# EQUATION OF STATE NEAR THE CRITICAL POINT ON THE BASIS OF THE VAN DER WAALS MODEL FOR A WIDE CLASS OF DIELECTRIC LIQUIDS

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The fluctuation part of the thermodynamic potential of a system near its critical point considered as a gas of fluctuations that obeys the van der Waals equation has been analyzed in the framework of the fluctuation theory of phase transitions (FTPT). The corresponding extended equation for the coexistence curve for liquid systems in the fluctuation region has been derived and verified, by using the experimental data on the temperature dependences of the liquid and vapor densities for dielectric liquids near their critical points, both for systems homogeneous and inhomogeneous under Earth's gravity.

The problem of finding an extended equation of state for substances in a wide range of thermodynamic parameters which includes a close vicinity of the critical point (CP) still remains challenging [1–3].

In this work, while developing the equation of state of a substance, we used the model of a system considered in the CP vicinity as a gas of fluctuations of the order parameter, the size of fluctuations being determined by the correlation length $R_c$ in the system [1, 2]. The fluctuation part of the thermodynamic potential $F_0$ of such a system looks similarly to the expression for the ideal gas energy $F_0 = N_f k_B T_c = C_0 R_c^{-3}$ [1,2]. Here, $N_f$ is the number of order parameter fluctuations per one mole of the substance.

Taking into consideration both the properties of non-interacting clusters of order parameter fluctuations in FTPT [1, 2] and the properties of a real van der Waals gas [4, 5], one can derive asymmetric equations of state which would be valid in a wider CP vicinity using the symmetric scale equations of state of a substance. According to work [6], it is necessary, for this purpose, to consider the own volume of fluctuation clusters and the interaction forces between them at distances $r \geq R_c$.

Then, the thermodynamic potential of such a system can be presented in the form $F_f = F_0(1 + \Delta F)$ [6, 7]. In this formula, the symmetric part of the FTPT thermodynamic potential $F_0 = N_f k_B T_c = C_0 R_c^{-3}$ [1, 2] is supplemented by the term $\Delta F$ that makes allowance for the own volume of order parameter fluctuations, the interaction forces between them at distances $r > R_c$, and the presence of complexes that consist of $n$ separate fluctuations in the system.

The analytical form of the fluctuation part of the thermodynamic potential and its analysis are presented in detail in works [6–8]. This potential was used as a base to obtain the equation of state of a substance along the thermodynamic direction of the interface $t = (T - T_c)/T_c < 0$:

$$\Delta \rho = (\rho - \rho_c)/\rho_c = \frac{dF_f}{d\mu} = \pm B_0|t|^\beta \pm B_1|t|^{\beta+\Delta_0}+$$

$$+B_2|t|^{2\beta} + B_3|t|^{1-\alpha} - B_4|t|^{\beta+\nu} + \dots . \tag{1}$$

By its view, this equation coincides with the results of other known extended equations of for the coexistence curve (CC) of a substance [3, 9–11]. At the same time, the parameters $B_n$ in Eq. (1) possess a well-defined physical content. Really, the asymmetric terms in expression (1) take the following contributions into account: the term $B_2|t|^{2\beta}$ is connected with the own volume of order parameter fluctuations $V_f$ in the system, the term $B_3|t|^{1-\alpha}$ is the entropy contribution to the formation of order parameter fluctuations, the negative term $-B_4|t|^{\beta+\nu} < 0$ is the contribution to the thermodynamic potential $F_f$ of attraction forces between order parameter fluctuations at distances $r > R_c$, and the non-asymptotic term $\mp B_1|t|^{\beta+\Delta_0}$ [10] is connected with the presence of complexes that are formed of $n$ order parameter fluctuations [7].
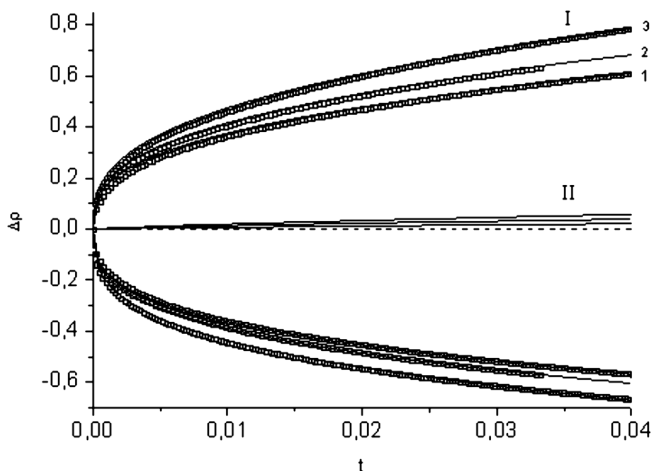
Fig. 1. Temperature dependences of the order parameter $\Delta\rho(t) = (\rho - \rho_c)/\rho_c$ (I) and the CC diameter $d = (\rho_l(t) + \rho_v(t))/(2\rho_c) - 1$ (II) of uniform liquids: carbon monoxide (1), carbon dioxide (2), and water (3)



Fig. 3. The same as in Fig. 1, but for alkanes: methane (1), ethane (2), pentane (3), and dodecane (4)
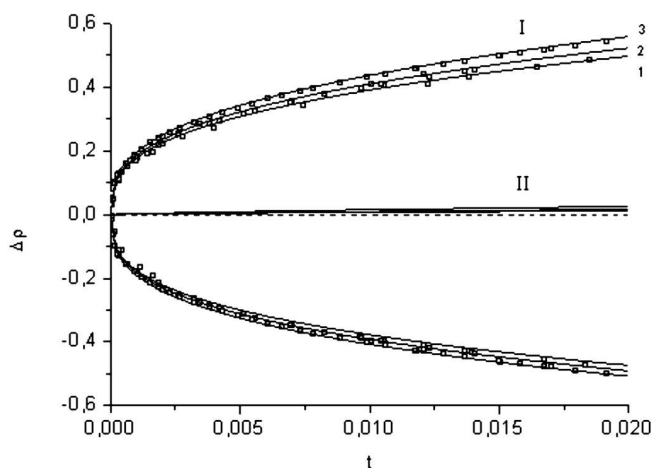


Fig. 2. The same as in Fig. 1, but for non-uniform liquids: ethane (1), benzene (2), and freon-113 (3)

In works [12–14], the derived Eq. (1) was tested, by analyzing experimental data obtained for binary solutions near the critical separation temperature. To continue the testing of the model proposed [6–8] and Eq. (1), we extended the list of objects to study in this work. Accordingly, we used Eq. (1) to analyze the temperature dependence of the density for a wide class of various one-component dielectric liquids near their critical vaporization temperatures. For this purpose, we used experimental data of our optical and neutron researches on the temperature dependence of the density $\Delta\rho(t)$ in such non-uniform systems as freon-113, ethane, and benzene in the gravitational field [15, 16]. In addition, we used literature data concerning $\Delta\rho(t)$ in various uniform di-
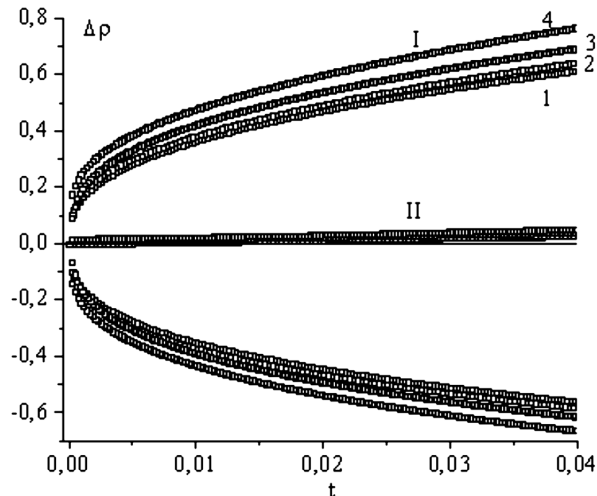
electric liquids: water, carbon dioxide, carbon monoxide [17–19], and a number of alkanes $C_nH_{2n+2}$ ($n = 1 \div 12$) [20–23].

In this work, the equation of state (1) was used to analyze the temperature dependence of the density $\rho(t)$ for researched objects [15–23] along the interface in the temperature range $t = 10^{-4} \div 10^{-2}$. This temperature interval, according to the Ginzburg criterion $t_f \ll Gi$ ($t_f \leq 10^{-2}$) [1], corresponds to the fluctuation region of temperatures $t_f$. This allowed the crossover terms [24] in the equation of state (1) to be neglected.

The experimental data obtained for the temperature dependences of the liquid, $\rho_l$, and vapor, $\rho_v$, densities are shown in Figs. 1 to 3. Their analysis testified that the order parameters $\Delta\rho_{l,v}(t) = (\rho_{l,v}(t) - \rho_c)/\rho_c$ and the density asymmetries $d = (\rho_l(t) + \rho_v(t))/(2\rho_c) - 1$ are considerably different for the objects under investigation. The largest values of the order parameters and the density asymmetry were observed in substances with higher critical temperatures (Tables 1 and 2), i.e. where the forces of intermolecular interaction are stronger. In addition, for a number of alkanes (Fig. 3) [20–23], an increase in the order parameter $\Delta\rho$ and its asymmetry occurs simultaneously, when the number of carbon atoms increases. These results qualitatively confirm conclusions that follow from the proposed model of a system near its CP as a gas of order parameter fluctuations [6–8] with the properties of a real van der Waals gas [4].

On the basis of data presented in works [15–23] (Fig. 1 to 3), we calculated the parameters $B_n$ in the CC equation (1) (Tables 1 and 2). For this purpose, we calculated

firstly the parameters $B_n$ in the symmetric part of the equation of state (1),

$$(\rho_{\mathrm{l,v}}^{-}\rho_{\mathrm{c}})/\rho_{\mathrm{c}} = \pm B_0|t|^{\beta} \pm B_1|t|^{\beta+\Delta_0}, \qquad (2)$$

and then in the asymmetric part

$$d = (\rho_{\mathrm{l}} + \rho_{\mathrm{v}})/2\rho_{\mathrm{c}} - 1 =$$

$$= +B_2|t|^{2\beta} + B_3|t|^{1-\alpha} - B_4|t|^{\beta+\nu} + \ldots \quad . \qquad (3)$$

In the calculations, we used the values of critical indices obtained in work [25] by introducing small parameters into FTPT relations [1, 2]: $\nu = 0.636$, $\beta = 0.338$, $\alpha = 0.091$, and $\Delta_0 = 0.5$ [10]. The application of this method allowed the values of critical indices to be determined to within an error of 1%.

The analysis of data for $\Delta\rho(t)$ presented in Figs. 1 to 3 demonstrated that the non-asymptotic term $B_1|t|^{\beta+\Delta_0}$ in Eq. (2) is much smaller than the term $B_0|t|^{\beta}$ ($B_0|t|^{\beta} \gg B_1|t|^{\beta+\Delta_0}$) in the temperature fluctuation interval $t \geq 10^{-4} \div 10^{-2}$. Moreover, the analysis of asymmetric terms in Eq. (3) implies that, owing to the equality $\beta + \nu \approx 1 - \alpha$ for critical indices [1], the contributions of terms can be estimated as $B_3|t|^{1-\alpha} - B_4|t|^{\beta+\nu} \approx B_3^*|t|^{1-\alpha}$. Therefore, only one term $B_0|t|^{\beta}$ of the symmetric equation (2) and the magnitudes of asymmetry parameters $B_2$ and $B_3^*$ from Eq. (3) are presented in Tables 1 and 2.

In Figs. 1 to 3, the solid curves illustrate the dependences $\Delta\rho(t)$ of researched substances [15–23] on the coexistence curve (1). The dependences were calculated using the parameters $B_0$, $B_2$, and $B_3^*$ presented in Tables 1 and 2. The figures clearly demonstrate that the

experimental data for $\Delta\rho(t)$ agree well with the extended equation for the equilibrium curve (1) which was derived on the basis of the model near the CP as a gas of order parameter fluctuations with the properties of a real van der Waals gas [6–8].

The experimental data on the temperature dependence $\Delta\rho(t)$ in a number of alkanes $C_nH_{2n+2}$ ($n = 1\div12$) (Fig. 3) [20–23] were analyzed in more details. On the basis of those data for $\Delta\rho(t)$, we established a relation between the parameters $B_n$ and the compressibility factor $Z_{\mathrm{c}} = P_{\mathrm{c}}V_{\mathrm{c}}/(RT_{\mathrm{c}})$ (see Table 2). From Table 2, it follows that the parameters $B_0$, $B_2$, and $B_3^*$ in Eq. (2) decrease, as the compressibility factor $Z_{\mathrm{c}}$ increases. These dependences can be described by the linear equations

$$B_0 = 4.2 - 8.5Z_{\mathrm{c}},$$

$$B_2 = 0.5 - 1.5Z_{\mathrm{c}},$$

$$B_3^* = 2.9 - 8.6Z_{\mathrm{c}}. \qquad (4)$$

On the basis of Eqs. (4), one can predict the equation of state for alkanes along the interface in the case where the number of carbon atoms $N_{\mathrm{c}} > 12$.

Hence, the analysis of the temperature dependences of the density along the liquid–vapor coexistence curve carried out in works [15–23] for a wide class of liquids showed that those data are adequately described by the extended equation of state (1), in which the model of a system near its CP as a gas of order parameter fluctuations [6–8] with the properties of a real van der Waals gas [4] is used. Equation (1) agrees, by its form, with modern equations that describe the substance state in the CP vicinity [4, 9–11] and are

**T a b l e 1.** **Parameters in the equation of state (1) for uniform and non-uniform dielectric one-component liquids**

| Liquid | $T_{\mathrm{k}}$ | $B_0$ | $B_2$ | $B_3^*$ |
|---|---|---|---|---|
| Uniform liquids | | | | |
| Water | 647.10 | 2.16 | 0.15 | 1.0 |
| Freon-113 | 487.21 | 1.96 | 0.15 | 0.6 |
| $CO_2$ | 304.13 | 1.91 | 0.11 | 0.6 |
| Ethane | 305.33 | 1.80 | 0.06 | 0.49 |
| CO | 132.86 | 1.75 | 0.07 | 0.4 |
| Non-uniform liquids | | | | |
| Freon-113 | 486.96 | 2.0 | 0.15 | 0.75 |
| Benzene | 561.80 | 1.9 | 0.05 | 0.5 |
| Ethane | 305.35 | 1.82 | 0.05 | 0.3 |

**T a b l e 2.** **Critical parameters and parameters in the equation of state (1) for a number of uniform alkanes**

| Substance | $N^C$ | $T_{\mathrm{c}}$, K | $Z_{\mathrm{c}}$ | $B_0$ | $B_2$ | $B_3^*$ |
|---|---|---|---|---|---|---|
| Methane | 1 | 190.56 | 0.286 | 1.75 | 0.05 | 0.42 |
| Ethane | 2 | 305.33 | 0.280 | 1.80 | 0.06 | 0.49 |
| Propane | 3 | 369.83 | 0.276 | 1.84 | 0.07 | 0.51 |
| Butane | 4 | 425.13 | 0.274 | 1.88 | 0.08 | 0.54 |
| Pentane | 5 | 469.70 | 0.268 | 1.93 | 0.09 | 0.6 |
| Hexane | 6 | 507.82 | 0.263 | 1.95 | 0.095 | 0.65 |
| Heptane | 7 | 540.13 | 0.261 | 1.98 | 0.102 | 0.64 |
| Octane | 8 | 569.32 | 0.259 | 2.00 | 0.105 | 0.67 |
| Nonane | 9 | 594.55 | 0.258 | 2.02 | 0.11 | 0.69 |
| Decane | 10 | 617.70 | 0.256 | 2.05 | 0.115 | 0.71 |
| Dodecane | 12 | 658.10 | 0.248 | 2.11 | 0.12 | 0.74 |

based on the extended variant of the algebra of fluctuating quantities and the application of renormalization group methods and parametric models of various types.

1. A.Z. Patashinski and V.L. Pokrovski, *Fluctuation Theory of Phase Transitions* (Pergamon Press, Oxford, 1982).

2. M.A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia, 1991).

3. Ch. Hongyuan, M.A. Anisimov, and J.V. Sengers, Fluid Phase Equilibr. **128**, 67 (1997).

4. J.D. van der Waals and Ph. Constamm, *Lehrbuch der Thermostatik* (Barth, Leipzig, 1927).

5. A.Ya. Kipnis and B.E. Yavelov, *J.D. van der Waals* (Acad. Sci. of the USSR, Leningrad, 1985) (in Russian).

6. A.D. Alekhin, Izv. Vyssh. Ucheb. Zaved. Fiz. **3**, 103 (1983).

7. A.D. Alekhin, Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauk **2**, 322 (2003).

8. O.D. Alekhin, A.K. Dorosh, and E.G. Rudnikov, *Critical State of Substance in the Earth's Gravitation Field* (Politekhnika, Kyiv, 2008) (in Ukrainian).

9. Y.C. Kim, M.E. Fisher, and G. Orkoulas, Phys. Rev. E **67**, 061506 (2003).

10. F.J. Wegner, Phys. Rev. B **5**, 4529 (1972).

11. J. Wang, C.A. Cerdeirina, M.A. Anisimov, and J.V. Sengers, Phys. Rev. E **77**, 031127 (2008).

12. A.D. Alekhin, B.Zh. Abdikarimov, L.A. Bulavin, Yu.L. Ostapchuk, and E.G. Rudnikov, Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauk No. 2, 215 (2009).

13. A.D. Alekhin, B.Zh. Abdikarimov, Yu.L. Ostapchuk, and E.G. Rudnikov, Ukr. Fiz. Zh. **54**, 995 (2009).

14. A.D. Alekhin, B.Zh. Abdikarimov, Yu.L. Ostapchuk, and E.G. Rudnikov, Zh. Fiz. Khim. **84**, No. 8, 1 (2010).

15. L.A. Bulavin, *Properties of Fluids in Critical Region* (Kyiv Univ. Publ. House, Kyiv, 2002) (in Ukrainian).

16. L.M. Artyukhovskaya, Ph.D. thesis (Kyiv, 1973) (in Russian).

17. W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data **31**, 387 (2002).

18. R. Span and W. Wagner, J. Phys. Chem. Ref. Data **25**, 1509 (1996).

19. R.D. McCarty, *Correlations for the Thermophysical Properties of Carbon Monoxide* (National Institute of Standards and Technology, Boulder, CO, 1989).

20. D.G. Friend, H. Ingham, and J.F. Ely, J. Phys. Chem. Ref. Data **20**, 275 (1991).

21. R. Span, *Multiparameter Equations of State – An Accurate Source of Thermodynamic Property Data* (Springer, Berlin, 2000).

22. E.W. Lemmon and M.L. Huber, Energy Fuels **18**, 960 (2004).

23. U. Setzmann and W. Wagner, J. Phys. Chem. Ref. Data **20**, 1061 (1991).

24. V.A. Agayan, M.A. Anisimov, and J.V. Sengers, Phys. Rev. E **64**, 026125 (2001).

25. A.D. Alekhin, J. Mol. Liq. **120**, 43 (2005).

РІВНЯННЯ СТАНУ ШИРОКОГО КЛАСУ
ДІЕЛЕКТРИЧНИХ РІДИН ПОБЛИЗУ КРИТИЧНОЇ
ТОЧКИ НА ОСНОВІ МОДЕЛІ ВАН-ДЕР-ВААЛЬСА

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Р е з ю м е

У роботі на основі флуктуаційної теорії фазових переходів і моделі системи поблизу критичної точки як газу флуктуацій параметра порядку, що відповідає рівнянню Ван-дер-Ваальса, застосовано вираз для флуктуаційної частини термодинамічного потенціалу такої системи. Виходячи з цієї моделі розроблено розширене рівняння кривої співіснування рідинних систем у флуктуаційній області. Це рівняння апробовано на основі експериментальних даних температурної залежності густини рідини і пари діелектричних рідин поблизу критичної точки в однорідних і неоднорідних системах у полі гравітації Землі.