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Supercritical heterogeneous nanostructure of fluids. Part 1. Diagram of fluctuation transitions in non-gibbsian phases

New concept of a supercritical fluid (SCF) region is proposed to recognize the set of the recent experimental observations and the numerical model results, in which the conventional asymptotic scaling theory and its crossover extension achieve the limit of applicability. An existence of the heterogeneous steady lattice-type nanostructure in the wide ranges of supercritical parameters termed the non-gibbsian fluid (NGF)-phase was hypothesized by one of authors (V.B.R.) in the framework of FT (fluctuational thermodynamics)-model. It was argued by FT-model that the similar NGF-phase exists also below the critical temperature in any real finite-volume VLE-transition. The present work establishes the location of exact boundaries for the supercritical lattice-type NGF-phase confirmed by the set of recently published experimental results and simulations. In brief, the total supercritical region consists of the dilute gas-like (gl) gibbsian (homogeneous) phase (GPh) and the dense liquid-like (ll) gibbsian (homogeneous) phase (GPh) separated one from another by the heterogeneous (at least, in nanoscales of a finite volume) vapor-like (vl) NGF-phase. The practical usage of a such structure may be quite promising in many areas of applications. It is certainly non-restricted by only the known advances of a supercritical extraction processing.

Keywords*: supercritical fluid, heterogeneous (non-gibbsian) phases, model of fluctuational thermodynamics.*

1. Introduction. There are several interesting evidences [1-8] that the certain global segment of the supercritical fluid (SCF) region in a pure substance phase diagram might be the *steady heterogeneous* by its physical nature, at least, in the nanoscales of volume. From the phenomenon of near-critical opalescence described by the *gaussian* Ornstein-Zernike theory one may suppose the existence of its extension in the wider range *f*-states. Such a *non-gibbsisan* bi- or tri-modal type of SCF-behavior can be termed *the region of a higher order (second) fluctuation phase transition* (FT2) to distinct it from the *deterministic* notion of a second order *phase transition* PhT2. It should be segregated by two specific boundaries from the region of *gibbsian phases* (GPh). The different attempts of the similar specification have been proposed. As a rule, the known *Widom's line* is involved by the adepts of the crossover transformation [1, 2] developed to extend the applicability of an asymptotic scaling theory to the wide CP (critical point)-vicinity. In this case, the complementary role of the *critical isochore* as the second boundary of SCF-peculiarities is usually adopted. Another example of a such construction is two coupled lines of the *excluded volume* (EV-) and the *available volume* (AV-) *percolation transitions* hypothesized recently in the SCF-region by Woodcock [3]. This author has rejected even the itself existence of a singular classical CP for the first-order phase transition (PhT1) (gas-liquid) related conventionally to the type of second-order (PhT2)-states. Authors [4] have gone far beyond the equilibrium concept of a general phase diagram. They postulated the

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existence of substances *without any presence of a gas phase* (ionic liquids or polymers, for example) as well as those (simple and/or complex fluids) in which the traditional vapor-liquid equilibrium (VLE) exists with an exact CP-location. In both cases the specific *dynamical Frenkel's line* has been predicted up to the extreme pressures, mainly by the Lennard-Jones' (LJ)-fluid simulations. It divides the whole fluid region onto the subregions of two liquid phases (I and II) with the essential distinctions in a dynamical liquid-type structure. This set of revelations can be added to the direct MD-observation of the heterogeneous density distributions in the widely extended "compressible" [5] SCF-region relevant to the processes of supercritical extraction.

The common feature of above works [1-5] is the adoption of deterministic VLE-transition which should be supposedly described below CP (if it exists, of course [4]) *only by the unified for both coexistent phases EOS*. This concept originated by van der Waals (vdW) himself fails, completely, at the description of *any heterogeneous states such as saturated, moist or overheated vapor,* for example. Nevertheless, it is implied by all aforementioned works, which indicate themselves, in fact, the reality of *heterogeneous* (*non-gibbsian*) *SCF-structures* and lattice-type *fluctuations*.

The aim of present work is to explain a possibility of the alternative approach to the SCF-description and to its promising usage stimulated by the FT (*fluctuational thermodynamics*) model [6-9]. It rejects, at the start of SCF-consideration, the widely spread classical vdW-concept of a unified EOS, which leads, exclusively, to the notion of a single homogeneous (gibbsian) SCF-phase. At the same time, the cubic form of the 3-coefficient modified vdW-EOS termed FT-EOS [6] may be applied, *separately*, to the both hypothesized here GPh-regions of supercritical *gas-like* (*gl*) and *liquid-like* (*ll*) behavior with two different sets of above coefficients. The present work is formed by two parts. Our goal below is to demonstrate the highly probable existence of a heterogeneous SCF-region (i.e. FT2) located between these about homogeneous *gl*- and *ll*-phases. Another goal is to discuss, in brief, the promising perspectives of its practical application arising due to the unique thermophysical properties observable in this region.

In Section 2 of this part the main features of the proposed global *congruent fluctuation FT-diagram* of a pure fluid extrapolated in SCF-region are represented. The simple methodology of the *vdW-geometric contours* has been used to specify approximately the external boundaries of FT2. The comparison with the results reported by other authors for LJ-fluid corroborates, in general (Section 3), the discussed here configuration of FT2-region. We represented our conclusions in Section 4. The fundamental role of vdW-fluid as the adequate reference physical model of SCF-region for real fluids has been elucidated.

2. Global congruent fluctuation diagram of vdW/LJ-fluid and location of FT2 in SCF-region.

2.1. Terminology and main definitions. The known classification of phase transitions (PhTs) proposed by Ehrenfest long ago separates the first from second order in the context of gibbsian homogeneous phases (GPh). The discontinuity of mass density and caloric densities along the coexistence curve (CXC) indicates the *first-order phase transition* (PhT1) while the smooth disappearance of such distinction leads to the van der Waals (vdW)-Andrews definition of a classical CP. It is conventionally related to the *second-order phase transition* (PhT2) but, more accurately, the coupled discontinuity (divergence) of the isothermal compressibility β_T and isobaric heat capacity C_P has to arise as its main sign. It is easily to demonstrate [3, 6] that the famous *Gibbs' phase rule* fails locally at CP just due to the above classical CP-definition derived by van der Waals from his main concept of a fluid (*f*) continuity. It implies the *continuous transformation of* local *density* at any temperature within *the interface layer* between two coexistent stable GPhs of gas (*g*) and liquid (*l*). Their metastable continuation is also admissible. The real steady *vl*-states located within the spinodal are described by the classical VLE-theory as unstable ones.

We have used in this work the alternative notations of FT-model [6-9]: *FT1* instead of PhT1 as well as FT2 instead of PhT2 (its presence as a NGF-phase in SCF-region has been earlier hypothesized). The aim is to emphasize their principle difference, since both FT-ones: FT1 and FT2 admit the existence of heterogeneous fluctuational NGF-phases at both *sub*- and *supercritical* states. Below T_c, the presence of a such subcritical NGF-phase termed the *interphase* was confirmed for many substances by our previous investigations [8, 9, 17, 18]. We have used for its presence the term of *congruent vapor-liquid* (CVL)-*diagram* to distinct it from the traditional VLE-diagram constructed, exclusively, for GPhs i.e. the gibbsian infinite-volume phases. The similar result above T_c follows directly from the main concept of FT-model [6, 7] developed to *study all types of a fluid state in a finite volume*. This approach is different from the well-known proposed by Fisher techniques of the *finite-size scaling*. The latter method is directed, mainly, to include the finite-volume effects in the methodology of an asymptotic CP-vicinity. In the framework of FT-model, one should suppose that the classical mean-field results of the fluid theory for gibbsian phases become applicable only at the thermodynamic infinite-volume limit of the statistical mechanics. In any real, i.e. *finite-volume f*-system a possibility of the heterogeneous fluctuations exists. Hence, it has to be taken into account, especially, in the regions of deterministic PhTs.

As a result of above arguments the traditional *binodal locus* of VLE-diagram is not shown in Figs. 1-3 where two other PhT-lines of *sublimation* and *fusion* are also absent. To provide the full view of hypothesized FT2-region we have represented it by three (π,ω)-, (π,τ)- and (τ,ω)-projections together with the other known contours. One can consider the reported below results as an attempt to construct the global congruent fluctuation FT-diagram on the base of *combined thermal and caloric EOSs* but without any appeals to the strictly equilibrium Helmholtz's and/or Gibbs' thermodynamic potentials.

For the convenience of readers, the used conditions of contours are recollected in Table 1 for all six comparable lines. They were applied here to the reference reduced PCS (principle of corresponding states)-form of vdW-EOS to found the basis for the further corrections in terms of FT-EOS [6-9]. The simplest vdW-form is discussable, as a rule, by a variety of authors as an example of the mean-field criticality. We claim now that this viewpoint is rather elusive. It is completely based on the adopted analytic asymptotic expansion of vdW-EOS. This procedure is, however, not

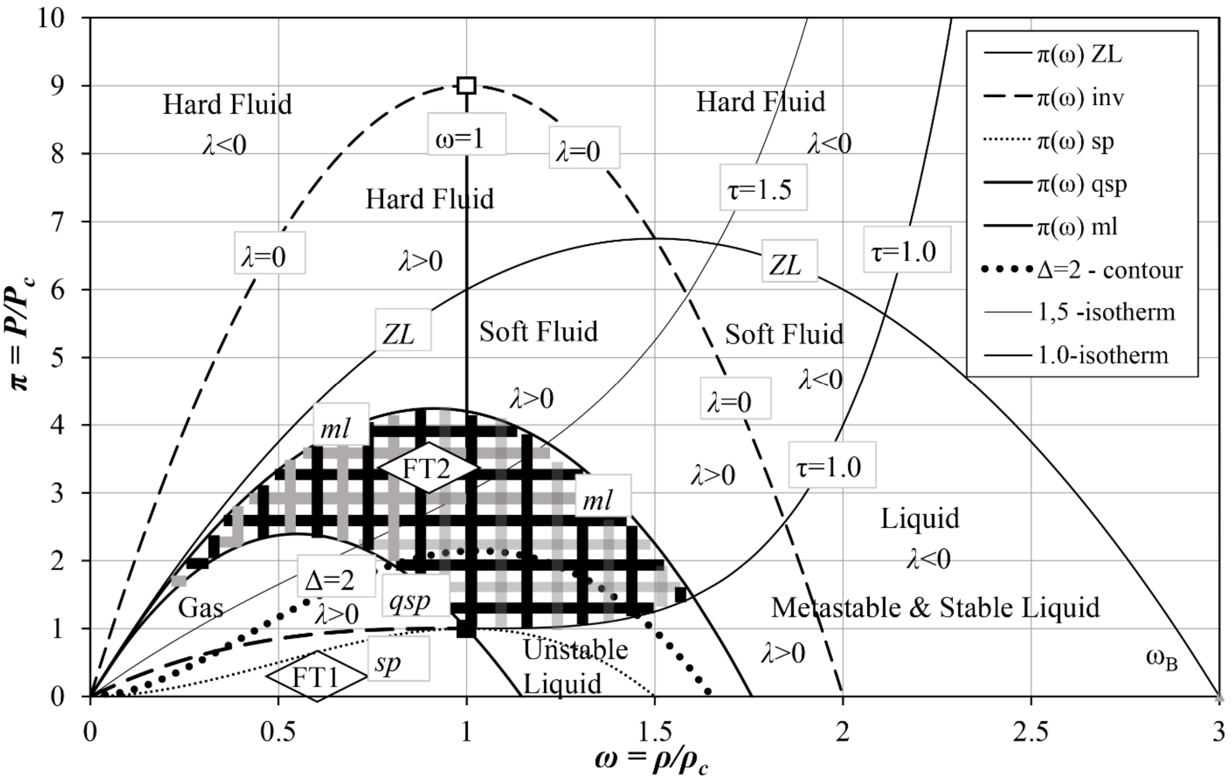


Fig. 1. Pressure-density (π, ω)-projection of FT2-region (shown by decorated lattice) represented in terms of reduced variables: $\pi = P / P_c$, $\omega = \rho / \rho_c$ for a real fluid (see Table 1 and text for its explanation)

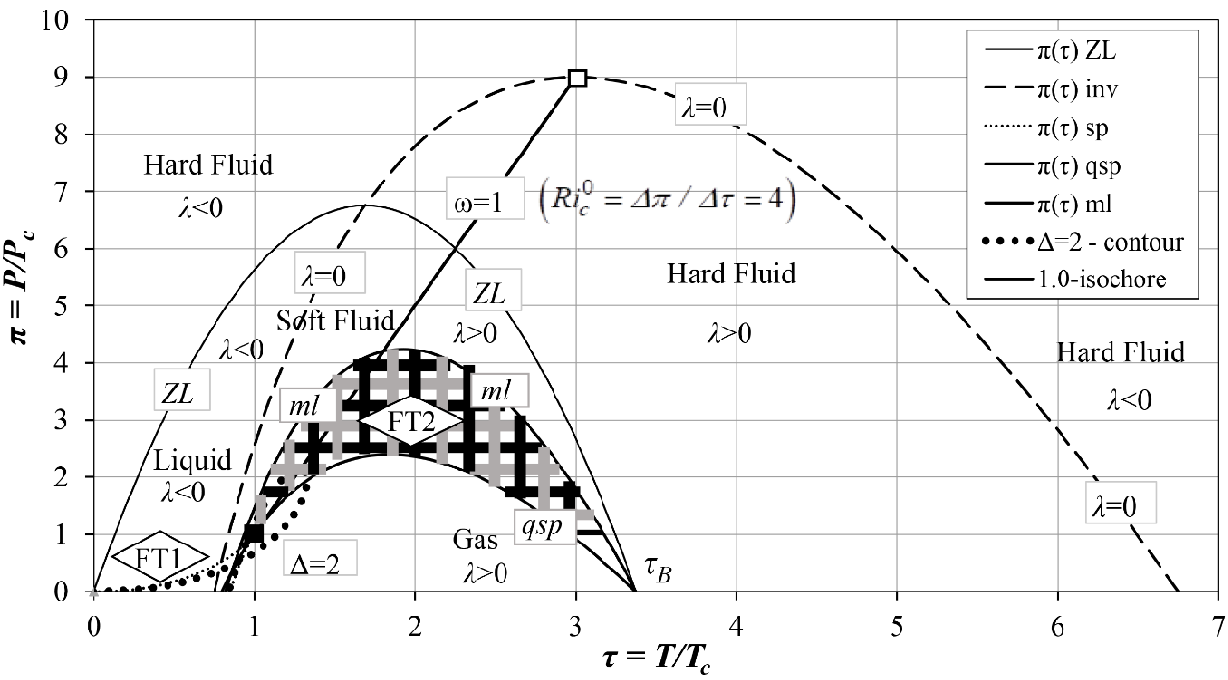


Fig. 2. Pressure-temperature (π, τ)-projection of FT2-region (shown by decorated lattice) represented in terms of reduced variables: $\pi = P / P_c$, $\tau = T / T_c$ for a real fluid (see Table 1 and text for its explanation)

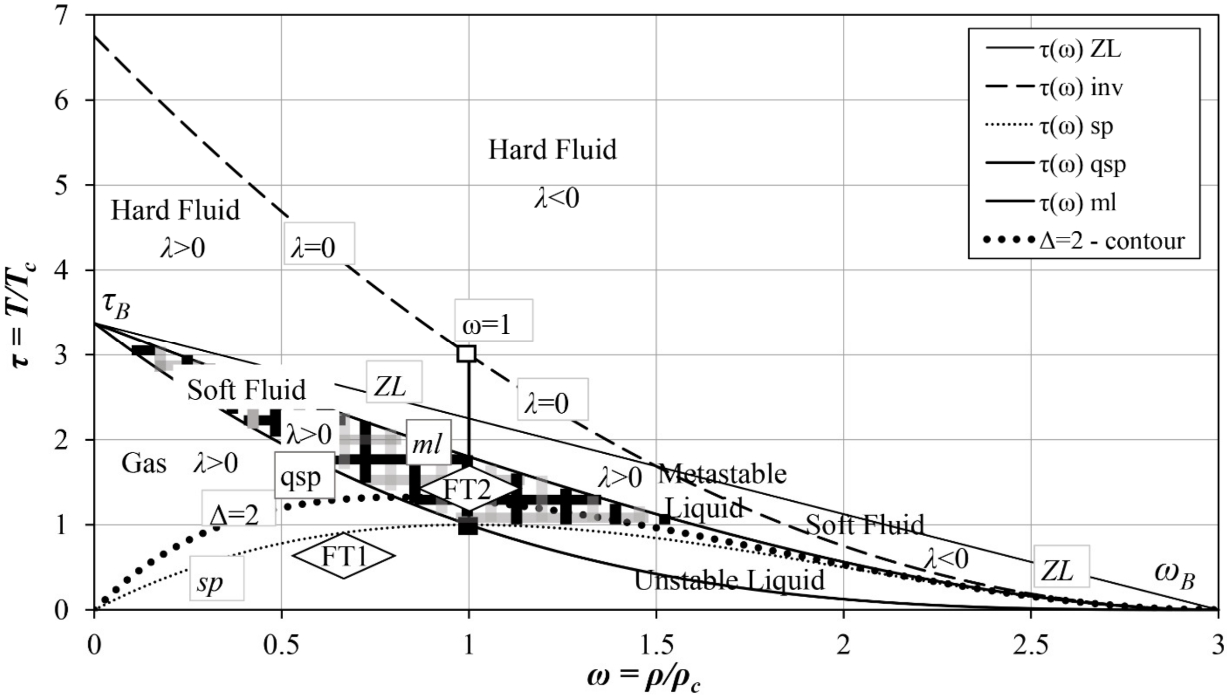


Fig. 3. Temperature-density (τ,ω)-projection of FT2-region (shown by decorated lattice) represented in terms of reduced variables: $\tau = T/T_C$, $\omega = \rho/\rho_C$ for a real fluid (see Table 1 and text for its explanation)

applicable just in the vicinity of actual CP. Hence, the known set of so-called classical critical indices: $\alpha_0 = 0$; $\beta_0 = 1/2$; $\gamma_0 = 1$; $\delta_0 = 3$ has nothing in common, strictly speaking, with the vdW-EOS itself. Besides, this famous PCS-form describes by its *subcritical part* of critical isotherm $\tau = 1$ the *actual g-branch of CXC* for many substances *within the experimental uncertainty* [6-9]. To illustrate such a striking vdW-feature of critical isotherm at $\pi \le 1$ we have shown it by the bold dashed curve together with the rest *supercritical part* of $\tau = 1$-curve at $\pi > 1$ on the single (π,ω)-projection.

2.2. Contours for definition of FT2-region in SCF-area. We start the discussion from the most usable in the heat energetics, for example, projection (π,ω). It contains in Fig. 1 six lines termed (see Table 1) by us: 1) quasispinodal (qsp); 2) metastable liquid (ml) boundary; 3) inversion curve (inv); 4) Zeno-line (ZL); 5) spinodal (sp); 6) contour of gaussian fluctuations (Δ). They form three characteristic pairs of coupled contours: *qsp/ml*, *ZL/inv*, *sp*/Δ. First one i.e. *qsp/ml* segregates FT2-region of NGF-phase depicted by the decorated lattice. Its lower boundary (*qsp*) has been often discussed as the smooth continuation in SCF-area of the special *ridge* for the contours of constant gaussian Δ-fluctuations [11, 12, 19, 20]. Another its plausible interpretation is provided by the known *Widom's line* with the expressible maxima of second derivatives β_T, C_P, α_P (isobaric expansion) following from the chemical potential $\mu(T,P)$ alongside the *qsp*-line. This interpretation is not completely consistent, however, [4] with the available near-critical experiment on $C_P(\pi,\omega)$-dependence, since it demonstrates the locus of maxima sooner alongside the critical isochore $\omega = 1$.

The upper boundary of FT2-region i.e. *ml*-contour was introduced by FT-model. It is crucial characteristic contour to confirm the important concept of a metastable *ll*-phase existing not only below T_c but, also, above it. In the certain meaning, *ml*-boundary of FT-model is the realization of the brilliant Bernal's idea [3, 20]. It is related to the hypothesized wide-range metastability of liquid existing up to the *gl*-phase states of a vanishing density $\omega \to 0$ too. Let us note also the evident common geometric similarity of two other characteristic pairs (*ZL/inv*- and *sp/*Δ-) of contours. This is observable only in (π,ω)-projection composed of the mechanical quantities. All six curves demonstrate in this case the domelike shape with the "*pseudo-critical maximum*" at the respective top-points.

This total similarity fails only for the classical *sp/*Δ-pair of gaussian contours in the next (π,τ)- and, especially, (τ,ω)-projection (Figs. 2,3). The closed loop of the chosen here, by chance, $\Delta = 2$-contour ($\Delta = 1$-contour corresponds to the *unrealistic ideal-gas EOS-model*) is degenerated into *a singular vdW-Andrews* CP at the top of classical *sp*-contour on the (π,τ)-plane. Such shape of CP-degeneracy is the common feature of any other gaussian Δ-contour at its trend to $\Delta \to \infty$. Just this simple observation provides, to our mind, the basis for the crossover expansion of any asymptotic nonclassical criticality [1, 2]. The particular phenomenological modification of vdW-EOS in the framework of the gaussian-contours (see below Fig. 5) approach was proposed long ago by Fox [10] to include the configurational heat capacity.

FT-model's pair of FT2-boundaries (*qsp/ml*) is *qualitatively different* from the above-discussed gaussian *sp/*Δ-pair of FT1 not only in the (π,τ)-plane (Fig. 2) but also in the (τ,ω)-plane (Fig. 3). The presence of non-mechanical thermal variable τ is here crucial. The latter is the widely discussable in the context of ZL-contour [13-16]. The used long ago by Nedostup [15] concept of the so-called ideal curves was extended, then, by Ben-Amotz and Hershbach [13] as well as by other authors, in particular [14, 16], for the CP-predictive aims. We represented ZL-contour of the pseudo-ideal-gas behavior $\left(Z^{ig} = 1\right)$ as well as the inversion curve (*inv*) with the sign of its effect ($\lambda \lesssim 0$) in Figs. 1-3 only for information of a reader. These curves intersect on all projections and their impact on the predicted global congruent FT-diagram with the supposed presence of NGF-phase is negligible. The only non-trivial thing, in this context, for vdW-fluid is the consideration of both Boyle's points: $T_B^{vdW} = (a/bR)$- and $\rho_B^{vdW} = (1/b)$-vicinities, namely, in the (π,τ)- and (τ,ω)-planes. It seems that the widespread belief in the crucial role of the second virial coefficient $B(T)$ at $T \to T_B$ can be, at least, called in question if one takes into account our results represented in Figs.2,3 [17] at the respective density limit $\omega \to 0$.

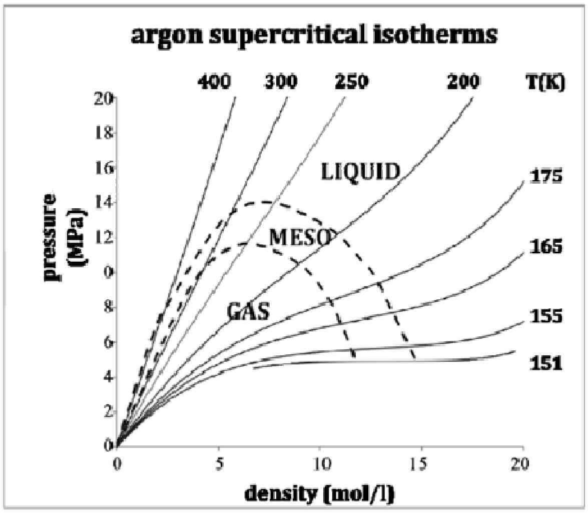
3. Comparison with the relevant SCF-investigations.

3.1. Simulated pro and con of NGF-existence in SCF-area. Let us note that it is impossible to discuss a variety of published relevant articles on SCF-problems ([1-

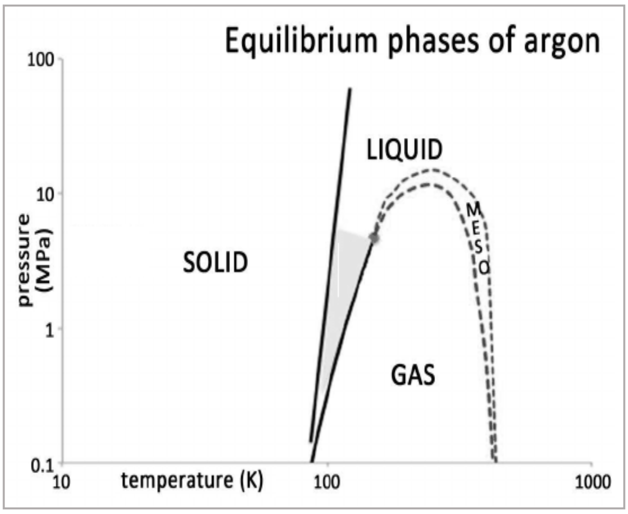
23] and many others) in any detail within this brief Section. However, their authors (we refer interested readers for detailed discussions to the list of cited works) have adopted, except for some exclusions [3, 5, 8], the orthodox vdW-Andrews concept of a supercritical behavior. Accordingly to it, one should consider above T_c and/or P_c only a single gibbsian phase (GPh) in which the supposedly continuous transformation of *gl*-states into *ll*-states and *vice versa* is possible along the supercritical isotherms and/or isobars. FT-diagram demonstrates (Section 2) that in a finite-volume *f*-system such a mean-field possibility is the highly idealized assumption in the wide ranges of (*P,T*)-parameters. We introduced the imaginable *decorated* lattice for the illustrative goal to emphasize the virtual heterogeneous structure of NGF-phase. It is formed, in accordance with FT-model, by two *coupled percolation transitions* depicted by black for *ll*-states and by grey for *gl*-states lattices. The white "voids" correspond to the about "empty" *ig*-states located inside of NGF-structure.

It is naturally to compare our construction with those for the heterogeneous SCF-states shown in Fig. 4ab and simulated by Woodcock [3] as the *meso-states*. Our interpretation of NGF- and *ll/gl*-states in Figs. 1-3 is the quite different from that proposed for the range located between upper and lower boundaries of AV- and EV-states, respectively, in [3]. The latter implies the crucial influence of a solid (*s*) molecular core on the *f*-behavior of vdW/LJ-systems. The standard vdW-terminology supposes namely a combination of "empty" (available) volumes (*v-b*) as well as of hard (excluded) volumes *b* in any *f*-state of vdW-fluid. This physically plausible concept is, however, too restrictive to imitate the heterogeneous phases. The overestimated role *either* of the only short-range attractive interactions in the asymptotic CP-vicinity [1, 2] *or* the only singular very short-range hard- (or soft-) core repulsions in the mean-field area of a triple point [3,4] is the typical feature of many SCF-investigations. Namely it leads, from our viewpoint, to the *made-up contradiction between the scaling and classical PCS-theories of CP*-vicinity and, even, to the "revolutionary" rejection from the CP-existence in the vdW-Andrews meaning [3]. In particular, we refer here the interested reader to the exciting polemics about itself CP-existence arisen recently between the adepts of the scaling theory [1, 2] and Woodcock [3] (he reported it in the open access journals). The latter author carried out the enormous set of SCF-investigations based on the comparison of the very accurate *but still unified* NIST-EOS of Ar, CO_2, H_2O with the set of the relatively simple molecular model's simulations (hard-spheres, square-well, augmented vdW, LJ-fluids) "to argue" the absence of a vdW-Andrews' CP. This fictitious concept is not completely novel because yet Michels et al [22] discussed its reality long ago in the well-known experimental work of 1936 on the criticality and CXC-properties of CO_2.

On the other side, it is remarkable, to our mind, result that the congruent FT-diagram (Section 2) based here on vdW-EOS corroborates by Figs. 1,2, at least, qualitatively, all bound-shapes reported in [3] (see Fig. 4) for the so-called *putative phase-diagram with the special region of mesophase* (in terminology proposed by Woodcock). This result has been obtained in the present work for Ar, CO_2, H_2O and any other *f*-system *without appeals to an absence of a singular CP*. Moreover, the well-studied experimentally and reliably approximated by the fundamental NIST-EOS real SCF-systems are adequately described in the present work by PCS-form of



a)



b)

Fig. 4. Scheme of mesophase [3] based on the fundamental NIST-EOS for argon in the (P,ρ)- and (P,T)-plane (in logarithmic coordinates) represented here for comparison with the predicted FT2-region in Figs. 1 and 2, respectively

Eqs.(1-9) from Table 1. They were derived for the simplest *supposedly mean-field vdW-EOS (!)*. It describes adequately at the condition $\tau = 1$ [7] the whole g-branch of Ar, CO_2, H_2O, … (see the bold dashed curve at $\pi < 1$ in Fig. 1):

$$\pi^{vdW} = \frac{8\tau\omega}{3-\omega} - 3\omega^2 . \tag{10}$$

Its known drawbacks are, of course, the universal and unrealistic values of two coupled vdW-criteria of similarity: $Z_C^0 = 3/8$, $Ri_c^0 = 4$ for all f-systems which need the revision. Let us note, in addition, that the logarithmic scales of P and T coordinates (Fig. 4b) used in [3] are the distorting factors which prevent from the more detailed comparison of Figs. 1,2 and Fig. 4ab.

3.2. Can NGF-concept be trusted for real SCFs - ? FT-EOS introduces the variant of vdW-EOS revision [6-8] for SCF-region performed in terms of two actual substance-dependent PCS-criteria [8, 18]: the crit-ical compressibility factor Z_c and the critical Riedel's factor Ri_c:

$$\pi^{FT} = \frac{Ri_c^2\tau\omega}{2\left(Ri_c - 1\right) - \left(Ri_c - 2\right)\omega} - \left(Ri_c - 1\right)\omega^2 . \tag{11}$$

The substitution of vdW-value $Ri_c^0 = 4$ transforms Eq.(11) into the original form of Eq.(10) but the respective transformations of gaussian Δ-fluctuations seems here to be even the more informative [8]:

$$\Delta^{FT} \equiv \frac{\left(\Delta N\right)^2}{\overline{N}} = \frac{\tau}{Z_c}\left(\frac{\partial\omega}{\partial\pi}\right)_\tau^{FT} = \frac{\tau A\left(Ri_c,\omega\right)}{2Z_c\left(Ri_c - 1\right)\left[Ri_c^2\tau - A\left(Ri_c,\omega\right)\omega\right]} , \tag{12}$$

where (see also Eq.(11)):

$$A\left(Ri_c,\omega\right) = \left[2\left(Ri_c - 1\right) - \left(Ri_c - 2\right)\omega\right]^2 . \tag{13}$$

It becomes the equality: $A(Ri_c, \omega = 1) = Ri_c^2$ along the *actual critical isochore*. Hence, FT-EOS (11-13) provides the asymptotic *gaussian* SCF-divergence in the vicinity of actual CP $(\omega_c = 1; \tau \to \tau_c = 1)$ and explains the phenomenon of near-critical opalescence:

$$\Delta^{FT}(T, \rho_c) = \frac{\tau}{2Z_c(Ri_c - 1)(\tau - 1)} = \frac{T}{2Z_c(Ri_c - 1)(T - T_c)}. \tag{14}$$

For comparison, Sengers and co-authors [2] had applied, as the first step of the crossover vdW-transformation the classical (*cl*) gaussian fluctuation contribution to the isothermal compressibility $\beta_T(T, \rho_c^0)$ calculated along the mean-field isochore: $\rho_c = \rho_c^0$ of Eq.(9) (see Table 1):

$$\Delta^{cl}(T, \rho_c^0) \equiv \rho_c^0 kT\beta_T = \frac{1}{6Z_c^0}\left(1 + \frac{C_v(T, \rho_c^0)}{2k_B Z_c^0}\right) \cdot \frac{T}{T - T_c}. \tag{15}$$

Then, the “shifted” critical temperature to its actual value: $(T_c - T_c^0)/T_c^0$ was used by the field variant of RG-theory. The aim had been to obtain the prescribed nonclassical exponent for compressibility ($\gamma > \gamma_0 = 1$) by the involvement of the actual Z_C-value instead of $Z_C^0 = 3/8$ from Eq.(15).

Another phenomenological attempt to convert vdW-EOS so as to incorporate the Ising-like criticality was performed by Fox [10]:

$$\pi^F = \frac{3\tau\omega}{(3 - \omega)Z_c} - \frac{3\omega^2}{\tau^{1/2}}. \tag{16}$$

This vdW-modification *of a unified EOS* provides the rather realistic estimates of the Riedel’s substance-dependent PCS-criterion of similarity at the actual CP $(\omega_c = 1; \tau \geq 1)$:

$$Ri_c^F = \frac{3}{2}\left(\frac{1}{Z_c} + \frac{1}{\tau^{3/2}}\right). \tag{17}$$

Comparison of the contours from [10] in the (π, τ)- and (τ, ω)-planes with the Δ-contour $\Delta = 2$ depicted in Figs. 2, 3 shows, however, the gaussian nature of such vdW-modification.

The equation derived long ago by Levanyuk for PhT2 in *s*-phases and used by Sengers and co-authors [2] for SCF supposes the divergence of $C_v(T, \rho_c^0)$ with the gaussian exponent $\alpha = 1/2$ too:

$$C_v(T, \rho_c^0) = C(Z_c^0, ...)\left(\frac{T}{T - T_c^0}\right)^{1/2}, \tag{18}$$

where the dimensional amplitude $C(Z_c^0, ...)$ is irrelevant for our discussion. Fig. 5 taken from [8] represents the detailed comparison of macro- and mesoscopic gaussian fluctuations of density. It confirms the concept of heterogeneous fluctuations existing in SCF-area. The respective Δ-contour was earlier called the *pseudospinodal* curve [8].

FT-model provides also the following system of two gaussian approximations for heat capacities along the actual ρ_c at $\tau \geq 1$:

$$C_P(T,\rho_c) = C_P^{ig}\left(\frac{\tau}{\tau-1}+1\right) \quad (a) \qquad C_v(T,\rho_c) = C_v^{ig}\left(\frac{\tau}{(\tau-1)^{1/2}}+1\right) \quad (b). \quad (19)$$

The index *ig* corresponds to the *ig*-model in which *i*-degrees of molecular freedom: $C_P^{ig} = (i/2+1)k_B$, $C_v^{ig} = (i/2)k_B$. These results are written for the simple approximate caloric EOSs based on the knowledge of $C_P(P,T)$-values for enthalpy *h* and of $C_v(T,\rho)$-values for internal energy *e*:

$$h(T,P) = e(T,\rho) + P/\rho \to h^{ig}(T,P^{ig} \to 0) = e^{ig}(T,\rho^{ig} \to 0) + k_B T. \quad (20)$$

It was interesting to compare in the (T,ρ)-plane of Fig. 3 the about linear contour for vdW-fluid $h^{ig}(T,P) \approx e^{ig}(T) + P^{vdW}/\rho$ with that predicted by Nedostup [15] and simulated by Desgranges and co-authors [14] for the LJ-fluid (including the additional electrostatic interactions adopted between the point-atom charges). While such comparison (it is not shown in Fig. 3) is only of passing interest for the main here discussion of FT-diagram, its results confirm qualitatively the thermodynamic consistency not only of FT-EOS (11) but also of vdW-EOS (10) itself up to the actual CP.

The comparison of Δ^{FT}-contours following from Eqs.(12-14) and represented in Fig. 5 (taken for C_2H_4, CO_2, C_6H_6, H_2O from [8]) with those calculated by Nishikawa et al [11,12] for vdW-fluid:

$$\Delta^{vdW} = \frac{4\tau(3-\omega)^2}{36\tau - 9\omega(3-\omega)^2} \quad (21)$$

seems to be also rather informative. Only the formers predict the supercritical divergence of gaussian fluctuation located between the actual T_c- and vdW T_c^0-values (see also the crossover approach of Eq.(15) developed in [2]). We termed earlier the Δ^{FT}-contours as *pseudospinodal* (*psp*) [8] since the similar divergence of gaussian fluctuations of density is observable alongside the classical *sp*-contour at $T \leq T_c$ shown in Figs. 1-3. At the same time *qsp*- and *ml*-contours of FT2-region demonstrate *the qualitatively different shape* in comparison with the gaussian Δ^{vdW}-contours (Table 1). Namely, these curves segregate the wide segment of SCF-plane identified by FT-diagram as the NGF-phase and FT-2 region, respectively. Taking into account their crucial role for the substance-dependent calculations, we represented below the FT-refinement of *ml*-contour Eq.(2) for vdW-fluid just in the (τ,ω)-plane:

$$\tau_{ml} = \frac{18Z_c(1-Z_c\omega)^2}{2-Z_c\omega}. \quad (22)$$

It seems that the revealed so point of intersection between the (not shown in Fig. 3) *saturated l-branch* $\rho_l(T)$ (see Fig.5) and this universal FT-boundary of a *liquid metastability* was the main cause for "*rejecting*" of a singular CP-existence in [3]. Two asymptotic trends following from Eq.(23) are obvious [17]:

$$\rho_B(T \to 0) = \rho_c / Z_c \quad (a) \qquad T_B(\rho \to 0) = 9T_c Z_c \quad (b). \tag{23}$$

They are widely discussible in the predictive ZL-methodology [13,16,18].

4. Conclusions. The notions of global FT-diagram including FT1- and FT2-regions of NGF-phase represented by Figs. 1-3 can be quite useful to develop the advanced combined theory of SCF. FT-diagram provides the fluctuation insight into the conventional PhT1- and PhT2-concepts and their idealized spatial structures too. In particular, both subcritical (FT1) and supercritical (FT2) regions are *two-dimensional* manifolds on the planes of all measurable volumetric PVT-variables: (P,ρ), (P,T) and (T,ρ). This distinction from PhT1-model is especially notable in the (P,T)-plane where NGF-interphase is bounded [7-9] by two *bubble* $P_b(T)$ and *dew* $P_d(T)$ curves instead of a single deterministic *vapor pressure curve* $P_v(T)$ implied by the classical VLE-theory. Both above curves cross one another at the actual singular CP in which the *gibbsian phase rule is, of course, fulfilled*.

It is interesting to note that some authors [19] have used even the rather controversial interpretation of the standard equilibrium abbreviation *PVT* (*physical-vapor transport*) to emphasize the hypothesized *dynamical* nature of criticality. The aim was to develop the "revised" dynamical version of vdW-EOS for the vicinity of vdW-Andrews CP in which one a priori adopts the adequacy of the equilibrium chemical potential $\mu(T,P)$. Simultaneously, this approach admits the reality of an Euler-Lagrange time-dependent equation for both conjugated densities of mass $\rho(T,P;t)$ and entropy $\sigma(T,P;t) = \rho(T,P;t)s$ interconnected by the differential thermodynamic Gibbs-Duhem identity for the First Law:

$$dP = \rho\, d\mu + \sigma\, dT. \tag{24}$$

The list of references cited in [19] shows that T.Ma and S.Wang had published, for the first time, their dynamical vdW-EOS' "version" *at 2008*. In particular, they introduced the combined *density/entropy order parameter* $u = (\rho - \rho_0, \sigma - \sigma_0)$ in their PVT-abbreviated dynamical model. They supposed in conclusion the existence of *general asymmetry principle of fluctuations* and PhT3-reality.

We inform a reader that the similar concepts were developed by one of us (V.B.R.) in detail about twenty years earlier (see, for example, [23] and its list of cited works). Besides, the essential but slightly changed notions used by Ma and Wang such as the *order-disorder parameter* and *global fluid asymmetry* may be easily found in the cited here works of FT-model [6-9]. In any case, it seems to be worthwhile to compare the final conclusions of aforementioned authors [19] with those reported in the present work.

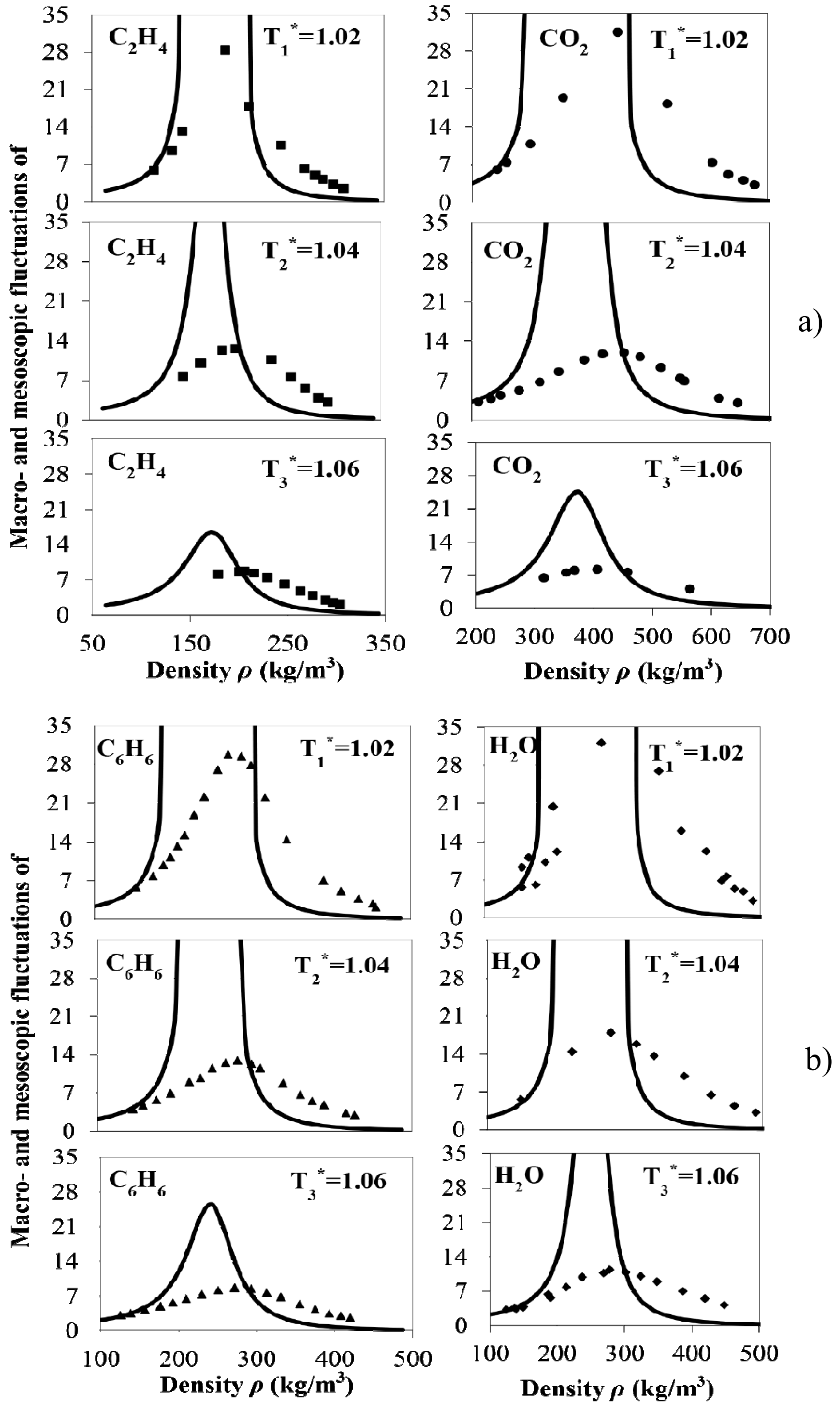


Fig. 5. Comparison of isothermal gaussian (macroscopic) and non-gaussian (mesoscopic) fluctuations predicted by FT-EOS [8] for Z_c, Ri_c (solid lines) with SAXS-experimental data (points) obtained by Nishikawa et al [11,12] and described by vdW-EOS [10] in which $Z_c^0 = 3/8$ and $Ri_c^0 = 4$. The locus of SAXS-ridge in [11,12] coincides, practically, with the supercritical *l*-branch of FT-EOS (see Conclusion)

To our mind, the attempt to expand the Ehrenfest classification of PhTs into SCF-region by the steps: 1) "the gas-liquid coexistence-curve can be extended beyond the Andrews critical point and 2) the transition is *first order* before the critical point, *second order* at the critical point, and the *third order* beyond the Andrews critical point" is, in general, erroneous due to its non-thermodynamic nature. Both thermodynamic potentials: $f(T,v)$ and $\mu(T,P)$ termed *the Helmholtz's and Gibbs' free energies*, respectively, are not applicable, strictly speaking to the description of *any* non-equilibrium states. Macroscopic fluctuation thermodynamics of a finite-volume [23] has to operate under the Second Law constraint, which requires only the positive values of heat capacities: $C_P \geq C_v > 0$ and compressibilities $\beta_T \geq \beta_s > 0$ at any temperatures. This requirement excludes, as a matter of fact, from the conventional equilibrium PhT-theory such anomalous vdW-area of PhT1 with the negative compressibility as the *spinodal decomposition segment* located between two branches of *sp*-contour in Figs. 1-3. From this viewpoint, the reference in [19] to the work of Nishikawa et al [11,12] on the vdW-ridge in SCF-region (see its discussion in Section 3 and Fig. 5 for comparison with FT-model) is not convincing. One should not consider such ridge as the "experimental discovery" which "seems to the locus of a higher-order phase transition". Moreover, any explicit (i.e. model-dependent) calculations of the third-order derivative with respect to the temperature (i.e. $\left[\partial C_P / \partial T\right]_{\rho_c}$) of the Gibbs' energy $\mu(P,T)$ cannot be *pro* or *con* proof of the PhT3-existence.

By contrast, FT-diagram identifies the above fluctuation ridge with *qsp*-contour, i.e. the lower boundary of NGF-phase. Its upper boundary, i.e. *ml*-contour separates the heterogeneous FT2-region from the *metastable* super- and subcritical *l*-phase. The structure of latter is evidently about homogeneous, i.e. gibbsian GPh's one. Below T_c, namely, FT-boundary of Eqs.(22,23) predicts with the reasonable accuracy the most reliable experimental data on a liquid metastability [20,21]. The main tool for its description in term of FT2-region is the reference model of vdW-fluid (Table 1) refined by FT-EOS (11-13). It is highly desirable to corroborate and confirm the reported here FT-estimates by the controllable relevant simulations of *mesoscopic* (nano-) *volumes*. The implied possibility of superposition of the a priori unknown global congruent PhT-diagram (with its *g*-, *l*-, s-GPhs-regions and the respective NGF-regions) on the predicted here FT-diagram seems to be quite promising and challenging problem for the further investigations.

The title of the fundamental Gibbs' work published 140 years ago was "About equilibrium of heterogeneous substances". The conventional notion of GPh complemented by the concept of NGF-existence provides the new insight into the "old" problem of VLE-transition occurred in the finite-volume real *f*-systems.

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Надкритична гетерогенна наноструктура флюїдів. Частина1. Діаграма флуктуаційних переходів у негіббсівських фазах

АНОТАЦІЯ

Запропоновано нову концепцію області надкритичної флюїдної поведінки щоб пояснити сукупність нових експериментальних і чисельних результатів, в яких загальноприйнята теорія асимптотичного скейлінгу та її розширення на більший інтервал параметрів досягають межі придатності. Існування гетерогенної стаціонарної наноструктури гратового типу в широких діапазонах надкритичних властивостей, що була названа не-гіббсівською фазою флюїду, було запропоноване В.Б.Рогонковим у рамках моделі ФТ (флуктуаційної термодинаміки). ФТ-модель стверджує, що аналогічна не-гіббсівська фаза існує і нижче критичної температури в будь-якому реальному (тобто скінченно-об'ємному) переході пара-рідина. Ця робота встановлює геометричну форму і положення точних границь для надкритичної не-гіббсівської фази на фазовій діаграмі, що підтверджується набором нещодавно опублікованих експериментальних і модельних результатів. Коротко кажучи, загальна надкритична область флюїду складається з розбавленої газоподібної гіббсівської гомогенної фази і щільної рідинноподібної гіббсівської гомогенної фази, відокремлених одна від одної гетерогенною (щонайменше, в наношарах скінченного об'єму) пароподібною фазою. Практичне використання такої структури може бути досить перспективним у багатьох сферах застосування. Це ствердження, звичайно, не обмежено лише відомими досягненнями в практичному здійсненні процесів надкритичної екстракції.

***Ключові слова**: надкритичний флюїд, гетерогенні (негібсовські) фази, модель флуктуаційної термодинаміки*

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Сверхкритическая гетерогенная наноструктура флюидов. Часть 1. Диаграмма флуктуационных переходов в негиббсовских фазах

АННОТАЦИЯ

Предложена новая концепция сверхкритической флюидной (СКФ) области с целью интерпретации ряда экспериментальных и полученных численными методами наблюдений, в которых использование принятой асимптотической теории скейлинга и ее кроссоверного расширения достигает предела применимости. Существование устойчивой, решеточного типа, гетерогенной наноструктуры в широких интервалах сверхкритических параметров, названной негиббсовской флюидной (НГФ)-фазой, было гипотетически сформулировано В.Б. Роганковым в рамках модели флуктуационной термодинамики (ФТ). С помощью ФТ-модели было доказано, что подобная НГФ-фаза существует также при температурах, меньших критической в любой реальной системе конечного объема, вблизи от наблюдаемого в ней паро-жидкостного равновесного (ПЖР) перехода. В настоящей работе установлены точные границы и расположение сверхкритической НГФ-фазы на диаграмме состояний, подтвержденные недавно опубликованными результатами эксперимента и численных симуляций. В главном, область СКФ образуется сегментами разбавленной газо-подобной (почти гомогенной) гиббсовской фазы и плотной, жидкостно-подобной (гомогенной) гиббсовской фазы, отделенных одна от другой областью гетерогенной (по меньшей мере, в наномасштабах конечных объемов) НГФ-фазы пар-жидкостного типа. Практическое использование информации о такой универсальной СКФ-структуре может быть очень перспективно для многочисленных прикладных задач. Данный подход явно не ограничен только известными преимуществами проведения процессов сверхкритической экстракции.

***Ключевые слова**: сверхкритический флюид, гетерогенные (не-гиббсовские) фазы, модель флуктуационной термодинамики.*