THEORY OF THE HETEROPHASE FLUCTUATIONS IN THE VICINITY OF GAS-LIQUID CRITICAL POINT

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Abstract

A theory of the heterophase fluctuations in the vicinity of the gas-liquid critical point is developed. The formulated fluctuon model of heterophase fluctuations is genetically connected with the Frenkel model but includes description of the fluctuaton interaction. As a result a mean-field theory of the heterophase fluid in critical and overcritical region is obtained. Solutions of the deduced equation of state describe thermodynamics and heterophase structure of fluid. It is shown that the continuation of the gas-liquid coexistence curve in the overcritical region is the Widom line on which the constant-pressure heat capacity has a maximum and diverges when temperature approaches the critical point.

1. Introduction

Physics of SCW is developing intensively due to specific properties of the water fluid states and because it is planned to be used as coolant in nuclear reactors of the next generation, in part, in the Supercritical Water Reactor [1]. Results from experimental and computer simulations show that SCW is essentially heterogeneous [2-5]. It is composed of dense regions with hydrogen-bonded (H-bonded) molecular clusters surrounded by less dense regions with non-bonded molecules of gas-like phase. It is naturally to assume that in the critical and overcritical region the fluid is a heterophase "mixture" consistent of gas-like and liquid-like molecular short-living clusters possessing different densities and short-range orders (SRO).

In spite H-bonds play an important role in formation of the liquid and fluid structure of water [6-8], it is clear that other substances, with different interaction of atoms or molecules, also have the heterophase structure of fluid state. Remarkably is that Van der Waals was the first who noted imperfections of his theory of fluid. In his Nobel Prize Lecture, *The equation of state for gases and liquids*, (1910) he has demonstrated that his equation fails to describe the high density fluid states and explained why. He conjectured that contribution of the molecular complexes, which are forming in gas at high densities, play an important role and has to be taken into account.

Meanwhile the known models of the gas-liquid transition have nothing to do with the heterophase fluctuations in the vicinity of critical point and in overcritical region. As an exception Frenkel's theory of the heterophase fluctuations has to be mentioned [9]. Frenkel has considered the isolated heterophase fluctuations in the vicinity of the phase coexistence curve far from the critical point. Later Fisher has developed a droplet model of the gas-to-liquid transition including the critical point [10] (see also [11]). The critical exponents for the gas containing the non-interacting droplets are considered. But this model fails to describe liquid state and the fluid in overcritical region.

In this communication a phenomenological model of the heterophase fluid states is proposed. It is based on ideas formulated at consideration of the heterophase fluctuations in liquid near the second critical point [12-16] but the fluid features are taken into account. The fraction of molecules belonging to the liquid-like fraction, c_l, plays the role of the order parameter which determines the heterophase structure of fluid. Below the critical point the theory gives a correct description of Frenkel's heterophase states. The gas-to-liquid transformation at passing around the critical point takes place due to continuous increase of c_l.

The paper is organized as follows. In Section 2. the heterophase fluctuations in the liquid and gas phases are considered and fluctuons (the liquid-like droplets and gas-like bubbles of a minimal size) are defined. The fluctuon model of heterophase fluid state in the mean field approximation is formulated in Section 3. The equation of the heterophase states is deduced. It has the well known Landau's form [17]. Its solutions are presented in explicit form. The Widom line is considered in Subsection 3.4. Brief discussion and conclusions are placed in the Sections 4 and 5 respectively.

2. Heterophase fluctuations: the gas-like and liquid-like fluctuons

To deduce equations of the heterophase fluctuations model of fluid we start from consideration of the heterophase fluctuations following approach developed in Ref. [9]. Near the gas-liquid coexistence temperature, the free energy of the spherical gas bubble in liquid or liquid droplet in gas is

$$\begin{aligned} g_i(r,T) &= \frac{4\pi}{3}\left(\frac{r}{a}\right)^3(\mu_k-\mu_i)+4\pi\left(\frac{r}{a}\right)^2\sigma \\ &= \frac{4\pi}{3}\left(\frac{r}{a}\right)^3(s_i-s_k)(T_e-T)+4\pi\left(\frac{r}{a}\right)^2\sigma \qquad (1) \\ i,k&=g,l; \quad i\neq k; \qquad T<T_e \end{aligned}$$

The subscripts "g" and "l" are denoting the quantities concerning the gas and liquids respectively; μ_g, s_g and μ_l, s_l is the free energy and entropy per molecule of the "pure" gas and liquid; σ is the interfacial free energy per molecule; a is the size of molecule; r is the embryo radius. All thermodynamics quantities are dependent of T and P but this dependence is not shown explicitly in (1). The Gibbs equation for the coexistence curve $T_e(P)$ is

$$\mu_l(P,T)=\mu_g(P,T) \qquad (2)$$

Eq. (1) is valid at $r>>a$. Eq. (2) determines the real coexistence curve at $T<T_c$, T_c is the critical temperature. Since $\mu_l(P,T)$ and $\mu_g(P,T)$ are continuous functions, they can be extrapolated from the under-critical into the overcritical region.

The lower limit of r, r_{0i}, at which Eq. (1) still makes sense, can be estimated as follows. Let us consider the bubble of volume $V\sim r^3$ which contains k_g molecules. It has the specific volume $v=V/k_g$. The specific volume fluctuations depend on V, k_g and T as follows [16]

$$\left\langle (\Delta v)^2 \right\rangle = \frac{vT\kappa_T}{k_g}, \qquad (3)$$

Here κ_T is the compressibility at constant *T*. For gas $\kappa_T \sim 1/P$.

We have to demand

$$\left\langle (\Delta v)^2 \right\rangle << v^2 \qquad (4)$$

Taking into account that $PV \sim kT$, we have from (3) and (4) that at $k_g >> 1$ the specific volume fluctuations within the bubble are small as compare to its mean value.

Considering the liquid droplet in gas, we have to put

$$r > r_{0l} \approx r_{c,l}\ , \qquad (5)$$

where $r_{c,l}$ is the correlation radius of molecules in the liquid. The thermodynamic properties of the droplet and bulk liquid are close only when the condition (5) is satisfied.

The range of the pair potential is $\approx a$. Because the many-particle interactions are also responsible for the molecular correlations, it occurs that $r_{c,l} > a$. Temperature and pressure dependence of $r_{c,l}$ can be determined (measured) in under-critical region and then extrapolated into the overcritical region.

The distribution of the droplets on r is

$$f_l(r,T) \sim \exp\left[-g_l(r,T)/T\right] \quad , \ r > r_{0l} \qquad (6)$$

Here and later on the Boltzmann constant is put 1. As it follows from (1) and (6), $f_l(r,T)$ has a sharp supremum at $r = r_{0l}$. Therefore for the mean droplet radius we have

$$\left\langle r_l \right\rangle \approx r_{0l} \qquad (7)$$

Since the droplet is a short-living transient cluster in gas we call it *l-fluctuon*. Considering the droplets as the structure elements of the heterophase state we therein neglect the variance of their sizes. The number of molecules per *l*-fluctuon is

$$k_{0l} \sim 4\pi (r_{0l}/a)^3 / 3 >> 1 \qquad (8)$$

Considering the gas bubbles in the same manner we determine the gas-like fluctuons (*g*-fluctuons) consisting of $k_{og} >> 1$ molecules. Both conditions (4) and (5) are satisfied simultaneously if we put that the fluctuons of both types are consisting of the same number of molecules,

$$k_{og} = k_{ol} \equiv k_0 \qquad (9)$$

This condition is not necessary and could be avoided but it simplifies formulation of the fluctuon model of the heterophase states.

3. The fluctuon model of the heterophase gas-liquid states

3.1 Basic equations

Previous consideration lead to the following formulation of this model. The heterophase system is consisting of $N_f = N / k_0$ fluctuons (*N* is the number of molecules). Each fluctuon is *l*-like or *g*-like. In the "pure" liquid or gas phase the fluctuons have free energies

$$g_l = k_0 \mu_l \quad \text{and} \quad g_g = k_0 \mu_g \tag{10}$$

respectively.

Let us denote by $N_{f,l}$ and $N_{f,g}$ the numbers of the *l*- and *g*-fluctuons respectively. Then the fractions of the fluctuons are

$$c_l = N_{f,l} / N \, ; \qquad c_g = N_{f,g} / N \tag{11}$$

and

$$c_l + c_g = 1 \tag{12}$$

Taking into account the interfacial fluctuon interactions, gradient term and mixing entropy, the density of the free energy of heterophase state can be presented as follows

$$\begin{aligned} g &= \frac{1}{v_f}\left[\frac{1}{2}A(r_{0l})^2(\nabla c_l)^2 + \sum_i c_i\, g_i + z c_l c_g g_{gl}^0 + T\sum_i c_i \ln c_i + g_0\right] \\ &\equiv \frac{1}{v_f}\left[\frac{1}{2}A(r_{0l})^2(\nabla c_l)^2 + \sum_i c_i\, g_i + c_l c_g g_{gl} + T\sum_i c_i \ln c_i + g_0\right] \end{aligned} \tag{13}$$

$$i,k = l,g$$

Here z is the coordination number of fluctuons, g_{gl}^0 is the free energy of the fluctuons pair interaction; c_l, c_g are slow varying fields. Since r_{0l} is the scale of characteristic short-range correlations, the gradient term, as usually, takes into account the contribution of the large scale heterogeneities, $(r_{0l})^2(\nabla c_l)^2 << 1$. It determines the spectrum of long-range fluctuations in the vicinity of critical point. v_f is the mean value of the fluctuon volume,

$$v_f = V / N_f \tag{14}$$

The coefficients A and g_{gl} are positive. g_0 is the independent of c_l, c_g part of the free energy per fluctuon.

The equilibrium equations (the saddle point equations, equations of state) one can get by varying the free energy functional

$$G = \int g(x) d^3x \tag{15}$$

Taking into account the condition (11), we have

$$\frac{\delta}{\delta c_i(x)} G(P,T) + \lambda \frac{\partial}{\partial c_i(x)} \sum_k c_k(x) = 0 \tag{16}$$

where λ is the Lagrange coefficient.

It follows from (13)-(16) that

$$-A(r_{0l})^2 \Delta c_l + (1 - 2c_l) g_{gl} + T \ln \frac{c_l}{1 - c_l} = h_{gl} \tag{17}$$

$$h_{gl} = g_g - g_l \approx \Delta s_{gl}(T_e - T) \tag{18}$$

where Δs_{gl} is the difference of entropies of g-fluctuon and l-fluctuon at the phase coexistence temperature T_e.

3.2 The most probable state

It follows from (13) and (16) that minimum of the free energy can be achieved with $\nabla c_l = 0$. i.e. the stable homogeneous solutions of Eq. (17) determine the most probable states of the system. The inhomogeneous solutions describe the order parameter fluctuations.

With $\nabla c_l = 0$ Eq. (17) reads

$$(1-2c_l)g_{gl} + T\ln\frac{c_l}{1-c_l} = \Delta s_{gl}(T_e - T) \tag{19}$$

Substitution

$$c_l = \frac{1}{2} + \alpha; \quad \alpha \le \frac{1}{2} \tag{20}$$

and subsequent expansion in series on α up to fourth power gives

$$4(T - T_c)\alpha + \frac{16T}{3}\alpha^3 = \Delta s_{gl}(T_e - T) + O(\alpha^5) \tag{21}$$

where

$$T_c = T_e(P_c) = g_{gl}/2 \tag{22}$$

Eq. (21) is the standard Landau equation for the gas-liquid phase transition in the vicinity of the critical point [16] but with specific order parameter, α. To connect it with the Van der Waals order parameter,

$$\tilde{v} = \frac{v(P,T) - v_c}{v_c}; \quad v_c = v(P_c, T_c) \tag{23}$$

one can note that the specific volume of the heterophase state is

$$v \approx c_l v_l + c_g v_g, \tag{24}$$

$v_{l,} v_g$ is the specific volume of liquid and gas respectively. In the critical point $v_c = (v_l + v_g)/2$ and in the vicinity of critical point

$$\tilde{v} \approx \frac{v_l - v_g}{v_c}\alpha \tag{25}$$

Let us start from consideration of the small heterophase fluctuations in the vicinity of coexistence curve below T_c. As it follows from Eq. (19), in the liquid ($c_l \to 1, T < T_e$)

$$c_g = \exp\left[\left(\Delta s_{gl}(T_e - T) - g_{gl}\right)/T_e\right] \tag{26}$$

In gas (with $c_g \to 1,\ T > T_e$)

$$c_l = \exp\left[\left(\Delta s_{gl}(T - T_e) - g_{gl}\right)/T_e\right] \tag{27}$$

With $T = T_e$

$$c_l = c_g = \frac{1}{2} \tag{28}$$

As it follows from (13), the solutions (26), (27) correspond to the stable states of the system while the solution (28) corresponds to the unstable state. Solutions (26), (27) are in accordance with the Frenkel result (6) describing the heterophase fluctuations.

Equation (21) describes the heterophase fluctuations in critical and overcritical regions. With that the coexistence curve (2) has to be extrapolated in the overcritical region, $T > T_c;\ P > P_c$,

$$T_e(P) = T_c + \left.\frac{dT(P)}{dP}\right|_{P_c}(P - P_c) \tag{29}$$

Stable homogeneous solutions of the state equation (21) in the vicinity of the coexistence curve are

$$\alpha(T) \approx \frac{\Delta s_{gl}(T_e - T)}{4(T_c - T)} \pm \frac{4}{\sqrt{3}}\sqrt{\frac{T_c - T}{T}}\,, \quad T < T_c \tag{30}$$

and

$$\alpha(T) \approx \frac{\Delta s_{gl}(T_e - T)}{2\left(2T_e - g_{gl}\right)}\left[1 - \frac{2\left[\Delta s_{gl}(T_e - T)\right]^2 T}{3\left(2T_e - g_{gl}\right)^3}\right] \tag{31}$$

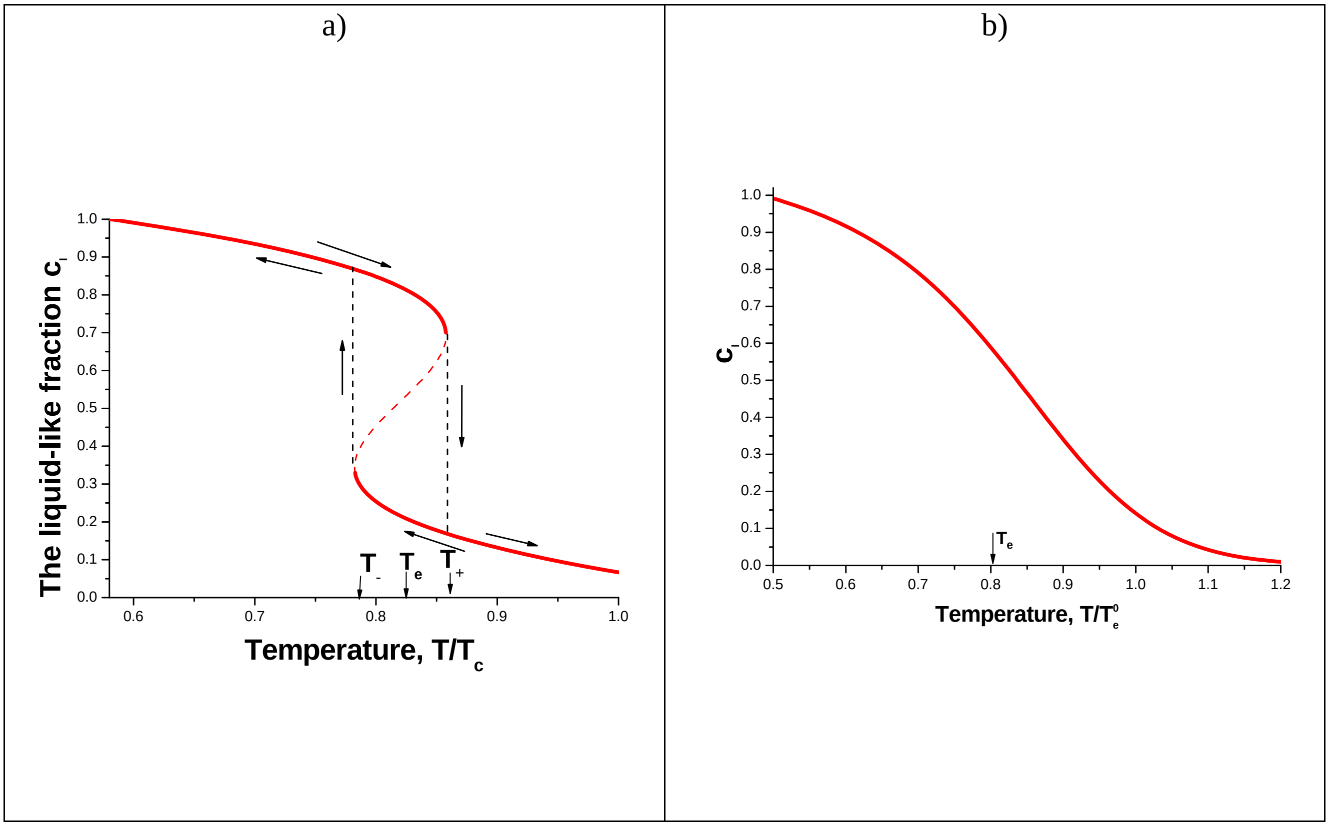

Figure 1 The isobaric temperature dependence of the liquid-like fraction of fluid, $c_l(T)$, at a) $P < P_c$ and b) $P > P_c$.

In Fig. 1 the isobaric solutions (30) and (31) are shown. In Fig.1a the unstable and metastable states within the temperature interval $T_- \le T \le T_+$ are shown too. $T_-(P)$ and $T_+(P)$ are branches of the spinodal.

3.2 Fluctuations of the order parameter and density

It is seen from (25) that the density fluctuations are directly connected with fluctuations of the order parameter. has to be added for completeness. As it follows from (21) [LL], the spectrum of the order parameter fluctuations is

$$\left\langle \left|\alpha_q\right|^2 \right\rangle = \frac{T}{V\left[A(r_{ol}q)^2 + 4(T-T_c)\right]} \tag{32}$$

Combining (32) and (25) we have

$$\left\langle \left|\rho_q\right|^2 \right\rangle = \rho_c^4 \left\langle \left|\tilde{v}_q\right|^2 \right\rangle = v_c^{-4}\left(\frac{v_g - v_l}{v_c}\right)^2 \left\langle \left|\alpha_q\right|^2 \right\rangle = \left(\frac{v_g - v_l}{v_c}\right)^2 \frac{T}{Vv_c^4\left[A(r_{ol}q)^2 + 4(T-T_c)\right]} \tag{33}$$

Here α_q and ρ_q are the Fourier components of $\alpha(x)$ and density $\rho(x)$, q is the wave vector, V is the volume.

The fluctuon-fluctuon correlation function is

$$K_{ll}(r) = \frac{T}{4\pi A r_{0l}^2 r}\exp(-r/\xi) \tag{34}$$

with the correlation length

$$\xi = \frac{r_{ol}}{2}\sqrt{\frac{A}{|T - T_c|}} \tag{35}$$

It is clear that Eqs. (33-35) describe the coarsened (on scale $r \sim r_{0l}$) density fluctuations. Therefore they make a sense at $q < 2\pi / r_{0l}$.

3.3 The Widom line

The coexistence curve continuation (29) makes a physical sense since the thermodynamic coefficients connected with the second order derivatives of the thermodynamic potentials have maxima on this line. The line on which the constant-pressure heat capacity, C_p, has maximum is named “the Widom line” [17]. It is easy to check that the line $T = T_e(P)$ is the Widom line. As it follows from (13), (19), the heat capacity of the fluid state at $T > T_c$ is

$$C_p = -T\frac{d^2 g}{dT^2} \approx \frac{1}{2}\left(C_{pl} + C_{pg}\right) + \left(C_{pg} - C_{pl}\right)\alpha + \frac{(1-4\alpha^2)\left(\Delta s_{gl}\right)^2}{4k_0\left[T - T_c(1-4\alpha^2)\right]}; \tag{36}$$

Here C_{pl} and C_{pg} is the heat capacity of liquid and gas.

Since on the coexistence curve $\alpha(T_e(P)) = 0$, the last term of r.h.s. of (36) has here maximum and becomes singular with $T \to T_c$.

3. Discussion

The developed fluctuon model of heterophase fluctuations gives a coarse grained phenomenological description of the fluid. Coefficients of this model, unlike to the Van der Waals model with two constant parameters, are *P,T*-dependent functions. The thermodynamic phenomenological coefficients can be determined experimentally below the critical point and continued in the overcritical region.

The model is symmetric with respect to both liquid and gas phase states, as in the Lee and Young lattice model of condensation [18] and other so called “two-state models” (see . [14] and references quoted). We have included in consideration interaction of the heterophase fluctuations. Therefore the formulated model is a generalization of Frenkel’s model of heterophase fluctuations. From the other hand, a mean-field formulation of the critical point in terms of the heterophase fluctuations is obtained. Thus this model is as generalization of the mean-field critical point description taking into account the structured fluid states.

As it is seen from the model formulation, it contains two characteristic correlation lengths, $r_{0,l}$ and ξ. The first one is the SRO correlation length of the *l*-fluctuons. The second one concerns the fluctuon-fluctuon correlations. The last one makes a sense if $\xi >> r_{o,l}$. To some extension $r_{0,l}$ can be treated as a parameter of the direct correlation function and ξ as parameter of the total correlation function introduced by Ornstein and Zernike [19] but validity of the Ornstein-Zernike assumption that the Fourier transform of the direct correlation function can be presented in form of q- expansion is disputable.

The completed consideration show that thermodynamic and dynamic properties of the fluids of different substances are expected to be similar but the equation of the corresponding states takes no place.

5. Conclusion

A theory of the heterophase fluctuations in the vicinity of the gas-liquid critical point is developed. The formulated fluctuon model of heterophase fluctuations is genetically connected with the Frenkel model but it is presented in a quantized form and includes the fluctuons interaction. As a result we have obtained a mean-field theory of the heterophase fluid in critical and overcritical region. Solutions of the deduced equation of state describe thermodynamics and heterophase structure of the fluid below and above the critical point.

It is shown that the continuation of the gas-liquid coexistence curve in the overcritical region is the Widom line on which the constant-pressure heat capacity has a maximum. This quantity diverges when temperature approaches the critical point.

The developed theory provides a theoretical base for further investigations of the structure and properties of SCW and fluids of other substances.

6. References

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