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Classic origin of mesoscopic critical and boyle's singularities simulated by fluctuational potential

We have used the developed recently methodology of the congruent vapor-liquid (CVL) diagram for prediction, in particular, of the entire vapor-liquid equilibrium (VLE) diagram in the test-fluid argon. The former is based on the proposed earlier principle of the global fluid asymmetry (GFA) which rejects the conventional concept of a unified fluid equation of state (EOS) in both sub- and supercritical regions. In contrast to the traditional VLE-locus applicable in the restricted (subcritical) range between critical (T_c) and triple (T_t) temperatures, the CVL-locus spans the much more wide ranges of fluid states located between the generalized Boyle's (B) points ($\rho \to 0, T_B^{FT}$], ($T \to 0, \rho_B^{FT}$] predicted by FT-model of fluctuational thermodynamics. The new shape, location and the opposite sign of curvature for the boundary of metastable liquid which does not pass over CP (critical point) have been revealed in the global fluid (f) temperature range ($0, T_B^{FT}$) including its supercritical segment. The classical GFA-origin of the asymptotic criticality is unambiguously established without any appeals to the non-classical scaling phenomenology but in accordance with its main findings, at least, in the regions of stable and metastable liquid. Since the fundamental concept of a homogeneous equilibrium Gibbsian phase achieves the limit of its applicability in the simulated discrete N,V-systems of the Lennard-Jones' particles, their metastable, at best, states are highly-probable in the conventional scales of VLE-simulation.

Keywords: *congruent vapor-liquid diagram, boundary of metastable liquid, global fluid asymmetry.*

1. Introduction. There is a set of objective difficulties in the various experimental and/or simulation methodologies usable for determination of an *actual* (i.e. *non-mean-field* (*mf*)) critical point's (CP-) position. At least two parameters from its EOS-thermodynamic set: $\{T_c, P_c$ (critical *fields* [1]) and $\rho_c, Z_c = P_c / \rho_c k T_c$ (*critical densities* or *volumes*: $v_c = 1/\rho_c)\}$ are hardly measurable by the direct experiment with an uncertainty better than one percent. The standard extrapolation of the coexistence-curve (CXC) data simulated *far away from CP* by a combination of the asymptotic scaling law and the so-called *mf-rectilinear diameter* is the rather arbitrary procedure. Its uncertainty becomes especially undesirable within the small asymptotic CP-vicinity: $\Delta\tau = |1 - T / T_c| \lesssim 10^{-3}$. The discrepancies between the recommended by different authors ρ_c-values can lead, in principle, to the significant uncertainties at the estimation of standard substance-dependent amplitudes *B, Γ, D* and the respective *universal* EOS-exponents: β, γ, δ [1, 2]. The isochoric heat capacity C_v-parameters *A, α* become especially elusive in this case. The common feature of the power-law definitions is an attempt to elucidate the asymptotic behavior of the strongly- or

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weakly-fluctuating [1] local densities (ρ, *v*, *s* – specific entropy) at the given subcritical $\left(T^{-},P^{-}\right)$- and/or supercritical $\left(T^{+},P^{+}\right)$-equilibrium state-points. One usually determines the non-classical CP-trends in terms of the smooth functions defined alongside either CXC or the CP-isolines: $\rho_g\left[T^- \to T_c, P_v\left(T^-\right)\right]$, $\rho_l\left[T^- \to T_c, P_v\left(T^-\right)\right]$, $\rho\left(P^{+/-} \to P_c; T_c\right)$, $\chi_T\left(T^+ \to T_c; \rho_c\right)$. The square branches denote here and below the implied functional dependences along CXC.

Strictly speaking, only the most problematic for an experiment CP-exponent δ implements an important *inverse* task in which the pressure $P^{+/-}$ (i.e. the thermodynamic field [1]) is considered as the function of independent density *ρ* given alongside the fixed *a priori* T_C-value. At a glance, just this choice should be appropriate to test the asymptotic scaling law $P\left(\rho^{+/-} \to \rho_c; T_c\right)$ with two above-mentioned parameters (*D*, δ) not only by the direct experiment but also by the most usable *NVT*-ensemble of MD (molecular-dynamical) simulations [3]. Obviously that both extensive but, at best, *mesoscopic* (Sect. II) parameters $N, V = L^3$ of a simulated box should be *simultaneously* fixed to study the realistic fluctuation dynamics of any equilibration in the CP-vicinity. However, there are some paradigms of the conventional non-classical criticality, which forbid to realize namely such plan.

One admits that all real fluids (*f*) (Ar, CO_2, H_2O,…) belong to the special *class of universal criticality* [1,2] which is determinable by the Ising-based *Ib-systems*. Its distinctive features follow from the adopted so basic Ib-model of a lattice gas:

(i) the imposed primitive thermodynamic Ib-symmetry between the respective liquid (*l*) and gas (*g*) CXC-densities at $T^{-} \le T_C$ with constant (vertical) *T*-independent "diameter": $\rho_d = \left[\rho_g\left(T^-\right) + \rho_l\left(T^-\right)\right]/2$;

(ii) the underlying "particle-hole" lattice-gas'-symmetry symbolized by the ± signs standing before both CXC-branches: $B_l = \left|-B_g\right|, \beta_l = \beta_g$ (it is usually postulated also for the other subcritical EOS-exponents: $\gamma_l = \gamma_g$; $\delta_l = \delta_g$);

(iii) the absence of an inherent for real fluids isothermal latent heat of (*g,l*)-transition: $h\left(T^{-}\right) = T^{-}\left[s_g\left(T^{-}\right) - s_l\left(T^{-}\right)\right]$ in the ordinary lattice-gas;

(iv) the implied external zero-field and the respective zero-value of its *T*-derivative (density) lead to the degeneracy of the thermodynamic Clausius-Clapey-ron's differential equality.

The remarks (i-iv) confirm the rather restrictive nature of the adopted basic Ib-model at the description of CP-vicinity in real *f*-states. On the other hand, the assumed by the original van der Waals' vdW-EOS concept of an *isothermal (g,l)-continuity* in both ($T^{+/-}$) *f*-regions leads unavoidably to the known vdW-loop with its conventional but rather controversial interpretation of the binodal-spinodal construction. We mean here the physically questionable for a finite-volume (*N,V*)-system of interacting particles predictions of the equilibrium unstable states ($\chi_T < 0$), the *negative* pressures ($P<0$) of *spinodal decomposition* (?) and the supposedly erroneous critical *mf-parameters* $\left(T_c^0, P_c^0, \rho_c^0, Z_c^0 = 3/8\right)$ for the so-called *Andrews-van der Waals' CP* [2,4]:

$$\left(\partial P / \partial \rho\right)_{T_c} = 0 \quad (a) \qquad \left(\partial^2 P / \partial \rho^2\right)_{T_c} = 0 \quad (b) . \tag{1}$$

The first condition of the type Eq.(1a) defines also the *mf*-spinodal at $T^- < T_C$. Simultaneously, it should be fulfilled along any two-phase *isotherm-isobar* $\left(T^-, P^-\right)$.

Some authors have exploited recently the similar vdW-formalism of (*g,l*)-continuity combined either with the oversimplified particle-hole model [5] or with the non-equilibrium gradient-type's [4,6] models of non-homogeneity. The common aim was to reveal the presumed existence of the *higher (third)-order* (*g,l)-transition* in the supercritical T^+-region of *f*-states. In one case [5] a combination of the precise tabular EOS-data for Ar, CO_2, H_2O with the modelistic percolation transition has led to the "disappearance" of a single *mf*-CP itself determined by Eq.(1). More accurately, it becomes the horizontal *critical* $\left(T_C, P_C\right)$ *isotherm-isobar-line*. Such construction resembles, of course, the coincidence of isotherms with isobars in a first-order transition. Their presumable critical "counterpart" termed *rigidity* [5] is limited, however, by two "spinodal" point-densities of the reversible percolation ($g \to l$)- and ($l \to g$)-transitions. In other case [6], a combination of the thermodynamic four-dimensional *phase space* formed by coordinates (fields) and momenta (densities) $\left(P,T;\rho,\sigma=\rho s\right)$ with the non-equilibrium gradient terms (defined only for *densities* of the number particles: $\rho = N/V$ and entropy $\sigma = S/V$) was used. Such approach has provided a possibility to discuss the *dynamical* (i.e. *t*-dependent) *PVT-behavior* (?) of the vdW-fluid's criticality in terms of its *extended* chemical potential: $\mu\left[T,P;\rho,\sigma\,|\nabla\rho|^2,|\nabla\sigma|^2\right]$. Besides, the proposed in [6] methodology introduces *on the ad hoc basis* the continuous dependence for both vdW-coefficients (*a,b*) defined along an *isotherm-isobar* too: $b(T,P)$, $a(T,P)$. Only *T*-dependent coefficients are admissible (Sect. II,III) in the framework of any cubic EOS.

The FT-(*fluctuational thermodynamics'*) model developed earlier [7-12] and used in the present work excludes the itself traditional notion of an *isotherm-isobar* determined as a line with the continuously variable densities. The latter leads not only to the formal divergences of compressibility χ_T and expansivity α_P everywhe-re within *mf*-binodal. Indeed, the choice of the standard grand-canonical ($V;T,\mu$) and isobaric (*N;P,T*)-ensembles *with two fixed coordinates-fields* cannot define comprehensively [4] the state of two-phase or, generally, heterophase assembly. Both pairs of their conjugated momenta-densities: $\rho, \sigma = \rho s$ or specific (per mole or per particle) quantities: *v,s* may vary locally within the given limits *without changing of the fixed fields*: μ,T or P,T respectively. In other words, the trans-formation of the measureable P,v,T EOS-surface into that determined exclusively by the fields: P,μ,T Gibbsian-surface [1] might, in principle, "wash off" the realistic heterophase structures of real fluids and their mixtures.

2. Fluctuational – thermodynamic nature of mesoscopic simulations. Thermodynamics assumes a possibility of the Gibbsian (i.e. macroscopic) isothermal differentiation applied to the thermodynamic *fields* of pressure P and chemical potential μ. The latter is determined for a pure substance as the specific (per particle) Gibbs' function: $G = N\mu(T,P)$. The methodology of unified EOS adopts that its inconsistent variable of the mean (i.e. uniform) number density $\rho = N/V = 1/v$ can be used as independent one either to realize the Maxwell's rule at $T^{-} < T_c$ or to define the "fundamental extensive state function" of "rigidity" [5] at $T^{+} \geq T_c$:

$$(dP/d\rho)_{T\geq T_c} = \rho(d\mu/d\rho)_{T\geq T_c} = w\left(T^{+}\right). \tag{2}$$

This local ρ-parametrization of the Gibbs-Duhem's differential form is based on the implied assumption of a smooth EOS-surface $\rho(P,T)$. It becomes not completely correct (due to the inconsistent choice of independent variable) if the finite-volume *small N-systems* (termed in [10-12] the *mesoscopic N,V*-systems) composed by the small number of constituent particles should be considered. In this case, one has to distinct [30] the uniform above-mentioned chemical potential $\hat{\mu} = G/N$ from its differential form $\mu = (\partial G/\partial N)_{T,P}$. Such distinction leads to the N-dependent difference, which one has to take into account at the simulation of two-phase *f*-states. The Gibbsian related to one particle model of a smooth field $\mu(T,P)$ implied, in particular, by Eq.(2) as well as by the conventional methodology of VLE-simulations [13] should be modified in this case by N-dependent equality:

$$(\partial\hat{\mu}/\partial N)_{T,P} = (\mu - \hat{\mu})/N \equiv \Delta\mu/N\ . \tag{3}$$

This refinement of the standard *test-particle* methodology proposed by Widom [31] is especially important due to the practically mesoscopic (*m*-) volumes of the mostly simulated VLE-diagram. Hill [30] emphasized that *small system effects in the regions of phase transition and criticality are especially noticeable*. In particular, an additional independent variable N (discrete by nature) appears in the generalized Clausius-Clapeyron's system of equalities [30]. It can be termed as the formal sign of mesoscopicity:

$$\left(\frac{\partial P}{\partial T}\right)_N = \frac{s_g - s_l}{v_g - v_l} \equiv \frac{\Delta s}{\Delta v}, \tag{4}$$

$$\left(\frac{\partial T}{\partial N}\right)_P = \frac{\Delta\mu}{N\Delta s} \quad (a) \qquad \left(\frac{\partial P}{\partial N}\right)_T = -\frac{\Delta\mu}{N\Delta v} \quad (b)\ , \tag{5}$$

where the left-hand sides and the difference $\Delta v = \left(\rho_l - \rho_g\right)/\rho_g\rho_l$ are measurable by experiment or by numerical simulation. Hence, the unmeasurable entropy-dependent differences $\Delta\mu$ and Δs may be appropriately estimated only by Eqs.(3-5) with the implied differential equality between two uniform chemical potentials $d\hat{\mu}_g = d\hat{\mu}_l$

taken alongside the unique CXC in the field space.

It was argued earlier [7-9] that the necessary thermodynamic choice of an extensive V-scale for f-state leads in the thermodynamic limit: $\rho = \lim\limits_{V\to\infty}(N/V)$ to the special role of its conjugated variable P-pressure. The respective *thermodynamic* FT-Hamiltonian determined in the four-dimensional phase space is degenerated on the thermodynamic Gibbs' surface: $H(P,T;v,s)=0$. The role of a new FT-Hamiltonian passes, as a result, just to $P(v,T)$-EOS with the exclusive role of a constant specific entropy s (as the path of "FT-motion"). We refer now the interested readers to the development of an alternative geometric concept by Maslov [16,17] in which just the alternative role of the Gibbs'-function $G = N\mu(P,T)$ was discussed. This main "tool" of classical WMG-phenomenology [9] originated to construct the actual VLE-diagram on the base of a *unified* (i.e. common for both coexisting f-phases) *EOS* is highly modelistic by nature for a real *mesoscopic* finite-volume (N,V)-system. One cannot realize the verification of the supposed equality $\mu_g\left(T^-,P^-\right)=\mu_l\left(T^-,P^-\right)$ by the direct VLE-experiment. Moreover, its plausible two-phase imitation in the widely usable numerical GEMC (Gibbs ensemble Monte Carlo) simulation [13] requires, to our mind, the serious oversimplifications. It arises just due to the implied isothermal $\mu_f\left(\rho_f,T\right)$-dependencies. *GFA-principle omits the described "μ-problem" at the construction of CVL-diagram.*

In the present work we intend to argue that some postulates of the classical WMG-phenomenology [9] should be rejected, at the study of realistic finite-volume (N,V)-systems. In their mesoscopic volumes (simulated at the given nano-scales of length and volume $V = L^3$) the main vdW-hypothesis of (g,l)-continuity and reversibility of its two variants ($g \to l$) and ($l \to g$) achieves the limit of its applicability. Hence, the impact of a discrete variable (number of particles N) cannot be negligible at any estimation of the two-phase thermodynamic field $(T,P;\mu)$ variables. Moreover, the different physical nature of *mechanical* ($\rho = N/V$-density, P-pressure (momentum flux), $H = E_{kin} + E_{pot}$ – Hamiltonian (total mechanical energy of a conservative force-field) *variables* and *thermal* (T – temperature, μ – chemical potential per particle, $e = E/N$ – internal energy per particle, $s = S/N$ – entropy per particle) *variables* has to be taken into account by the appropriate simulation f-models. As a result, the unavoidable distinctions in the local discrete structures of g- and l-states might be presumably described in terms either the *different interparticle effective potentials* $\phi^f(r)$ accepted separately for every f-phase or by the distinguishable primary effective parameters (well-depth ε^f and/or collision-diameter σ^f, first of all) determined for the *same* $\phi^{g,l}(r)$-function. At last, a possibility of metastable, at best, local heterogeneous f-states, simulated by the conventional MD- and MC-techniques should not be excluded from analysis of the predicted thermodynamical properties (in spite of the formal, highly-modelistic signs of the attained equilibration).

To test and corroborate the proposed FT/LJ-methodology of CXC-simulations carried out in the framework of CVL-diagram, the choice of argon in Sections III,IV seems to be the most appropriate . Its experimental and correlated by the empirical EOS data [18,19] as well as simulated [20] CXC-data incorporated in the fundamental EOS [21] are plentiful. Thus, the detailed classical and non-classical variants of a *unified* EOS are also well-known. The widespread belief in the similarity of real Ar to the model LJ-fluid is here noteworthy. Its correctness will be discussed below in the context of comparison with the FT/LJ-predictions of the present work.

3. Main concepts and hypotheses of cvl-diagram. The above-mentioned attempts to lay the foundations of the third-order phase (*g,l*)-transition at T^{+},P^{+}-states (see, for example, [5,6]) are similar to the long-standing problem of supercritical *quasi-spinodal* (locus of zero-curvature: $\left(\partial^2 P / \partial\rho^2\right)_{T^{+}} = 0$) formulated by Semenchenko [22]. This author introduced the notion of *above-critical phase transition* in spite of the unified EOS and the Gibbsian concept of a homogeneous equilibrium phase used in consideration. The manifold of gas-like $\left(T^{+},P^{+}\right)$-states at $\rho^{-} \le \rho_c$ located within this locus was termed by him [22,23] *the region of a lowering f-stability*. However, this appro-ach needs the high-level accuracy of EOS to be convincing in its conclusions.

The same problem arises if the widely discussable construction of so-called Zeno-line (locus of the unit *quasi-ideal-gas* (*qig*) compressibility factor $Z_{qig} = 1$) should be obtained [23-25]. It was used by many authors [24-29] for CP-predictions. The construction of Zeno-line covers continuously the whole *f*-range between two asymptotic Boyle's points $\left(T_B, \rho_{Z=1} \to 0\right)$ and $\left(\rho_B, T_{Z=1} \to 0\right)$. Its original definition of T_B-parameter [23] is based on the Boyle's condition accepted for the model-dependent second virial coefficient: $B\left(T_B\right) = 0$ chosen for (*N,V*)-system. So one can use either its approximate estimate for the vdW-fluid, for example, or the more sophisticated interpretation for the LJ-fluid [24,25] and so on:

$$B_{vdW} \approx b - a/kT \qquad (a) \qquad\qquad T_B^0 = a/kb = \left(a/k\right)\rho_B^0 \qquad (b) \qquad\qquad (6)$$

$$\rho_{Z=1} \Big/ \left[\frac{T_B}{C\left(T_B\right)} \left(\frac{dB}{dT}\right)_{T_B} \right] \approx \frac{\rho_{Z=1}}{\rho_B} = 1 - \frac{T}{T_B} \; . \qquad (7)$$

The restrictions of the hardly available accurate knowledge of the third virial coefficient $C\left(T_B\right)$ as well as of the *T*-derivative of the second coefficient calculated at the sought-for Boyle's temperature T_B are obvious. They lead, often, to the rather rough estimates of *B*-parameters and CP-position by Eqs.(6,7) complemented by the rule of «rectilinear diameter».

It was shown recently [15] that such model-dependent uncertainty including that arisen due to the fit of empirical data is inherent for the prescribed linearity of Zeno-line. This feature makes the related Zeno-line with the other prescribed line of rectilinear diameter to be the rather ambiguous methodology. The latter points out supposedly the position of $\rho_c(T_c)$ -value on the actual CXC. Even the rather unrealistic classical variant of the symmetric lattice gas has been exploited [26] for real fluids to develop the predictive scheme for estimation of Z_c-values.

Unfortunately, the relative failure of such formalism in the certain CP-predictions is recognizable not only by the asymptotic singularity of CXC-diameter [32] and/or its evident curvature for such polar fluids as methanol or water [26-28]. Its implicit but essential constraint is just the attempt to connect by the continuous Zeno-line the region of a very dilute fluid $(\rho_{Z=1}\to 0)$ near $(T_B, P_{Z=1}\to 0)$-point with a practically incompressible low-temperature [15,17] liquid $(T_{Z=1}\to 0)$ in the vicinity of $(\rho_B, P_{Z=1}\to 0)$-point. FT-model considers both asymptotic *qig*-uncertainties of the type 0/0 in the formal $Z_{qig}=1$-definition as the questionable consequences of such attempt.

4. The fluctuational type of potentials. We have recently argued [14,33] that even the role of a dominant variable in above *f*-regions ($1/kT$ in the former gaseous *f*-region and ρ in the latter liquid-like *l*-region) is drastically distinctive. The distinction should be reflected in the respective forms of *f*-dependent EOS. We report below the well-known [35-37] virial EOS for g-phase at the very small density truncated after the second virial coefficient $B\left(T^*=kT/\varepsilon\right)$ to emphasize the dominant effect of *a scaled reverse temperature* (l/T^*):

$$Z_{LJ}^{g}-1\simeq\frac{2\pi\rho^*}{3}\left[\left(\frac{l}{T^*}\right)^{D/n}\gamma\left(1+\frac{D}{n}\right)-\left(\frac{l}{T^*}\right)^{D/m}\gamma\left(1+\frac{D}{m}\right)\right]. \tag{8}$$

Here the implied infinite-range Lennard-Jones (*l,n/m*)-potential is:

$$\phi_{LJ}(r)=l\varepsilon\left[(\sigma/r)^n-(\sigma/r)^m\right], \tag{9}$$

$D=3$ – dimensionality; $\gamma(x)$ – Euller's gamma-function, ($l=4, n=12, m=6$) – the realistic most popular set of universal LJ-parameters and the reduced density ρ^*: $2\pi\sigma^3\rho/3=(4v_0)\rho\equiv b\rho$ is equivalent to the vdW-excluded volume.

The FT-estimates of the substance-dependent molecular parameters are principally different from those based just on the experimental *B(T)*-data for *g*-states [36]. One should know CP-parameters and two main PCS-factors ($Z_c, A_c\equiv Ri$) of similarity to predict the standard pair (ε^f, σ^f) of molecular characteristics in *any f-phase for any simple or complicated substance* [11,12,14,15]:

$$\varepsilon^{g,l}=kT_c(1-Z_c)=kT_c-P_c/\rho_c, \tag{10}$$

$$\sigma^g = \left(3b_g / 2\pi\right)^{1/3} = \left\{3\left(A_c - 2\right) / \left[4\pi\rho_c\left(A_c - 1\right)\right]\right\}^{1/3}, \qquad (11)$$

$$\sigma^l = \left(3b_l / 2\pi\right)^{1/3} = \left[1 / \left(2\pi\rho_c\right)\right]^{1/3}. \qquad (12)$$

The last FT-definition is quite important for the formulation of GFA-principle and for its realization by the CVL-diagram methodology. Eq.(12) can be derived from Eq.(11) by the substitution of the universal for all vdW-fluids critical slope $A_c^0 = 4$. So to determine the value of effective diameter σ^l in *l*-phase one should use not only three actual CP-parameters (T_c, P_c, ρ_c or Z_c) from Eq.(10) but also the implied classical vapor-pressure slope: $\left(dP_v^0 / dT\right)_{T \to T_c}$. This FT-definition elucidates the meaningful inherent correlation between two fundamental *vdW*- and *LJ*-models of f-states.

To illustrate this important conclusion of FT-model let us note that Eq.(8) must lead to the Boyle's condition $Z_{LJ}^g \to 1$ by two concomitant trends: $\rho^* \to 0$ and:

$$T_B^* \to l\left[\gamma_{att}\left(3/2\right) / \gamma_{rep}\left(7/4\right)\right]^4 \simeq 3.441. \qquad (13)$$

This known LJ-result [34] provides the following. FT-estimate of the Boyle's temperature:

$$\tau_B = T_B^* / T_c^* = T_B^*\left(1 - Z_c\right) \simeq 2.437. \qquad (14)$$

Its distinction from the larger estimate ($\tau_B = 2.627$) reported by Ben-Amotz and Herschbach [24] is explainable by the “universal” LJ-estimate: $T_c^* \simeq 1.31$ [20,21]. It corresponds to FT-estimate: $T_c^* \simeq 1.412$ obtained namely for Ar. Thus our estimate: $T_B^{Ar} = \tau_B \cdot 150.66$ K $\simeq 367.2$ K is significantly lower than that reported in [24]: $T_B^{Ar} = 408$ K – estimate based on the hardly available data from Eq.(7). At the same time, the vdW-variant ($A_c^0 = 4$) extended on the entire range of *f*-densities $\rho \in \left(0, \rho_B\right]$ leads independently to the similar values of vdW-estimates following from Eq.(6): $\tau_B = 9Z_c \simeq 2.627$. It gives the value $T_B = 395.8$ K usable by many authors [23, 25-27, 29].

The inherent correlation between vdW- and LJ-models [11,12] becomes especially apparent at the discussion of ρ_B-magnitudes. FT-estimate of $\omega_B = \rho_B\left(T \to 0\right) / \rho_c$-value is independent on Zeno-methodology (as well as, the above-discussed FT-estimate of τ_B) and is based on the local FT-EOS derived [14,33] for *l*-phase of LJ-fluid:

$$Z_{LJ}^l - 1 = \frac{l}{T^*}\left(\frac{n}{D}\rho^{*n/D} - \frac{m}{D}\rho^{*m/D}\right). \qquad (15)$$

Its solution at the condition $Z_{LJ}^l = 1$ and the arbitrary T^* provides the value:

$$\omega_B = \rho_B^* / \rho_c^* = \left(\frac{n}{m}\right)^{-D/(n-m)} / 0.1905 \simeq 3.711. \qquad (16)$$

It is the physically meaningful quantity ($\rho_B^* = 1/\sqrt{2}$). It corresponds to the estimate: $2.63/0.713 = 3.689$ (~0.6 %) obtained by Ben-Amotz and Herschbach [24]. They derived it from the theoretical virial coefficients [36] for the infinite-range (i.e. *mf*-) LJ-potential (used at the estimate of $\tau_B = 2.63$ and Zeno-slope 0.713). For Ar these authors obtained the essential deviation: $2.70/0.775 = 3.484$ from the supposedly basic LJ-fluid. Their estimate of ω_B is closer to the Timmermans-vdW estimate [23] $\omega_B = 1/Z_c = 3.42$ which fails, however, for the recommended in [20,21] the "best" estimates: $Z_c^{LJ} \equiv P_c^* / \rho_c^* T_c^* = 0.126/(0.314 \cdot 1.31) = 0.3063$ ($\omega_B^{LJ} = 3.265$).

The independent FT-predictions by Eqs.(15,16) are based on the realistic FT-values of critical density $\rho_c^* = 0.1905$ and critical temperature $T_c^* = 1.412$ for Ar ($Z_c = 0.2919$). They will be used below instead of the conventional LJ-set [20] as the reference LJ-parameters of *mf*-criticality. The aim is to introduce then the well-established FT/LJ-procedure of a *short-range LJ-potential*. It follows from GFA-principle and from FT-estimate of σ^g-diameter by Eq.(11). Hence, the inherent interrelationship between the properties of *g*- and *l*-phases implied by Zeno-methodology does exist in FT-model too. However, it is much more subtle in the latter, which rejects completely the predictive methodology of a *unified* EOS.

In particular, the shape of Z_{LJ}^l-contours for the local FT-EOS (15) derived exclusively for liquid is the very different from that illustrated by [24] for CH_4. Nevertheless, the locus of maxima for the set of Z_{LJ}^l-contours *coincides with the unique FT-predicted isochore*: $\omega_t = 2.624$. It seems to be passing through or nearly the real triple point: $\tau_t = 2.639$ of Ar [18,19]. This FT-isochore of a triple point ω_t forms together with the isochore of a closed-packed solid ω_B the *specific for every substance* range of densities: $\omega_B \div \omega_t = 3.711 \div 2.624$ in which the liquid might certainty exist only as the *metastable* one. Such simple and plausible FT-estimate of two boundaries restricting the acceptable range for a variety of phase transitions between the crystal solid (*cs*), amorphous solid (*as*) and metastable liquid (*ml*) can be very useful for the model calculations.

One may conclude that the common *mf*-restrictions of above EOS-forms are:

(i) the implied infinite range of pair interactions;

(ii) PCS-concept of only two main molecular scales (ε, σ) or thermodynamic scales (*a,b*) while, at least, three independent critical parameters (T_c, ρ_c, P_c) are necessary to indicate the fluids with the interactions deviated a substantially from the reference, *mf*-based LJ-potential;

(iii) the unspecified, strictly speaking, region of EOS-adequacy because, in practice, one compares the theoretical values of *T*-dependent virial coefficients in a step-by-step manner with their "experimental ρ –dependent counterparts" to fix such regions;

(iv) the loss of important thermodynamic information in any two-term EOS arisen due to the restrictive (physically oversimplified) nature of the conventional ideal-gas (*ig*) reference EOS: $Z_{ig}=1$ [34];

(v) an unsatisfactory choice of the more sophisticated but *singular reference models* of *f*-states (hard or soft spheres (*hs* or *ss*), rectangular (*square*) or triangular potential wells (*sw* or *tw*) and so on) in the frameworks of more advanced perturbation expansions.

5. The fluctuational nature of correlation integrals. To explain the general concept of CVL-diagram, let us remind that Zeno-line does not provide any information concerning either the *metastable f*-phases or solid *cs*- and *as*-phases. Its approximate linearity of Eq.(7) in the (T,ρ)-plane stems from the elimination of one $b\rho\equiv\rho/\rho_B^0$-root due to the adopted classical *qig*-condition $Z_{vdW}=1$ in the original vdW-EOS;

$$Z_{vdW}-1=\frac{b\rho}{1-b\rho}-\frac{a\,b\rho}{bkT}=\frac{\rho}{\rho_B^0}\left(\frac{1}{1-b\rho}-\frac{a}{bkT}\right). \tag{17}$$

The same *qig*-condition applied to the local LJ-EOS (8) for *g*-phase and to the local Eq.(15) for *l*-phase leads either to the similar artificial T_B^*-isotherm (instead of T_B^*-point at $\rho_g^*\to 0$) or to the artificial ρ_B^*-isochore (instead of ρ_B^*-point at $T^*\to 0$), respectively. Their artificial alternative is the strict linearity of Zeno-line and the interchangeable role of reduced density $\bar\rho=\rho/\rho_B^0$- and reduced *field* $\bar T=T/T_B^0$-variables following from Eq.(7). Thus, the used by many authors [23,24,29] definition of second virial coefficient $B_{vdW}(T)$ by *T*-hyperbola from Eq.(6a) does not exclude the existence of curvature in the supposedly "rectilinear" CXC-diameter for the original vdW-EOS. GFA principle consider that the main shortcoming of this cubic equation is its implied concept of a unified EOS. One should avoid it to retain the advantages of simplicity and to provide the physically-motivated *f*-description.

Recently we have proposed [12,14,33] to distinguish three different fluctuation (*f*-), mesoscopic (*m*-) and gaussian (*g*-) regimes in dependence on their finite-volume scales chosen at the study of (*N,V*)-system. The respective scale of ranks (from the complicated FT-EOS to its simplest variant) is:

$$Z_{FT}^{f}-1=\frac{b_f(T)\rho-c_f(T)}{1-b_f(T)\rho}-\frac{a_f(T)\rho}{kT}, \tag{18}$$

$$Z_{FT}^{m}-1=\frac{b_f(T_c)\rho-c_f(T_c)}{1-b_f(T_c)\rho}-\frac{a_f(T_c)\rho}{kT}, \tag{19}$$

$$Z_{FT}^{g}-1=\rho\left[\frac{b_f}{1-b_f\rho}-T\left(\frac{\partial B^0}{\partial T}\right)_{\rho}\right], \tag{20}$$

where $B^0(T,\rho)$ corresponds [37] exactly to the original vdW-EOS (17). Its introduction refines the definitions of Boyle's parameters in comparison with Eqs.(6,7):

$$\rho_B=\rho_B^0-\left[T\left(\partial B^0/\partial T\right)_{\rho}\right]^{-1}, \tag{21}$$

$$T_B/T=\rho_B^0 T\left(\partial B^0/\partial T\right)_{\rho}. \tag{22}$$

The smallest volumes are located in the range of *locally-heterophase fluctuations* (*f*-regime) formed by two limits of volume. The lowest boundary is compatible with the incompressible hard-core volume: $\sim d^3$ of the FT-modified *short-range FT/LJ-potential* [11, 14, 33] with three characteristic constants ($\varepsilon,\sigma>d,r_c$ – the cut-off radius of direct interparticle attraction). The reduced value of latter ($\lambda=r_c/\sigma$) normalized by either CP-dependent σ^g from Eq.(11) or by ρ_c-dependent σ^l from Eq.(12) is assumed to be *f*-independent. It forms the highest natural boundary of *f*-regime: $\sim r_c^3$. Any simulations of (*N,V*)-system performed within the above boundaries of volume $V\in\left(\sim d^3,\sim r_c^3\right)$ should be *controllable by the most general FT-EOS* (18) *with the known set of f,T-dependent coefficients* (see [9-12]).

Its specific form of Eq.(19) for *m*-regime (its volumes are less than the correlation volume ξ^3 implies the persistence of *qig*-fluctuations. Thus the conventional *ig*-asymptotic trend at ($\rho\to 0,P\to 0$) [35] is modified in the discussed *f,m*-regimes where $Z_{qig}\to 1-c_f(T)$ or $Z_{qig}\to 1-c_f(T_c)$, respectively. We emphasize, once more, that FT-model, in contrast to the other fluctuation methodologies in which only one extensive quantity *N* or *V* is fixed, studies and simulates the real single-phase *f*-systems with the average density $\rho=N/V$. The posed aim is an investigation of the field fluctuations $\delta T,\delta P$ without any attempts to use the basic *ig*-model of statistical mechanics formulated for the system of material non-interacting point-particles [35] ($\varepsilon\to 0,\sigma\to 0$). Its formal trend to the infinite isothermal compressibility: $\chi_T^{ig}=(\rho kT)^{-1}=P^{-1}\to\infty$ is obvious.

The classical WMG-phenomenology of a first-order phase transition introduces the similar and unrealistic from our viewpoint locus of infinite values $\chi_T\left(\rho,T^{-}\right)$ *termed* spinodal [23]. Such a highly-model definition for a finite-volume *(N,V)-system* at a given density leads to its inaccessibility by experiment [37]. Moreover, itself χ_T-"indicator" of the fluctuation behavior can be formally excluded [12] from the statistical-mechanical system of equations written for the total pair $H(\rho,T)$- and direct $C(\rho,T)$-*correlation integrals* [2,35]:

$$\frac{\rho C(\rho,T)}{1-\rho C(\rho,T)}-\rho H(\rho,T)=0. \tag{23}$$

The spectacular similarity of Eq.(23) with the right-hand-side of vdW-EOS (18) taken under the *qig*-constraint $Z_{vdW}=1$ demonstrates unambiguously that the above-mentioned exclusion of an "extra"-root $\rho C(\rho,T)$ at this condition well lead at $\rho\to 0$ to the apparent *congruous relation* denoted below by the double arrow:

$$H(\rho,T)/C(\rho,T)\Leftrightarrow T_B^0/T. \tag{24}$$

It does not realized along the classical spinodal where: $H_{sp}(\rho,T)\to\infty$ due to its definition. The refinement achieved by Eq.(22) becomes of great importance.

This observation was one of the main stimulus for FT-model [12] to introduce the physically-realistic finite limits of action for correlation integrals (i.e. the *total* correlation radius: $\xi(\rho,T)$ for $H(\rho,T)$ and the *direct* correlation radius of attraction r_c for $C(\rho,T)$). Hence, the implied FT-correction to the *total correlation integral* arisen due to the introduction of fluctuation coefficient $c_f(T)$:

$$C_{FT}(\rho,T)\Leftrightarrow b_f(T)\ (a)\quad H_{FT}(\rho,T)\Leftrightarrow\frac{a_f(T)}{kT}+\frac{c_f(T)}{\rho\left(1-b_f(T)\rho\right)}(b) \tag{25}$$

has everywhere the finite value in the wide compressible *f*-regime even if the inequality $\xi>r_c$ is fulfilled. Respectively, the divergence of $H_{FT}(\rho,T)$ can be realized only in the singular CP ($\rho\to\rho_c,T\to T_c$) for which the limiting correlation radius tends unquestionably to infinity: $\xi_c\to\infty$.

Let us note that the *ρ*-dependent denominator of Eq.(25b) can be expressed [33] in terms of the reduced pressure P/kT_B^0 too due to the interchangeable role of $\bar{\rho}\equiv\rho/\rho_B^0$- and $\bar{T}\equiv T/T_B^0$-variables along Zeno-line:

$$\bar{P}\equiv\frac{P}{\rho_B^0 kT_B^0}=\frac{\rho}{\rho_B^0}\left(1-\frac{\rho}{\rho_B^0}\right)=\frac{T}{T_B^0}\left(1-\frac{T}{T_B^0}\right). \tag{26}$$

This symmetric bifurcation of Zeno-variables noticed and discussed by many authors (see, in particular, [16,17]) makes the proposed in [24] separability by Zeno-line of the region of "soft" fluid from the region of "hard" fluid to be not enough informative. It is interesting to note, in this context, that the proposed by Ben-Amotz and Herschbach interpretation of ρ_B in terms of $C(T_B)$ from Eq.(7) will lead to its divergence $C(T_B)=b/\left[\rho(1-b\rho)\right]$ at $\rho\to 0$.

One should consider undoubtedly the other $(\bar{P},\bar{T})$- and $(\bar{P},\bar{\rho})$-projections at the construction of CVL-diagram. Besides, the alternative dividing line located between *f*- and *l*-regions should avoid the evident crossing of the *cs*- and *as*-regions by the standard Zeno-line. This rather complicated problem is solvable, in principle, by the non-classical FT-notion of an *universal ml-boundary*. It was introduced in the frameworks of CVL-diagram by the *unit relative compressibility line* (i.e. not by the unit compressibility factor line) related to the chosen unit: $\tau = V_0 / V_\tau$ [12] of a fixed initial volume V_0:

$$\frac{\left\langle (\Delta N)_\tau^2 \right\rangle}{\langle N \rangle_\tau} = \left(\frac{\chi_T}{\chi_T^0} \right)_\tau^{ml} = kT\left(\partial \rho / \partial P\right)_{T^{+/-}} = 1 . \qquad (27)$$

This boundary of a metastable liquid (*ml*) is independent on the absolute value of density ρ_{ml}. It corresponds to the achievable balance of *qig*-compressibility and *ml*-compressibility at any local density and local temperature from the total *f*-ranges ($\rho \to 0, \rho_B$) and ($T \to 0, T_B$), respectively. There are two possible strategies of its estimation. The first type corresponds to FT-EOS (19) with three constant T_c-dependent coefficients. They are determinative in the *m-regime of mesoscopic volumes* located between $\sim r_c^3$- and $\sim \xi^3$-limits: $\sim r_c^3 < V <\sim \xi^3$ (of course, if the respective difference $(\xi - r_c)$ exists). It appears undoubtedly in the small near-critical region in which the density fluctuations of range longer than that of the intermolecular attraction become significant. The second type relates to the much wider *g-regime of gaussian fluctuations in the macroscopic finite volumes*: $V >\sim \xi^3$. It corresponds to vdW-EOS (20) which is applicable, however, in accordance with GFA-principle [11] to both *g*- and *l*-phases *separately*. Only in this *g*-regime as well as in its local realizations for a dilute *g*-phase and for a low-temperature *l*-phase by Eq.(15) the *qig*-constraint: $Z_{qig} = 1$ is fulfilled.

Conclusions. The proposed finite-range type of fluctuation potential provides the promising tool for the simulation mesoscopic study of heterogeneous systems. In the small vicinities of a critical point and coexistence curve the obtained by the standard MD- or MC- simulations information can be, in principle, inaccurate or even qualitatively distorted. The reason of both potential drawbacks is the possible misinterpretation of the simulated runs and properties. One assumes usually that the standard nano-scales of volume and the typical pico-scales of time concern to the average properties of a macroscopic system. This assumption needs, however, the verification in the above hardly testable by the direct experiment regions of a phase transition. The ap plication of the classical *binonal/spinonal* concepts based on the gibbsian strictly homogeneous phases becomes asymptotically questionable in the scales of mesoscopicity. More accurately, the traditional mean-field VLE-diagram of equilibrium between the model coexistent infinite-volume/ infinite-lifetime phases of the different but homogeneous densities and entropies is the highly model concept. The physics of aerosol systems seems to be the appropriate field for the thorough verification of the proposed fluctuation formalism.

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Источник мезоскопических, критических и Бойлевых сингулярностей симулированных флуктуационным потенциалом.

АННОТАЦИЯ

Предложенная недавно методология конгруэнтной пар-жидкостной диаграммы, использована для предсказания всего интервала равновесия жидкость-пар в тестовом флюиде-аргоне. Методология основана на сформулированном ранее принципе глобальной флюидной асимметрии, в котором отвергнута распространенная идея единого уравнения состояния, обшего для обеих, как подкритической, так и надкритической областей существования. В противоположность обычной пар-жидкостной диаграмме, локализованной между критической точкой и тройной точкой, конгруэнтная диаграмма описывает значительно более широкий интервал флюидных состояний, простирающийся между двумя обобщенными точками Бойля (при исчезающе-малой плотности при исчезающе-малой температуре), предсказанный с помощью модели флуктуационной термодинамики. Установлено новое расположение, форма и обратный знак кривизны для характеристик классической спинодали. Новая граница метастабильной жидкости не проходит через критическую точку и может быть определена во всем интервале флюида, включая его сверхкритическую часть.

Классический, но не соответствующий теории среднего поля источник сингулярностей на основе глобальной асимметрии может быть установлен без привлечения феноменологии скейлинга. Тем не менее, полученные данные (уплощение в околокритической области зависимости температуры от ортобарических плотностей) соответствуют результатам теории критической области. Основные идеи гибссовской теории равновесий между двумя идеализированно-однородными сосуществующими фазами достигает в этой области предела своей применимости.

Ключевые слова: *конгруэнтная пар-жидкостная диаграмма, граница метастабильной жидкости, глобальная флюидная ассиметрия.*

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Джерело мезоскопічних, критичних і Бойлевих сингулярностей симульованих флуктуаційним потенціалом.

АНОТАЦІЯ

Запропонована недавно методологія конгруентної пар-рідинної діаграми, яка використана для передбачення всього інтервалу рівноваги рідина-пар в тестовому флюїдіаргоні. Методологія заснована на сформульованому раніше принципі глобальної флюїдної асиметрії, у якій відкинута поширена ідея єдиного рівняння стану, загального, як для підкритичній, так і надкритичної області існування. На протилежність звичайній пар-рідинній діаграмі, яка локалізована між критичною точкою і потрійною точкою, конгруентна діаграма описує значно ширший інтервал флюїдних станів, що тягнеться між двома узагальненими точками Бойля (при зникаюче-малої густини і при зникаюче-малої температурі), передбаченої за допомогою моделі флуктуаційної термодинаміки. Встановлено нове розташування, форма і зворотний знак кривизни для характеристик класичної спінодалі. Нова межа метастабільної рідини не проходить через критичну точку і може бути визначена в усьому інтервалі флюїду, включаючи його надкритичну частину.

Класичне, але не відповідне теорії середнього поля джерело сингулярностей на основі глобальної асиметрії може бути встановлено без залучення феноменології скейлінга. Проте, отримані дані (сплощення у близько критичної області залежності температури від ортобаричної густини) відповідають результатам теорії критичної області. Основні ідеї гібссівській теорії рівноваг між двома ідеалізовано-однорідними існуючими фазами досягає в цієї області межі своєї застосовності.

Ключові слова: *конгруентна пар-рідинна діаграма, межа метастабільної рідини, глобальна флюїдна асиметрія.*