\rho}_{l,g} = \pm B_0 \bar{T}^\beta + \rho_{d,l}^* - 1 \quad \text{(a)} \quad \rho_{d,l}^* - 1 = D_0 \bar{T}^{1-\alpha} + D_1 \bar{T} + D_2 \bar{T}^{2\beta} \quad \text{(b)}
\]

CXC-asymmetry corresponds presumably to the supposed divergences of \( \rho_{d,l}^* \) [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 \(2\beta\)-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:

\[
\bar{\rho}_l = B \bar{T}^{1/3} + (B - 1) \bar{T}.
\]

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

\[
\bar{\rho}_{l,g} = \pm B \bar{T}^\beta + (B - 1) \bar{T}.
\]

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 EOSs 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 CO₂ and C₃H₈, 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 CO₂ and/or C₂H₆ [16] (the latter substance is very similar on the molecular level just to C₃H₈).

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 (super-script zero) latent heat \( x^0 = \left( s_g - s_i \right) / 2 k_B \) 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 \( x(\rho_g^*) \)-branch to the symmetric constant negative value along \( x(\rho_l^*) \)-branch. Such replacement corroborates but in the quite different \( (x, \rho^*) \)-plane (!), the underlying asymptotic symmetry of the lattice gas. The latter is usually discussable only in the \((T, \rho)\)-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 \( (\bar{T}, \rho^*) \).

It is important to note that the discussed here asymptotic linearity of both branches \( x(\rho_g^*) \) and \( x(\rho_l^*) \) exists for the actual (i.e. measurable by direct experiment) parameter of disorder \( x = \left( s_g - s_i \right) / 2 k_B \) 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: \( A_c = \left( T_c / P_c \right) \left( dP_c / dT \right)_c \) revealed unambiguously by FT-model. Thus the 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: \( x'^{\theta} \equiv \rho_c \left( s_g - s_l \right)^{\theta} / 2k_B \rho_{g,l} \) 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 \( \rho_{l,j}\left( \rho_{l} \right) \) is only asymptotically tangent to the critical isochore \( \rho_c \) from the side of the liquid-like \( \left( \rho_{l} \geq \rho_c \right) \) densities (See also Figs.2-4).

scaling variable instead of original one \( \left( \bar{T} / \bar{\rho}^{1/\theta} \right) \) 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-data represented 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 (\( j \))-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 \( \varepsilon_0, \sigma_0 \) from another. The latter have been expressed by \( FT\)-equations in terms of the reported in Table I new effective \( FT/LJ\)-parameters \( \varepsilon, \sigma \). These parameters are recommended in the present work for the
common approach to the consistent simulation of the realistic coexisting phases. Indeed, the \( F_T \)-correlation are based exclusively on the respective substance-dependent (i.e. actual) critical data:

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

\[
\sigma_g^3 = 3 \left( A_c - 2 \right) / \left[ 4 \pi ( A_c - 1) \rho_c \right] \quad \text{(a)} \quad \sigma_i^3 \left( A_i^0 = 4 \right) = 1 / 2 \pi \rho_c \quad \text{(b)}.
\]

The same unusual split of the predicted effective diameter \( \sigma_f \) onto the very close but still distinctive values \( \sigma_g > \sigma_i \) is related in Eq.(13) to the revealed by FT-model [20, 21] asymptotic difference between the above-mentioned \( A_c (\rho_g \rightarrow \rho_c) \) - and \( A_i^0 (\rho_i \rightarrow \rho_c) \) -trends of slopes. The recommended \( LJ \)-parameters for the generalized short-range \( FT/LJ \)-potential \( \varphi_{LJ} (r ; \varepsilon , \sigma , \rho) \) with the third, a priori unspecified parameter of cutoff radius \( r_c \) are represented in Table I, II for the actual CPs of several substances.

One may see that the conventional constant values \( \varepsilon_o / k_B = 119.8 \) K, \( \sigma_o = 0.3405 \text{nm} \) of \( Ar \), for example, obtained from the second-virial \( B(T) \)-data at small 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 \( P_v^* (T) \) 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)

<table>
<thead>
<tr>
<th>Substances</th>
<th>( T_c , K )</th>
<th>( P_c , \text{MPa} )</th>
<th>( \rho_c , \text{mol/dm}^3 )</th>
<th>( \varepsilon_{g,l} / k_B , K )</th>
<th>( \sigma_g , \text{nm} )</th>
<th>( \sigma_g / \sigma_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>150.66</td>
<td>4.860</td>
<td>13.29</td>
<td>106.68</td>
<td>0.2877</td>
<td>1.062</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>305.33</td>
<td>4.872</td>
<td>6.870</td>
<td>220.04</td>
<td>0.3610</td>
<td>1.069</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>304.14</td>
<td>7.373</td>
<td>10.62</td>
<td>220.65</td>
<td>0.3147</td>
<td>1.078</td>
</tr>
<tr>
<td>SF\textsubscript{6}</td>
<td>318.71</td>
<td>3.718</td>
<td>5.155</td>
<td>230.98</td>
<td>0.4012</td>
<td>1.080</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>647.14</td>
<td>22.06</td>
<td>17.89</td>
<td>498.80</td>
<td>0.2667</td>
<td>1.087</td>
</tr>
<tr>
<td>Rb</td>
<td>2017</td>
<td>12.45</td>
<td>3.416</td>
<td>1578.7</td>
<td>0.4715</td>
<td>1.106</td>
</tr>
<tr>
<td>Cs</td>
<td>1924</td>
<td>9.25</td>
<td>2.852</td>
<td>1533.9</td>
<td>0.5010</td>
<td>1.107</td>
</tr>
</tbody>
</table>
Table II. The set of reduced \( \text{LJ}/\text{CP} \)-parameters recommended at any \( \text{MD} \)- or \( \text{MC} \)-simulations of criticality by the short-range \( \text{FT}/\text{LJ} \) \( [l, n/m] \)-potential. Its advantage is the possibility of iterative calibration determination of the \( r^*_c \)-value just by simulations in the actual \( \text{CP} \). It becomes the well-established third \( \text{PCS} \)-parameter.

<table>
<thead>
<tr>
<th>Substances</th>
<th>( Z_c )</th>
<th>( A_c )</th>
<th>( T_{cLJ}^* )</th>
<th>( P_{cLJ}^* )</th>
<th>( \rho_{cLJ}^* )</th>
<th>( \rho_0(\varepsilon_0^+) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LJ} )</td>
<td>0.3073</td>
<td>5.531</td>
<td>1.31</td>
<td>0.1264</td>
<td>0.314</td>
<td>0.1775 [33]</td>
</tr>
<tr>
<td>( \text{Ar} )</td>
<td>0.2919</td>
<td>5.943</td>
<td>1.412</td>
<td>0.0785</td>
<td>0.1905</td>
<td>0.2293 [3]</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>0.2793</td>
<td>6.400</td>
<td>1.388</td>
<td>0.0754</td>
<td>0.1946</td>
<td>0.1808 [33]</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>0.2745</td>
<td>7.044</td>
<td>1.378</td>
<td>0.0753</td>
<td>0.1993</td>
<td>0.1832 [33]</td>
</tr>
<tr>
<td>( \text{SF}_6 )</td>
<td>0.2722</td>
<td>7.210</td>
<td>1.370</td>
<td>0.0747</td>
<td>0.2004</td>
<td>0.1576 [3]</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.2292</td>
<td>7.860</td>
<td>1.297</td>
<td>0.0607</td>
<td>0.2043</td>
<td>0.1861 [3]</td>
</tr>
<tr>
<td>( \text{Rb} )</td>
<td>0.2173</td>
<td>11.27</td>
<td>1.278</td>
<td>0.0598</td>
<td>0.2155</td>
<td></td>
</tr>
<tr>
<td>( \text{Cs} )</td>
<td>0.2028</td>
<td>11.39</td>
<td>1.254</td>
<td>0.0549</td>
<td>0.2159</td>
<td></td>
</tr>
</tbody>
</table>

with the adjustable coefficients \( A,B,C \). At higher subcritical temperatures the dew non-ideal-gas’ density \( \rho^*_g \) as well as the respective vapor pressure \( P^*_v \) may be already well 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 \( \gamma(T) \) between \( g \)- and \( l \)-phases. This factor explains an appearance of a third peak by the sharp decrease \( \gamma_{LJ}(T^*) \) 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 \( (T^*, \rho^*) \)-plane. The hypothetical \( \text{FT}/\text{LJ} \)-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 $\rho^*_c$-density.

The GFA-phenomenology developed in the present work provides, in principle, the possibility of independent test for all above suppositions by the thermodynamic-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:

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

were $\xi_o$ is the standard amplitude of a correlation length $\xi (T \geq T_c)$. The promising-comparison of the $\rho_o^*$-values taken from [3] (0.2293 for $C_2H_6$, 0.1861 for $H_2O$, 0.1576 for $SF_6$) with the similar $\rho_c^*$-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 $\rho_o^*$ 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 $\rho_o^*$ and $\rho_c^*$ 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 $\rho_c = 5.012 \text{ mol/dm}^3$ 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: $\rho_c = 6.87 \text{ mol/dm}^3$. 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 $\varepsilon_g, \sigma_g / \sigma_i$-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 ex-
planation 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 changeable in the manner of PCS-description. Hoover et al. [38] have simulated long ago at \(T^* = 1\) the restricted class of purely repulsive pair potentials \([l = 1; n/(m = 0)]\):

\[
\varphi / \varepsilon = r^{-n}
\]

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 \(\xi_0\) from Eq.15(b) with the thermodynamic amplitude of the isochoric heat capacity \(C_v(T \leq T_c) A_0^c : (2\xi_0)^3 \approx 2.62 k_B / (A_0\rho_c)\) can be reliably represented in terms of \(FT\)-Eqs.13(a, b) due to the above-discussed similarity of cubic volumes: \((2\xi_0)^3 \approx \sigma^3 (A_c, \rho_c)\) or \(\approx \sigma^3 (A^0_c, \rho_c)\). Such usage also on the FT-model’s approximate correspondence: \(B_0 \approx A^{1/3}_c\) [19] provides the apparently testable possibility for an additional estimate \(A_0^+\) for \(C_v(T \geq T_c)\) by the other accepted correlation in the complete scaling: \(A_0^+ \approx 0.523 A_0^c\) [3].

II. Curvilinear diameter cannot be tangent to the elongate ecx in both \((x, \rho)\)- and \((z, \rho)\)-planes. It was earlier shown [19] that in the physically informative \((x, \rho)\)-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 \(\rho_c\);

(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: \((x \rightarrow y\) or \(x \rightarrow T)\) while the role of density remains unchangeable? The negative answer to this question follows immediately from the description of singular \(1b\)-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: \(x \rightarrow T\). Obviously, that the experimental and, even, theoretical determination of critical density \(\rho_c\) is the hardly realizable procedure in the \((T, \rho)\)-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 \(Z_\sigma\) – value dimensional pseudo-densities:

\[
Z_\sigma \rho = P_\sigma / k_B T
\]

determined along the implied CXC near its actual \(CP\). The isothermal and isobaric derivatives should give the straight lines asymptotically 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 \( \alpha_p = -(1/\rho) (\partial \rho / \partial T)_p \):

\[
(\partial Z_\sigma / \partial \rho)_T \rho + Z_c = \left( \chi_T^0 / \chi_T \right)_c \quad \text{(a)} \quad (\partial Z_\sigma / \partial \rho)_P \rho + Z_c = \left( \alpha_p^0 / \alpha_p \right)_c \quad \text{(b)}.
\] (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:

\[
\chi_T^0 = 1 / (\rho \cdot k_B T_c^0) = Z_c / P_c \quad \text{(a)} \quad \alpha_p^0 = Z_c / T_c \quad \text{(b)}
\] (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:

\[
\chi_T = \frac{1}{P_c} \cdot \frac{Z_\sigma}{Z_\sigma + (\partial Z / \partial \rho)_T \rho} \quad \text{(a)} \quad \alpha_p = \frac{1}{T_c} \cdot \frac{Z_\sigma}{Z_\sigma + (\partial Z / \partial \rho)_P \rho} \quad \text{(b)}
\] (20)

Both quantities \( (Z_\sigma, \rho) \) should tend to their critical values \( (Z_c, \rho_c) \) 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), \( [C_4mim][BF_4] \) (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 \((Z, \rho)\)-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 feature hardly testable by experiment. This restriction is also typical for all measurements directed to determine either \( \rho_c \) 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 \( (Z_c^0, \rho_c^0) \) too if one uses preliminarily the more reliable estimates of actual fields \( P_c, T_c \) to calculate the constant coefficients \( a_0, b_0 \). In accordance with PCS-phenomenology \([6, 7]\) one should substitute, on the ad hoc basis, the actual third parameter \( Z_c \) instead of universal but unrealistic \( Z_c^0 \)-value 3/8 to obtain the correct estimate of \( \rho_c \). 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 \( Z_c, \rho_c \) 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:
19

\[ \rho_d^* \approx 3/2 - T^*/2 \quad (a) \quad P_\sigma^* \approx \rho_i \rho_g^* T^* \quad (b) \quad (21) \]

**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 \((T, \rho)\)-projection to the visible anomaly of compressibility factor. Inset demonstrates schematically the singular diameter of *Ib*-phenomenology.

**2(b)** – The elongate *CXC* and its curvilinear diameter in the \((Z, \rho)\)-projection of *GFA*-transformation as the “inversion” counterparts of *CXC*-diameter and *CXC* itself, respectively. The rectilinear part of *l*-branch shown by thin tangent line crosses the curvilinear diameter 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]:

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

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

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

\[
Z_g = \frac{P_g}{\rho_g k_b T} = \rho_c^* Z_c \frac{P_c^0}{P_c} \quad \text{a)}
\]

\[
Z_l = \frac{P_l}{\rho_l k_b T} = \rho_g^* Z_c \frac{P_c^0}{P_c} \quad \text{b)}
\]

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:
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 $A_{n}(T)$:

$$A_{n}^{0} = 1 + 3/T^{*} = 4(T_{c}^{*} = 1).$$

The respective Clapeyron’s-type equation similar to that in Eq. (14):

$$\rho_{c}^{*} = \rho_{g}(T) \cdot P_{c}^{0} = \rho_{g}(T) \cdot P_{c}^{0} / Z_{g}(T) \cdot P_{c}. \quad (24)$$
\[ \ln P_\sigma^* = \ln T^* + 3\left(1 - 1/T^*\right) \]  \hspace{1cm} (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:

\[
Z_g(T, \rho_g \leq \rho_c) = \frac{P_\sigma}{\rho_g k_B T} = \left[a(T)\rho_g(T) / k_B T\right][1 - 2b(T)\rho_d(T)], \hspace{1cm} \text{(27)}
\]

\[
Z_l(T, \rho_l \geq \rho_c) = \frac{P_\sigma}{\rho_l k_B T} = \left[a^0(T)\rho_g(T) / k_B T\right][1 - 2b^0(T)\rho_d(T)]. \hspace{1cm} \text{(28)}
\]

The aim is here (see, for comparison Eq.(24)) to take into account the difference of \( A_c(T) \) and \( A^0_c(T) \)-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 \( A^0_c = 4 \) arise due to the described GFA-distinction:

\[
a_c = \frac{P_c(A_c - 1)}{\rho_c^2}, \hspace{1cm} b_c = \frac{(A_c - 2)}{2\rho_c(A_c - 1)}, \hspace{1cm} c_c = 1 - Z_c A_c^2 / \left[2(A_c - 1)\right], \hspace{1cm} \text{(29)}
\]

\[
a^0_c = 3\rho_c^2, \hspace{1cm} b^0_c = 1 / 3\rho_c, \hspace{1cm} c^0_c = 1 - Z_c / Z_c^0 = 1 - 8Z_c / 3. \hspace{1cm} \text{(30)}
\]

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 \( \overline{\rho}_l = 1 - \rho^*_l << B^0 / 2 = 1 \) accepted for the critical isobar \( \overline{P}_c = 1 - P^* = 0 \) (it forms the \( l \)-branch of \( CXC \) in the \( (T, \rho) \)-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-gases. They tend to zero \( \rho_g \to 0 \) simultaneously with the vapor pressures \( P_\sigma \to 0 \) while their ratio becomes about unit \( (Z_g \to 1) \). Simultaneously at low temperatures of \( l \)-branch the Boyle’s-locus \( Z_B = 1 \) coincides, practically, in the \( (T, \rho) \)-plane with the \( CXC \)-locus \( Z_l \approx 0 \) (see Figs 2(a)-4(a)) arising due to the respective negligible-values \( P_g \approx 0 \). 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 \( \rho_B \) and \( T_B \):

\[
P_{Z=1} = k_B \rho_B T \left(1 - \frac{T}{T_B}\right) \hspace{1cm} (a) \hspace{1cm} P_{Z=1} = k_B T_B \rho \left(1 - \frac{\rho}{\rho_B}\right) \hspace{1cm} (b) \hspace{1cm} \text{(33)}
\]
become inapplicable alongside the isolines $\rho_B$ and $T_B$ of a low-temperature CXC. The revealed by $FT$-model asymptotic discontinuities of the disorder parameter $x = \left(s_g - s_l\right)/2k_B$ and the reduced slope $A_n = \left(T/\sigma\right)d\sigma/dT$ are also interconnected at each point of $VLE$-transition by the thermodynamic Clausius-Clapeyron’s equation:

$$x = A_n \left(Z_g - Z_l\right)/2 \quad (34)$$

The asymptotic behavior of compressibility factor $Z_g,f$ is presumably (see Figs 2(b)-4(b)) smooth, at least, for its first derivative $\left(\partial Z / \partial \rho_g\right)_{T_c} = \left(\partial Z / \partial \rho_l\right)_{T_c}$ 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 $A_n(\rho)$ changeable from the non-universal value $A_c\left(\rho_g \rightarrow \rho_c\right)$ to the universal one $A^0_c\left(\rho_l \rightarrow \rho_c\right) = 4$. The Clausius-Clapeyron’s Eq.(35) is reduced at low temperatures to the quite simple approximate form termed the Clapeyron’s equation ($T_b$ is the normal boiling point):

$$A_n \left(T \leq T_b\right) = 2x. \quad (35)$$

Thus the critical isochore $\rho_c$ is asymptotically tangent to the CXC-diameter. This is similarly to that observable in the $(x,\rho)$-plane of Fig. 1. Since the critical isotherm $T_c$ is supposedly tangent to CXC [39, 40] in both $(T,\rho)$- and $(Z,\rho)$-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 $(T,\rho)$-plane is crucial, in accordance with $FT$-EOS [20, 21], to explain the singular CP-nature. Indeed, in the $(T,\rho)$-plane $P_c$-curve is asymptotically tangent to CXC only at $\rho_g \leq \rho_c$ but for the higher densities $\rho_l > \rho_c$ it coincides with the l-branch $\rho_l(T)$ of CXC. Analogously, in the $(P,\rho)$-plane $T_c$-curve is asymptotically tangent to CXC only at $\rho_l \geq \rho_c$ but for the lower densities $\rho_g < \rho_c$ it coincides with the g-branch $\rho_g \left(P_\sigma\right)$ 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 questionable in 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 $(T, \rho)$-plane. The situation can be essentially revised, from our viewpoint, by the long-range linear extrapolation to zero temperature only the reliable experimental data $\rho_0\left(T \leq T_b; P_0\right)$ 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 $\rho_B$ introduced by Eq.(4) in the context of Zeno-methodology.
Table 3. GFA-variants of the Boyle’s temperature predicted by Eqs.(36a,b).

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

It is interesting to note that the restrictions of the basic lattice-gas model implied by the I^b-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 $(T,\rho)$-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 diameter for the $vdW$- and $LJ$-fluids in the $(T,\rho)$-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 $Z_c$ ($\omega$ – 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:

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

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 $(Z,\rho)$-plane (see text); d) – to point out the approximate lower boundary $Z_l/\rho_l$ of anomalous liquid state (see insertion).

$$\alpha_{FT} = 1/6, \quad \beta_{FT} = 1/3, \quad \gamma_{FT} = 7/6, \quad \delta_{FT} = 9/2$$ 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 restrictivemf criticality) and theem-pirical rectilinear (only coincidentally) CXC-diameter are main obstacles to wake to the understanding GFA-concept and to the respective discussed here FT/LJ-simulation. 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-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 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.

REFERENCES:


42. V. B. Rogankov and V. I. Levchenko Towards the equation of state for neutral (C$_2$H$_4$), polar (H$_2$O), and ionic ([bmim][Bf$_4$], [bmim][Pf$_6$], [pmmim][Tf$_2$N]) liquids // Journal of Thermodynamics. – 2014.


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

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

Анотація
Розглянуто ряд неузгодженоності в прийнятих методологіях передбачення, використовуваних в районі пара-рідінного співіснування і критичної точки. Як правило, вони виникають у зв'язку з різними тлумаченнями концепції «прямолінійного діаметра» в площині температура-густинність. Він часто викривлений 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 вимірюваннях рівноважних даних, одержаних вдалою зоною критичної області.

Запропоновано в цій роботі, воно дозволяє з прийнятною точністю визначати положення критичної точки, яке відповідає перетину між витягнутими кривою співіснування в площині фактор стисливості-густинність і її виражено-криволінійним 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 пряме змірювання вкрай утруднене або неможливе.