International Journal of Thermophysics, Vol. 17, No. 3, 1996

Scaling, Crossover, and Classical Behavior in the Order Parameter Equation for Coexisting Phases of Benzene from Triple Point to Critical Point[1]

Yu. I. Shimansky[2,3] and E. T. Shimanskaya[2]

The temperature dependence of the density along the coexistence curve of benzene in the vicinity of the critical point and in a wide temperature range down to the triple point was investigated. The original results as well as literature data were statistically treated. A regression analysis of data on the critical exponents and critical amplitudes used as fitting parameters in a model equations was carried out. An adequate description of the order parameter by the three-term scaling equation in the entire two-phase (liquid–gas) region of benzene was obtained with experimental values of $\beta_0 = 0.352 \pm 0.003$ and $\Delta = 1.3 \pm 0.2$, which are inconsistent with the Ising model ($\beta_0 = 0.325$) and the Wegner exponent ($\Delta = 0.5$), respectively. It is shown that the equation with fixed classical exponents does not adequately describe the experimental data even far from the critical point.

KEY WORDS: benzene; coexistence curve; critical behavior; critical point; Ising model; order parameter; scaling laws; triple point.

1. INTRODUCTION

During the past 25 years, experimental and theoretical investigations of critical phenomena were carried out to check the hypothesis of similarity and universality of asymptotic behavior for second-order phase transitions and critical phenomena. According to the opinion of the authors of a review [1], there is consensus among the investigators that theory and experiment are in agreement. In particular, it is generally accepted that

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Physics Department, Kiev Taras Shevchenko University, pr. Glushkova 6, Kiev 252022, Ukraine.

[3] To whom correspondence should be addressed.

0195-928X/96/0500-0651$09.50/0

fluids belong to three-dimensional Ising-like systems with short-range forces and scalar order parameter. In Ref. 1, it was concluded that for the coexistence curve (CC) of fluids, the critical index $\beta = 0.326 \pm 0.002$ is the universal value; asymptotic scaling is valid in the region $\tau = (T_c - T)/T_c \sim 10^{-4}$–$10^{-3}$, and for the description of data in a wider region, corrections are necessary.

Among the unsolved problems, reviewed in Ref. 1, there are the determination of the region of classical equations validity and the crossover from singular nonclassical critical behavior to classical Van der Waals-like behavior.

Previously, we have carried out the statistical analysis of literature data on the order parameter temperature dependences for ethylene [2], Ne and HD [3], and N_2 [4] in the vicinity of the critical point and showed that, for these substances, a better description corresponds to an experimental critical exponent $\beta_0 = 0.355 \pm 0.003$.

The purpose of the present paper is the investigation of the temperature dependence of the coexisting densities of benzene in the entire region of liquid–gas coexistence from triple to critical point.

2. THE CHOICE OF THE EXPERIMENTAL DATA ARRAY

The data array for the investigation of the temperature dependence of the coexisting densities of benzene from triple point to critical point is based principally on our experimental results on the density obtained from the measurements of gravity effects in the vicinity of the critical point [5] and on refractive index data obtained in a wide temperature region [6]. To obtain the values of coexisting liquid (ρ_l) and gas (ρ_g) phase densities several methods (including the optical Toepler method, prisms, and microfloat methods) were used. In Refs. 5 and 6 temperature was measured by means of platinum thermometer. The absolute temperature uncertainty was $\delta T = \pm 0.001$ K. The precision of the control of the thermostat was 0.01 K. The densities were calculated from refractive indices values using Lorenz–Lorentz formula. The uncertainties of the refractive index and density were estimated to be $\delta n = \pm 0.0001$ and $\delta \rho = \pm 0.001\ \text{g} \cdot \text{cm}^{-3}$, respectively. Our data on the density of liquid ρ_l far from critical point were complemented with data by others [7], while in the vicinity of the triple point the data calculated according to Ref. 8 were also used. Data for the vapor density ρ_g far from the critical point were generated according to Ref. 9. The array includes 79 conjugate values ρ_l and ρ_g. The data array is presented in Table I. The experimental data *N* 54–78 (Table I) can be found in Ref. 10 as well. Preliminary analysis of all data showed consistency.

Table I. The Liquid ρ_l and Gas ρ_g Coexistence Phase Densities of Benzene from Triple Point to Critical Point

N	T (°C)	ρ_l ($g \cdot cm^{-3}$)	Ref. No.	ρ_g ($g \cdot cm^{-3}$)	Ref. No.
1	6.00	0.89366	8	0.00017	9
2	6.85	0.89278	8	0.00018	9
3	10.00	0.88948	8	0.00022	9
4	16.85	0.88228	8	0.00032	9
5	20.00	0.87896	8	0.00036	9
6	26.85	0.87170	8	0.00047	9
7	30.00	0.86896	8	0.00053	9
8	36.85	0.86101	8	0.00072	9
9	40.00	0.85763	8	0.00080	9
10	46.85	0.85023	8	0.00102	9
11	50.00	0.84681	8	0.00112	9
12	56.85	0.83935	8	0.00145	9
13	60.00	0.83591	8	0.00159	9
14	19.96	0.87936	7	0.00036	9
15	19.98	0.87938	7	0.00036	9
16	20.03	0.87933	7	0.00036	9
17	36.95	0.86125	7	0.00072	9
18	56.92	0.83962	7	0.00145	9
19	76.95	0.81745	7	0.00268	9
20	96.89	0.79505	7	0.00460	9
21	126.86	0.75950	7	0.00912	9
22	156.92	0.72085	7	0.01689	9
23	186.94	0.67821	7	0.02697	6
24	216.24	0.63016	7	0.04639	6
25	236.91	0.58937	7	0.06745	6
26	246.87	0.56651	7	0.08092	6
27	266.79	0.50888	7	0.11970	6
28	276.96	0.46588	7	0.15246	6
29	18.00	0.87961	6	0.00033	9
30	27.50	0.86937	6	0.00049	9
31	90.04	0.80312	6	0.00380	9
32	100.83	0.79070	6	0.00506	9
33	107.21	0.78308	6	0.00580	9
34	123.04	0.76444	6	0.00849	9
35	134.03	0.75075	6	0.01069	9
36	145.12	0.73677	6	0.01342	9
37	155.37	0.72405	6	0.01644	9
38	165.91	0.70917	6	0.01855	6
39	174.94	0.69586	6	0.02204	6
40	176.33	0.69433	6	0.02262	6

Table I. *(Continued)*

N	T (°C)	ρ_l ($g \cdot cm^{-3}$)	Ref. No.	ρ_g ($g \cdot cm^{-3}$)	Ref. No.
41	186.23	0.67942	6	0.02707	6
42	196.23	0.66392	6	0.03266	6
43	206.17	0.64778	6	0.03900	6
44	216.38	0.62996	6	0.04745	6
45	226.12	0.61139	6	0.05546	6
46	235.67	0.59283	6	0.06572	6
47	245.18	0.57050	6	0.07840	6
48	254.47	0.54649	6	0.09254	6
49	263.89	0.51792	6	0.11072	6
50	272.04	0.48869	6	0.13380	6
51	275.65	0.47320	6	0.14681	6
52	278.15	0.46027	6	0.15670	6
53	280.03	0.44970	6	0.16414	6
54	280.76	0.4417	5	0.1720	5
55	280.99	0.4407	5	0.1738	5
56	281.75	0.4346	5	0.1774	5
57	281.86	0.4370	5	0.1756	5
58	282.73	0.4272	5	0.1841	5
59	282.80	0.4274	5	0.1841	5
60	283.02	0.4274	5	0.1841	5
61	283.22	0.4243	5	0.1868	5
62	284.02	0.4185	5	0.1912	5
63	284.75	0.4117	5	0.1978	5
64	284.77	0.4093	5	0.1989	5
65	285.53	0.4019	5	0.2050	5
66	285.77	0.3989	5	0.2081	5
67	286.31	0.3914	5	0.2145	5
68	286.51	0.3895	5	0.2165	5
69	286.74	0.3887	5	0.2188	5
70	287.18	0.3797	5	0.2258	5
71	287.52	0.3708	5	0.2323	5
72	287.62	0.3682	5	0.2385	5
73	286.86	0.3602	5	0.2403	5
74	288.10	0.3551	5	0.2477	5
75	288.13	0.3534	5	0.2488	5
76	288.30	0.3473	5	0.2547	5
77	288.49	0.3345	5	0.2674	5
78	288.50	0.3352	5	0.2680	5
79	288.62	0.3164	5	0.2832	5

3. STATISTICAL TREATMENT OF DATA, RESULTS, AND DISCUSSION

The coexistence curve and the symmetrical part of the CC equations read as

$$\rho_{\mathrm{l,g}} = \rho_{\mathrm{c}}(1 \pm B_0 \tau^{\beta_0} + B_1 \tau^{\beta_1} \pm B_2 \tau^{\beta_2} + \cdots) \tag{1}$$

$$(\rho_{\mathrm{l}} - \rho_{\mathrm{g}})/2\rho_{\mathrm{c}} = B_0 \tau^{\beta_0} + B_2 \tau^{\beta_2} + B_4 \tau^{\beta_4} + \cdots \tag{2}$$

where ρ_{c} is the critical density, $\tau = (T_{\mathrm{c}} - T)/T_{\mathrm{c}}$ is the dimensionless temperature, and β_i and B_i are critical exponents and amplitudes. The odd terms accounting for the asymmetry of CC are not considered here.

A direct fit of the experimental data by Eqs. (1) and (2) with adjustable parameters is complicated by the correlations which emerge among these parameters. In particular, the values β_i and B_i in Eq. (2) are strongly influenced by the choice of the numerical value of T_{c} within the range of measurements error. Usually, the critical temperature is measured with an experimental error which exceeds the uncertainty of the measuring equipment by an order of magnitude or even more. It is caused by problems with identification of the critical state.

To obtain the numerical values of all parameters in the fitting of Eq. (2) a stepwise regression method was used [11]. For adequate fitting of the experimental data three regressive equations, with one, two, and three terms on the right-hand side of the equation, Eq. (2), respectively, were used. In the process of data treatment the statistical weight of each point,

$$W = \left[2(\delta\rho/2\rho_{\mathrm{c}})^2 + \left(\sum_{k=0,1,2} \beta_{2k} B_{2k} \tau^{\beta_{2k}-1} \right)^2 (\delta T/T_{\mathrm{c}})^2 \right]^{-1} \tag{3}$$

was taken into account; here δT and $\delta\rho$ are the errors of temperature and density measurements, respectively. To estimate the quality of the fit we calculated

$$\chi^2 = \sum_{i=1}^{N} W_i (y_{\mathrm{exp},i} - y_{\mathrm{calc},i})^2/(N-M) \tag{4}$$

where

$$y_{\mathrm{exp},i} = (\rho_{\mathrm{l},i} - \rho_{\mathrm{g},i})/2\rho_{\mathrm{c}}, \qquad y_{\mathrm{calc},i} = \sum_{k=0,1,2} B_{2k} \tau_i^{\beta_{2k}} \tag{5}$$

N is the number of points and M is the number of adjustable parameters.

We also calculated the departures

$$\Delta R_i = \left(y_{\mathrm{exp},i} - \sum_{i=0,1,2} B_{2k} \tau_i^{\beta_{2k}} \right) \rho_c \tag{6}$$

and the value of root-mean-square $\bar{S}$

$$\bar{S} = \left[\sum_{i=1}^{N} \Delta R_i^2/(N-M) \right]^{1/2} \tag{7}$$

During the statistical treatment the refinement of the experimental value T_c was carried out simultaneously with the determination of true values β_0 and B_0. The latter values were obtained from the analysis of the dependence of effective values β_{eff} and B_{eff} on the temperature intervals in which the fit by the first regression equation,

$$(\rho_l - \rho_g)/2\rho_c = B_{\mathrm{eff}} \tau^{\beta_{\mathrm{eff}}} \tag{8}$$

was carried out. For this purpose two mutually complementary methods were used.

The first method deals with the definition of the asymptotic range and its size. The authors are of the opinion that the asymptotic range of the order parameter [or symmetrical part of CC; Eq. (2)] is the temperature range where the experimental data are described adequately by the first asymptotical term $B_0 \tau^{\beta_0}$. We determine the size of the asymptotic range in the same way as the authors of Ref. 12, by requiring that the first correction $B_2 \tau^{\beta_2}$ should contribute not more than 1% to the property in question. In the first method, the criterion for the attainment of correct asymptotic values β_0 and B_0 was the independence, in the asymptotic region, of β_{eff} and B_{eff} of the temperature interval. The horizontal portion of the temperature dependences β_{eff} vs $\lg \tau$ (i.e., the range where β_{eff} is independent of the temperature interval of approximation) was obtained for the choice $T_c = 288.643°\mathrm{C}$. The latter value was accepted to be the true value of the critical temperature. The corresponding values of β_0 and B_0 were equal to 0.352 and 2.04, respectively. At any other values of T_c the dependences $\beta_{\mathrm{eff}} = f(\lg \tau)$ and $B_{\mathrm{eff}} = f(\lg \tau)$ had no horizontal portions. For the order parameter of benzene [Eq. (2)] we found an asymptotic range $\tau \leqslant 6.9 \times 10^{-2}$; it included 32 experimental points.

In the second method, the criterion of the correctness of choice of T_c was the minimum of χ^2 and $\bar{S}$ when fitting experimental data in the asymptotic range at adjustable (within the range of experimental error) value T_c. Figures 1a and b show that the best fit ($\min \chi^2$) for the interval containing 15 points in the vicinity of the critical point can be achieved at

$T_c = 288.643°\mathrm{C}$ and $\beta_0 = 0.352$. Note that for this interval one cannot obtain $\beta_0 = 0.325$ by any means. The latter value could be artificially obtained if one would premeditatively omit the experimental point ($\tau = 4 \times 10^{-5}$) which is the nearest one to the critical point (Figs. 1a and b). However, the value 0.325 does not correspond to min χ^2, i.e., this value cannot be regarded as a true value (for our definition of the asymptotic range). Thus both methods of data analysis gave the values $T_c = (288.643 \pm 0.002)°\mathrm{C}$, $\beta_0 = 0.352 \pm 0.003$, and $B_0 = 2.04 \pm 0.02$.

The correctness of the chosen values β_0, B_0, and T_c is corroborated by Fig. 2, which shows the temperature dependences of scaling combinations for CC branches,

$$|\psi_{l,g}| = |(\rho_{l,g} - \rho_c)/\rho_c \tau^{\beta_0}| = |\pm B_0 + B_1 \tau^{\beta_1 - \beta_0} \pm B_2 \tau^{\beta_2 - \beta_0} + \cdots| \tag{9}$$

As shown in Fig. 2, the liquid and gas branches of CC near the critical point have linear portions which are symmetrical with respect to the horizontal and intersect with the ordinate axis at B_0.

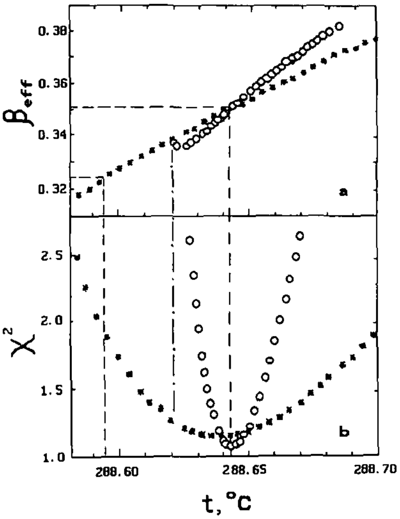

Fig. 1. Influence of the variation of T_c on the values β_{eff} (a) and χ^2 (b) for two temperature intervals, containing 15 (○) ($285.53 < t < 288.62°\mathrm{C}$) and 14 ($*$) ($285.53 < t < 288.50°\mathrm{C}$) experimental points in the vicinity of the critical point. The dashed-dotted line indicates the temperature corresponding to the experimental point nearest to the critical point.

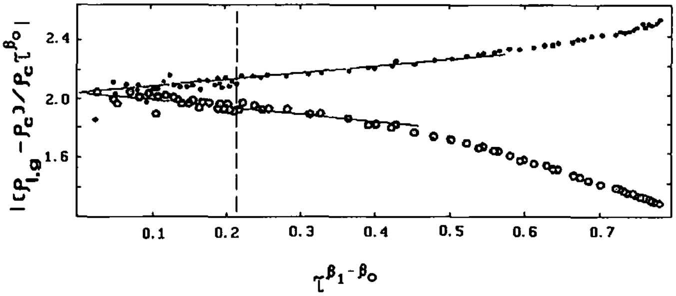

Fig. 2. Coexistence curve for benzene from triple to critical point in coordinates $(\rho_{l,g}-\rho_c)/\rho_c\tau^{\beta_0}$ and $\tau^{\beta_1-\beta_0}$, where the values $\beta_0=0.352$, $\beta_1=0.65$, $t_c=288.643°\mathrm{C}$, and $\rho_c=0.3006\ \mathrm{g\cdot cm^{-3}}$ were used. The data shown at the left of the dashed vertical line were obtained from gravity effect measurements.

Application of a two-term regression equation [Eq. (2)] permitted us to expand the temperature range of adequate fitting, but adequate description of the entire coexistence region was not attained.

The fitting of the data from triple point to critical point by the three-term regression equation [Eq. (2)] with $T_c=288.643°\mathrm{C}$ and $\rho_c=0.3006\ \mathrm{g\cdot cm^{-3}}$ gave the following results:

$$\begin{aligned} &\beta_0=0.35172\pm0.0014, &&B_0=2.0366\pm0.014\\ &\beta_2=1.871\pm0.23, &&B_2=-1.734\pm0.69\\ &\beta_4=2.47\pm1.5, &&B_4=1.41\pm0.76\\ &\chi^2=1.02, &&\bar{S}=0.00069\ \mathrm{g\cdot cm^{-3}} \end{aligned} \tag{10}$$

In this case the value $\beta_0=0.3517(14)$ coincides within limits of error with the value $\beta_0=0.352(3)$ obtained from the analysis of the dependences $\beta_{\mathrm{eff}}=f(\lg\tau)$ and $\beta_{\mathrm{eff}}=f(T_c)$ (Fig. 1). Figure 3 shows the departures of the experimental $(\rho_l-\rho_g)/2$ from a three-term regression equation in the range $4\times10^{-5}<\tau<0.5$. It is seen that the three-term equation describes the data rather well and the fourth term is not necessary.

We have also tested the fitting of the entire data array by the equation with the Wegner-type correction Δ:

$$(\rho_l-\rho_g)/2\rho_c=B_0\tau^{\beta_0}+B_2\tau^{\beta_0+\Delta}+B_4\tau^{\beta_0+2\Delta} \tag{11}$$

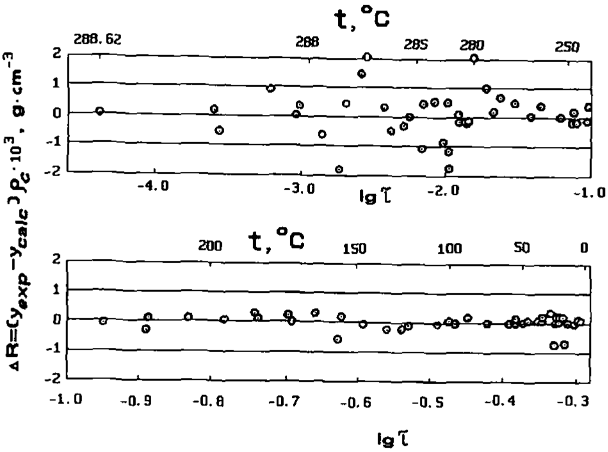

Fig. 3. Departures of the experimental order parameter of benzene from the three-term Eq. (2) with the values of parameters given by Eq. (10) in the range $4\times 10^{-5} < \tau < 0.503$.

The value $\beta_0 = 0.352$ (as the experimental asymptotic exponent) was fixed, while B_i and Δ were the fitting parameters. The best fitting was obtained at

$$\begin{gathered} B_0 = 2.0401, \qquad B_2 = -0.6830, \qquad B_4 = 0.7919, \\ \bar{S} = 0.00069\ \mathrm{g\cdot cm^{-3}}, \qquad \Delta = 1.3 \end{gathered} \tag{12}$$

Figure 4 shows the temperature dependences of the first, second, and third terms (curves 1, 2, and 3, respectively). Curve 4, being the temperature dependence of the sum of all three terms, pretty well describes the experimental data. According to the definition of the asymptotic temperature region (see above), one can conclude that for benzene the asymptotic region is $0 < \tau < 6.88\times 10^{-2}$ ($288.643 > t > 250$°C), because the contribution of the second term in this region is less than 1%. Two terms pretty well describe the region $0 < \tau < 0.238$ ($t_c > t > 155$°C); three terms, the region $0 < \tau < 0.503$ ($t_c > t > 6$°C). These regions are denoted in Fig. 4 as I, I + II, and I + II + III.

We have tested the fitting of the entire array of the coexisting density data with three-term equations which follow from theoretical papers [13–16]. Approximation under the assumption $\beta_0 = 0.352$ showed that only the equations of Green et al. [14] and Chalyi [15] permit us to describe the entire region of phase coexistence. When β_0 is assumed to be 0.325, none of the models gives an adequate fit. Note that the comparison

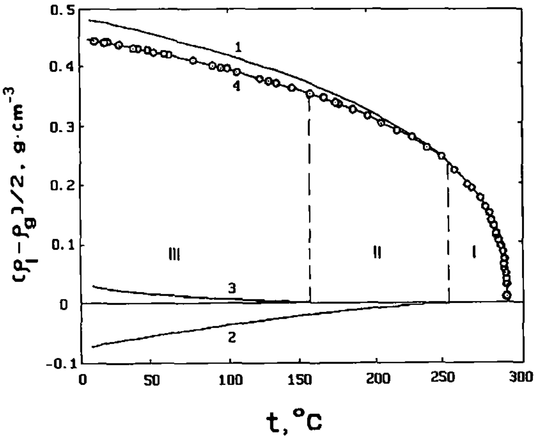

Fig. 4. Temperature dependences of the order parameter of benzene (experimental data) and of the first $(\rho_c B_0 \tau^{\beta_0})$, second $(\rho_c B_2 \tau^{\beta_0+\Delta})$, and third $(\rho_c B_4 \tau^{\beta_0+2\Delta})$ terms—curves 1, 2, and 3, respectively—and of the sum of all three terms —curve 4 [see Eq. (11) and parameter values, Eq. (12)].

of Eq. (11) with the equation from Ref. 15 shows that our value $\Delta = 1.3$ is none other than 2ν in the model [15]. It follows from our data that $\nu = 0.65$, which is approximately equal to the value discussed in the literature.

Assuming mean field (classical) behavior of fluids far from the critical point, we tried to fit the experimental data by the formula

$$(\rho_l - \rho_g)/2\rho_c = b_0\tau^{0.5} + b_2\tau^{1.5} + b_4\tau^{2.5} \tag{13}$$

and to determine the range of its validity. To obtain a description of experimental data by Eq. (13), we were forced to use higher values of the critical temperature than the measured ones. Note that these effective values of T_c increased with the increase in the temperature range, where the fitting was carried out toward the triple point. In any temperature range, Eq. (13) gave a worse fit than Eq. (2) with parameters given by Eq. (10) or Eq. (11) with parameters given by Eq. (12).

4. CONCLUSIONS

Investigations of the temperature dependence of the order parameter (or the symmetrical part of coexistence curve) over the entire range of liquid–gas coexistence from the triple point to the critical point were carried out. The following was shown.

1. The experimental data (both the original and the literature data) for the order parameter of benzene are adequately described by a three-term scaling equation over the entire liquid–gas coexistence region. This means that the total region of coexisting phases (liquid and gas) for benzene ($\Delta T = T_c - T = 282.643°C$, $4 \times 10^{-5} < \tau < 0.503$) may be regarded as the fluctuation range of the critical point.
2. The main term in the order parameter equation with the critical index $\beta_0 = 0.352 \pm 0.003$ describes the asymptotic region $5 \times 10^{-5} < \tau < 6.88 \times 10^{-2}$. The second and the third terms, with critical indices $\beta_0 + \Delta$ and $\beta_0 + 2\Delta$ (where $\Delta = 1.3 \pm 0.2$), are the corrections for the nonasymptotic region.
3. The description of the order parameter by the expansions with fixed values of the critical index $\beta_0 = 0.325$ and the indices of correction terms, obtained by means of the numerical renormalization group solution, is inadequate.
4. Approximation of experimental data by a classical equation for the order parameter with indices $\beta_i = 0.5$, 1.5, and 2.5 appears to be invalid in any temperature region.

Thus the entire experimental region can be described better by experimental exponents rather than by an asymptotic scaling power law even if the Wegner corrections are included. Far away from the critical point approximation by the classical (analytic) expansion requires effective values of T_c which are higher than the experimental ones. This is characteristic for crossover from Van der Waals-like behavior to scaling behavior [17]. Therefore crossover treatment of experimental data on the coexistence curve would be interesting.

ACKNOWLEDGMENTS

This work was supported, in part, by a Soros Humanitarian Foundations Grant (UG 271) awarded by the American Physical Society and Ukrainian Physical Society and by a Ukraine State Committee on Science and Technology Grant (N 23/101). The authors are thankful to Dr. J. M. H. Levelt Sengers, Prof. J. V. Sengers, and Prof. M. A. Anisimov for the reprints and for discussion of critical exponent values.

REFERENCES

1. J. V. Sengers and J. M. H. Levelt Sengers, *Annu. Rev. Phys. Chem.* **37**:189 (1986).
2. E. T. Shimanskaya, Yu. I. Shimansky, A. V. Oleinikova, and M. N. Zhukova, *Ukr. Fiz. Zh. (Ukraine)* **35**:1029 (1990).

3. E. T. Shimanskaya, A. V. Oleinikova, and Yu. I. Shimansky, *Sov. J. Low Temp. Phys.* **16**:780 (1990).
4. E. T. Shimanskaya, Yu. I. Shimansky, and A. V. Oleinikova, *Zh. Fiz. Khim. (Russia)* **66**:1054 (1992).
5. L. M. Artyukhovcskaya, E. T. Shimanskaya, and Yu. I. Shimansky, *Ukr. Fiz. Zhurn. (Ukraine)* **15**:1974 (1970).
6. E. T. Shimanskaya, *Optica Spectrosc.* (Russia) **29**:27 (1970).
7. J. L. Hales and H. A. Gundry, *J. Phys. Ser. E Sci. Instrum.* (England) **16**:91 (1983).
8. G. Hradetzki, A. Gikas, and H. J. Bittrich, *Z. Phys. Chem.* (Leipzig) **266**:165 (1985).
9. N. P. Kroopsky and M. B. Yeselev, *Ing. Fiz. Zh.* (Russia) **50**:487 (1986).
10. R. D. Goodwin, *J. Chem. Ref. Data* **17**:1541 (1988).
11. D. M. Himmelblau, *Process Analysis by Statistical Methods* (Wiley, New York, 1970), p. 957.
12. J. M. H. Levelt Sengers and J. V. Sengers, in *Perspective in Statistical Physics, M. S. Green Mem. Vol.*, H. J. Raveché, ed. (North Holland, Amsterdam, 1981), pp. 239–271.
13. M. J. Cooper, *J. Res. Natl. Bur. Stand.* **75A**:103 (1971).
14. M. S. Green, M. J. Cooper, and J. M. H. Levelt Sengers, *Phys. Rev. Lett.* **26**:492 (1971).
15. A. V. Chalyi, *Ukr. Fiz. Zh.* (Ukraine) **21**:474 (1976).
16. F. J. Wegner, *Phys. Rev.* **5B**:4529 (1972).
17. M. A. Anisimov, S. V. Kiselev, J. V. Sengers, and S. Tang, *Physica A* **188**:487 (1992).