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A New Similarity Found from the Correspondence of the Critical and Zeno-Line Parameters

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We find a new similarity based on the relation between the critical and unit compressibility line (Zeno-line) parameters. Our study relies on the fact that the Zeno-line must be tangential to the extension of the binodal liquid branch at the zero temperature domain. We show that this similarity faithfully describes both the numerical simulation data and experimental data for a wide class of real materials (17 gases, water, and 5 metals). Finally we make some predictions for metals which have critical parameters in the phase diagram domain still inaccessible for experiment.

Introduction

It is well-known that the critical point coordinates of the phase diagram determine specific features of liquids and depend on the interaction potential. For more than a century, in addition to this fact, researchers have recognized that liquid–gas systems exhibit several regular and scalable volumetric features, such as the principle of corresponding states or the law of rectilinear diameter states.^{1,2} Presently there is considerable experimental evidence confirming a third feature besides the two described above. This feature characterizes the states where the compressibility factor is unity (i.e., $Z = P/\rho T = 1$, where P is the pressure, ρ is the density, and T is the temperature). These states form a straight line on the density–temperature plane.

This empirical regularity is referred to as the Zeno-line. Corresponding data are presented for noble gases, hydrocarbons,³ and water and other nonmetallic materials.^{4,5} In our earlier works,^{6,7} we studied the experimental data for Hg and Cs and showed that the Zeno-line is a straight line for these metals as well. Recently we showed⁸ that this empirical regularity has a theoretical verification, at least for a Lennard-Jones (LJ) liquid. We also showed⁷ that (a) the straight line of the unit compressibility factor (Zeno-line) tends asymptotically to the liquid branch of the binodal at low temperatures and (b) the phase coexistence curves are inscribed into the right triangle in the density–temperature plane, which is formed by the Zeno-line and by the segments which this line cuts off at the axes. These statements were confirmed for model systems and for a wide group of real substances (for the first time including metals Hg, Cs, and Cu).

The present paper is based on the further development of the previous considerations. First, we construct a general expression for the liquid branch of the binodal which tends asymptotically to the Zeno-line at low temperature. It should be noted that we do not consider the solid region below the triple point, since the behavior of the $Z = 1$ line in the sublimation region deserves separate consideration.

We show that this general expression provides a good description of the liquid branch of the binodal for a Lennard-Jones system, for which there is a wealth of numerical information on the phase coexistence curves and critical and Zeno-line parameters. Then, on the basis of the analysis of experimental and model data, we find a new similarity based

on the universality of the factor $1 - T_c/T_B - \rho_c/\rho_B$, where the subscripts “B” and “c” are related to the Zeno-line and critical point, respectively. This factor weakly depends on the substance or model, and we assume that it equals the constant determined from the most reliable data of the Lennard-Jones liquid.

This assumption was checked for a wide group of real substances for which the critical parameters are known. We suggest a self-consistent method of determination of the Zeno-line parameters. This method gives the description of the liquid branch of the coexistence curve. For substances with unknown critical parameters, this similarity makes it possible to find the critical density and temperature. To apply it to a particular substance, it is enough to know (for example, from experiment) the low-temperature part of the liquid binodal. Then we suggest the procedure to find the position of such a Zeno-line that provides the best agreement between the calculated binodal and the experimental one. Thus, we have calculated the critical parameters for several metals (Al, Cu, and W). Note that these parameters are still inaccessible for direct measurements. Finally, we have compared our present results with previously known ones and with the data of other researchers.

Descripton of the Liquid Branch of the Binodal Curve

The expression which we will use for describing the liquid branch of the binodal is very similar to one proposed by Reid et al.:⁹

$$\rho(T) = \rho_c + \alpha\tau + \beta\tau^{1/3} \quad (1)$$

where T and ρ are the temperature and density, respectively. Here and below we denote the critical point values by the subscript “c”, and $\tau = 1 - T/T_c$. There are many ways^{9,16} to determine the coefficients in eq 1. Here we find the coefficients α and β using the condition that this equation has to tend to the Z-line equation at $T \rightarrow 0$. The equation for the Z-line is

$$\rho/\rho_B + T/T_B = 1 \quad (2)$$

where T_B is the Boyle point temperature (the second virial coefficient tends to zero when $T \rightarrow T_B$) and ρ_B is the density along the Zeno-line at $T \rightarrow 0$. It should be noted that the Boyle temperature is determined by the intermolecular potential and depends significantly on its form. For example, for the Lennard-

Jones potential $T_B = 3.418$, whereas for the modified Buckingham potential (6-exp) it depends on the parameter a (see refs 6 and 14). This potential with $a = 9.8$ –13 was used to describe the properties of Hg. It also describes the phase diagram of methane at $a = 15$ (see ref 28). Corresponding Boyle temperatures for the 6-exp potential are $T_B(a=9.8) = 5.631$ and $\rho_B(a=9.8) = 3.16$, $T_B(a=13.0) = 3.564$ and $\rho_B(a=13.0) = 1.29$, and $T_B(a=15.0) = 3.098$ and $\rho_B(a=15.0) = 1.23$. (Molecular units are used for both the LJ and Buckingham systems.)

Using eq 2 at $T \rightarrow 0$, we obtained from eq 1 that

$$\rho(T) = \rho_c + \frac{1}{2} \left[\rho_c - \rho_B + 3\rho_B \frac{T_c}{T_B} \right] \tau + \frac{3}{2} \left[\rho_B - \rho_c - \rho_B \frac{T_c}{T_B} \right] \tau^{1/3} \quad (3)$$

Equation 3 can also be rewritten as

$$\rho(T)/\rho_B = 1 - T/T_c + \rho_c T/T_c \rho_B - \gamma f(T/T_c) \quad (4)$$

where $f(x) = 1 - x - (1 - x)^{1/3}$ and the parameter γ is equal to

$$\gamma = \frac{3}{2} (1 - T_c/T_B - \rho_B) \quad (5)$$

Thus, if $T/T_c \rightarrow 1$ (critical point), then $\rho \rightarrow \rho_c$, and if $T \rightarrow 0$, then $\rho \rightarrow \rho_B$. Besides, eq 4 transforms into eq 2 if $T/T_c \ll 1$.

Calculations of the Phase Coexistence Curves

First, we check the validity of eq 3 for the Lennard-Jones liquid. This model plays a peculiar role in our investigation because it quite adequately describes the thermodynamical properties of a wide group of real substances that satisfy the corresponding states law, and there is a wealth of calculated information on the phase coexistence curves and critical and Zeno-line parameters for this model. It should be noted that this model is internally self-consistent and can serve as a test for our theoretical consideration. One more convenient theoretical model is the Buckingham potential liquid.^{6,14,28} The phase diagram for the Buckingham potential was studied in ref 28 with the Gibbs ensemble Monte Carlo technique. It was shown that the phase diagram of the Buckingham system almost perfectly describes the phase diagram of methane for $a = 12$ –16 (the most optimal value was $a = 15$). Below we will show the validity of our findings for methane. This means that they are also valid for the 6-exp potential. Consequently we will consider further only an LJ liquid.

The Boyle temperature (molecular units) is well-known and is equal to $T_B = 3.418$. The Zeno-line density and critical parameters according to the results of refs 10 and 11 are slightly different and are $\rho_B = 1.14$, $T_c = 1.314$, and $\rho_c = 0.314$ and $\rho_B = 1.05$, $T_c = 1.311$, and $\rho_c = 0.279$, respectively. The comparison of the phase coexistence curves according to the data of refs 10 and 11 with our calculations according to eqs 2 and 3 is presented in Figure 1. One can see that there is good agreement.

The parameter of similarity

$$1 - T_c/T_B - \rho_c/\rho_B \quad (6)$$

will play a very important role in our further consideration. Table 1 lists the values of this parameter and the critical and Boyle point parameters for (a) the Lennard-Jones and van der Waals systems, (b) a wide group of real substances that obey the corresponding states law,³ and (c) the metals Hg and Cs, their critical parameters measured in refs 12 and 13 and the approximate Boyle point parameters found in refs 6 and 7.

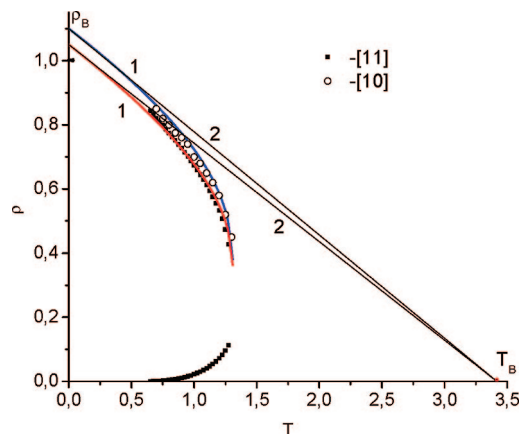


Figure 1. Phase coexistence curves and Zeno-lines for the Lennard-Jones model. The symbols are numerical data on the binodal. Lines 1 and 2 correspond to our calculations (eqs 2 and 3) of the liquid branch of the binodal and the Zeno-line, respectively. T_B and ρ_B are the Zeno-line parameters.

TABLE 1: Critical and Zeno-Line Parameters for Different Models and Substances^a

	LJ	vdW	corresponding states law	Hg	Cs
T_c	1.314 ^b 1.311 ^c	1	1.05	1751	1938
ρ_c	0.314 ^b 0.279 ^c	1	0.3	5.8	0.41
T_B	3.418	27/8	3	6500	4000
ρ_B	1.1 ^b 1.05 ^c	3	1	14	1.96
$1 - T_c/T_B - \rho_c/\rho_B$	0.332 ^b 0.328 ^c	10/27	0.35	0.317	0.315

^a For the LJ and corresponding states law models, the values are dimensionless. For Hg and Cs the density and temperature are expressed in grams per cubic centimeter and Kelvin, respectively.

^b Reference 10. ^c Reference 11.

From Table 1 one can see that the values of the similarity factor $1 - T_c/T_B - \rho_c/\rho_B$ depend weakly on the substances or models (at least for this group of materials). They are exact and consecutive for the Lennard-Jones and van der Waals models only. As for metals Hg and Cs, we do not know the exact form of the interaction potential and cannot find the exact values of the Zeno-line point parameters. Our earlier work^{6,7} used experimental data for that. Nevertheless, the values of this similarity factor presented above are very close to each other. This circumstance suggests that this factor can be (in some approximation) set equal to the value following from the Lennard-Jones model as the most consecutive one and the one closest to the real substances, i.e., $1 - T_c/T_B - \rho_c/\rho_B = a = 0.33$. The latter expression can also be written as a general relation:

$$\frac{\rho_c}{\rho_B(1-a)} + \frac{T_c}{T_B(1-a)} = 1 \quad (a=0.33) \quad (7)$$

Equation 7 can be treated as an equation describing the line of the critical points on the density–temperature plane. This line is parallel to the Z-line and cuts off the segments on the density $\rho_B(1-a)$ and temperature $T_B(1-a)$ axes. We should note that the value $a = 0.33$ is not a consequence of the van der Waals equation. Let us consider the van der Waals equation written in dimensionless units ($\rho = \rho/\rho_c$ and $T' = T/T_c$). In this case the Boyle point parameters⁸ are $T_B = 27/8$ and $\rho_B = 3$. The

exact value of a is $10/27$ ($1 - a = 17/27$). If we choose $a = 1/3$, then we find that the left side of eq 7 is equal to $17/18$ instead of unity. Similarly for the Lennard-Jones liquid (calculated Lotfi¹⁰ and $a = 1/3$) the left side of eq 7 is equal to 1.004 instead of unity.

Below we show that the similarity found above allows us to describe the phase coexistence curves and the critical and Z-line parameters on the density–temperature plane for a wide group of real substances and that this description corresponds well to the experimental data. Besides, we make several predictions concerning metals, which have critical parameters in the phase diagram domain still inaccessible for experiment.

Calculations of the Liquid Branches of the Binodals and Z-Line for Substances with Known Critical Parameters

The binodal of a substance can be calculated according to eqs 3 and 4 if the critical and Zeno-line parameters are known. The measurements and calculations of the critical parameters have received much attention in the literature.¹⁴ Let us describe in detail the definition of the Zeno-line parameters. These parameters, T_B and ρ_B , can be found in several ways.

First, the Zeno-line can be calculated if the interaction potential corresponding to the substance of interest is known. This approach is applicable to the model system (see above), but this potential as a rule is unknown for the real substance.

Another approach is based on the fact that the Zeno-line is an asymptote relative to the binodal at $T \rightarrow 0$ and has to tend to the tangent to an imaginary extension of this line up to the zero temperature domain (as we noted above). However, the liquid branch of the binodal at $T \rightarrow 0$ does not exist because the substance attains the solid state, so all the measurements of binodals exist for finite temperatures $T > 0$. Nevertheless, we can construct the liquid branch of the binodal using eq 3 and extend it till the zero temperature. Then a tangent to this line at $T \rightarrow 0$ will be the Z-line. Therefore, we require that the deviations of the binodal thus constructed from the experimental part of the binodal must be minimal. Consequently, we can use the least-squares method in our calculations. In this case the parameters T_B and ρ_B are dependent on the number of points used in the least-squares method. For example, we used the binodal measurements for ammonia presented in the NIST database¹⁵ and applied the least-squares technique for 2–25 points starting from the lowest temperature. The variation of ρ_B was not great, 0.94–0.95 g/cm³ (i.e., $\sim 1\%$). However, the variation of the Boyle temperature was 850–890 K (i.e., $\sim 4\%$). Therefore, this approach has some error.

A third approach considered here is the proposition that the relation between the Boyle and critical parameters (eq 7), as obtained for the Lennard-Jones system, is valid for various other systems, including real substances. We also suggest that the liquid branch of the binodal can be described by eq 3.

It should be noted that eq 1 was checked for 107 different substances¹⁶ (with α and β different from ours). In ref 16 there were also additional considerations allowing for a description of the gas branch of the binodal. Here we will use only the fact that eq 3 (as a partial case of eq 1) can successfully describe the liquid branch for a wide range of substances.

First, let us consider the substances with known critical parameters, where measurements of the binodal exist. We set ρ_B in the range obtained by the least-squares method. Then we find T_B using eq 7. After that, we calculate the dependence of the density upon the temperature along the binodal $\rho(T)$ according to eq 3. Then we compare $\rho(T)$ with the measured data $\rho_{\text{exp}}(T)$, i.e., calculate the value δ : $\delta = \sum_i |1 - \rho(T_i)/\rho_{\text{exp}}(T_i)|$.

TABLE 2: Critical and Zeno-Line Parameters for Different Substances

	T_c , K	ρ_c , g/cm ³	T_B , K	ρ_B , g/cm ³
Ar	150.69	0.536	392.84	1.87
Ne	44.49	0.482	118.85	1.63
Kr	209.48	0.909	537.98	3.24
Xe	289.73	1.100	740.02	3.95
ammonia	405.40	0.225	935.92	0.95
CO ₂	304.13	0.468	741.37	1.80
ethane	305.33	0.207	779.35	0.74
ethene	282.35	0.214	714.12	0.78
fluorine	144.41	0.593	385.06	2.01
hexane	507.82	0.233	1235.84	0.90
methane	190.56	0.163	498.06	0.57
N ₂	126.19	0.313	327.62	1.10
O ₂	154.58	0.436	401.14	1.53
propene	365.57	0.223	894.42	0.86
R13	302.00	0.583	763.31	2.13
R22	369.30	0.524	907.89	1.99
R32	351.26	0.424	823.92	1.74
Cs	1924	0.39	4114.47	1.96
Hg	1751	5.8	6552.60	14.40
water	647.3	0.32	1268.0	1.2

If $\delta < 10^{-3}$, we can consider that the calculated $\rho(T)$ is in agreement with the measured data $\rho_{\text{exp}}(T)$. Otherwise, we change ρ_B and repeat the procedure until $\delta < 10^{-3}$. The Boyle parameters obtained in this way are presented in Table 2. We considered 17 gases, water, and 5 metals. The data for the gases, Cs, and Hg are presented in Table 2. (The critical parameters of the gases were taken from the NIST database,¹⁵ those for Cs and Hg were taken from refs 12 and 13, those for water were taken from refs 5, 24, and 25, and the water Zeno-line was obtained for the first time in ref 5.)

For the gases considered here, the procedure above was always successful. In Figure 2 we present the results of the binodal calculation for the substances which satisfy the corresponding states law (a), ammonia (b), CO₂ (c), and hexane (d). One can see how for these substances the similarity formulated here is satisfied (i.e., eqs 3 and 7) and the condition of coincidence of the Zeno-line and the tangent to the binodal at $T \rightarrow 0$.

The situation for the metals is in many ways similar to that for the gases. The analysis of the measurements carried out in our previous work^{6,7} showed the existence of a straight Zeno-line for Hg and Cs. However, the construction of the binodal according to eq 3 was somewhat less exact in comparison with that of the gases. In Figure 3 we present the corresponding results for Cs. Here the best fit of the binodal corresponds to $\delta = 1.1 \times 10^{-3}$ (this value is somewhat greater than for the gases). This greater inaccuracy can appear due to additional terms in the Cs equation of state near the critical point (see ref 13). This is a term of type $\sim \tau^{1-\alpha}$, where α is the critical exponent, characterizing the temperature dependence of the heat capacity near the critical point. Therefore, this term should be accounted for at the points far from the critical one, but with another pre-exponent coefficient. We also draw the Zeno-line calculated in our previous work⁷ on the basis of the corresponding measurements. This line has a slope different from the one calculated here. The reason for this discrepancy, apparently, is the uncertainty in the ionic composition of Cs used in the calculation of ref 7. Here we do not consider the Cs composition. Therefore, the new Zeno-line should be more accurate.

For Hg, there is a discrepancy between the calculated and measured binodals for $T > 1000$ K (see Figure 3). The best fit corresponds to the parameter $\delta \approx 10^{-2}$. Therefore, it seems that

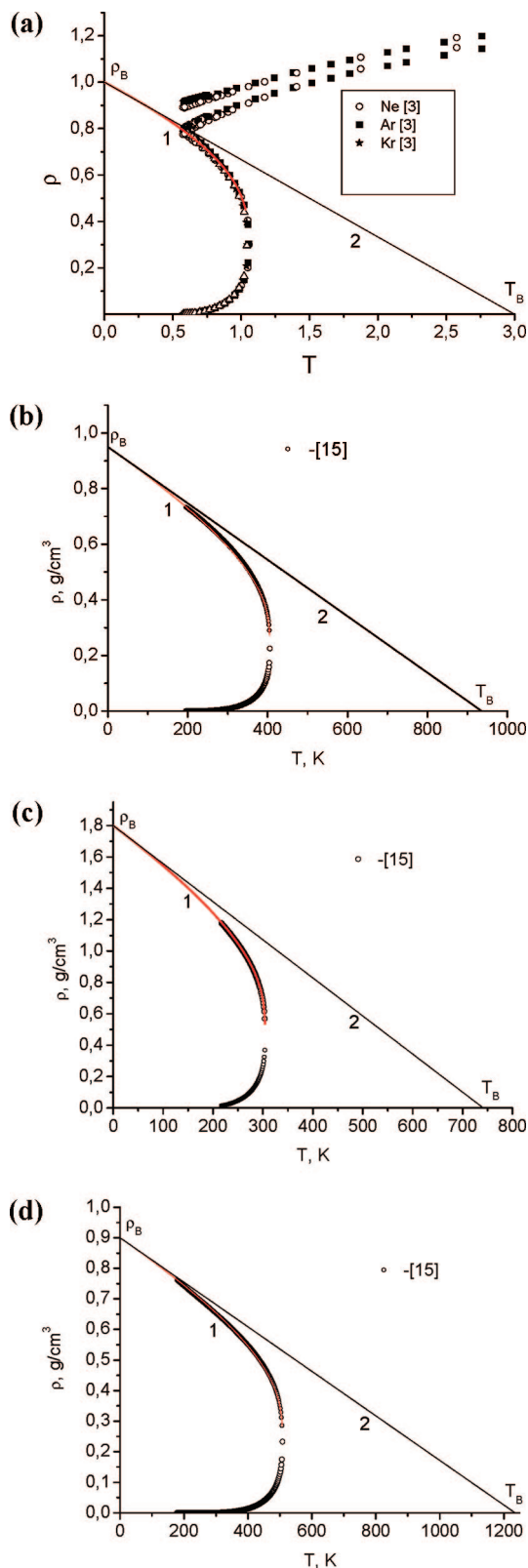


Figure 2. Phase coexistence curves and Zeno-line for the substances obeying the corresponding states law (a), ammonia (b), CO₂ (c), and hexane (d). The symbols are experimental data on the binodal. Curve 1 is the results of our calculations of the liquid branch of the binodal according to eq 3. Straight line 2 is the Zeno-line. T_B and ρ_B are the Zeno-line parameters.

eq 3 has a lower accuracy for Hg in comparison with other substances. This is not a surprise since Hg has different properties in comparison with many other metals.¹² Conse-

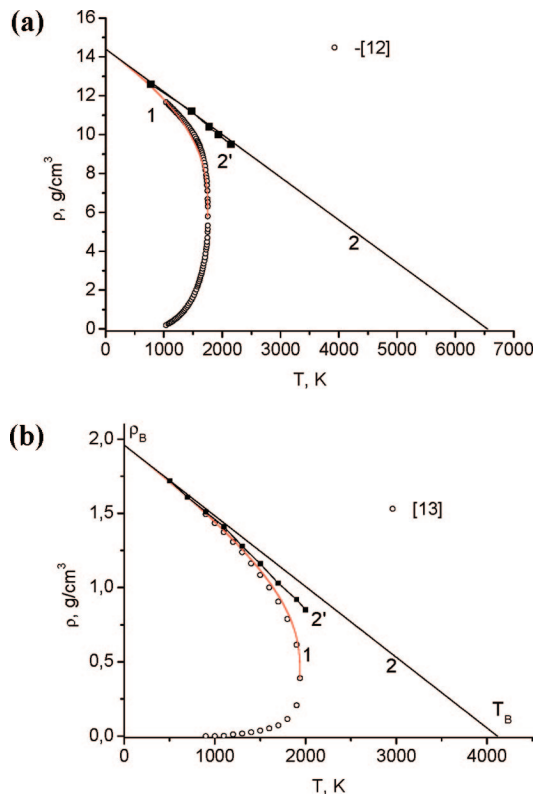


Figure 3. Phase coexistence curves and the Zeno-line for metals Hg (a) and Cs (b). The symbols are experimental data on the binodal. Line 1 is the results of our calculations of the liquid branch of the binodal according to eq 3. Straight line 2 is the Zeno-line of the present work and line 2' is the previous one presented in refs 6 and 7. T_B and ρ_B are the Zeno-line parameters.

quently, the binodal equation for Hg can also be different. However, the Zeno-line regularity also likely applies to Hg. Our previous results of the Zeno-line calculation⁷ are in good agreement with the present one. Thus, eq 7 can also be possibly true for Hg.

Calculations of the Liquid Branches of the Binodals and Z-Line for Substances with Unknown Critical Parameters

It is a challenge to use the method suggested above when we know the low-temperature branch of the binodal only and have no information concerning the critical and Boyle point parameters. This is the current state of knowledge for many metals, which have critical parameters in the phase diagram domain still inaccessible for experiment. Let us consider, for example, metals Al, Cu, and W. The low-temperature branches of the binodals found on the basis of the experimental data for these substances are presented in Figure 4. The tangent to the low-temperature part of the binodal allows us to find the Boyle point parameters (as shown in Figure 4). After that we again can suppose that the binodal can be described by eq 3.

The Zeno-line parameters are unknown as well as the critical ones. Consequently, the procedure described above cannot be applied directly to these metals. However, we can find the Zeno-line parameters independently using the least-squares method. After that we can use the analogous procedure to obtain the critical point parameters. Now for given Zeno-line parameters we set some value of ρ_c . Then we can calculate T_c with the help of eq 7. After that we can calculate δ as in the previous section. Further we obtain the necessary value of δ by the variation of ρ_c . It should be noted that the experimental data

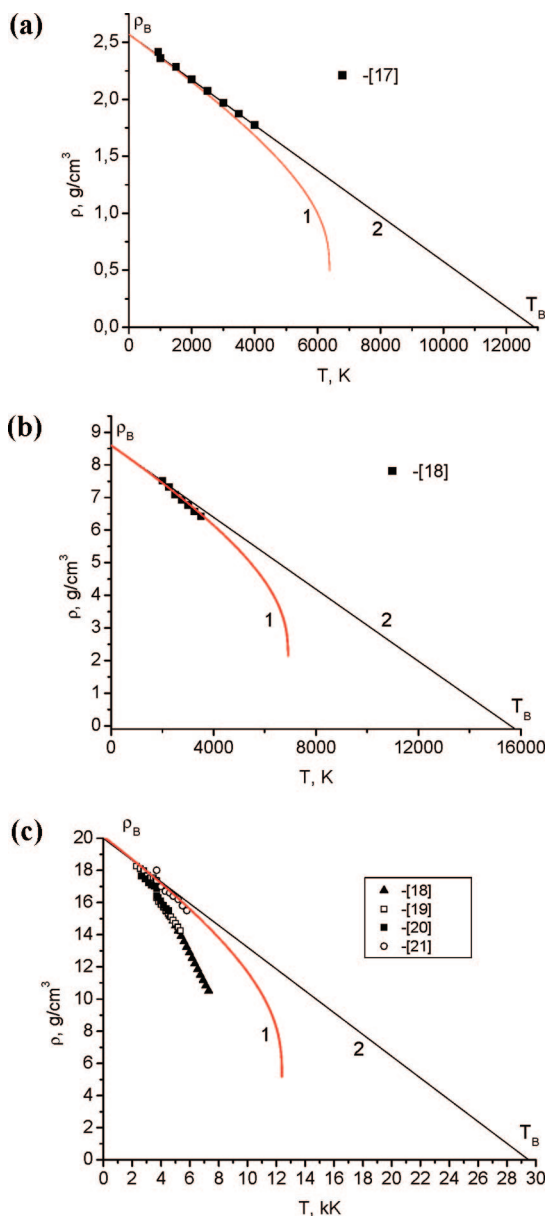


Figure 4. Phase coexistence curves, Zeno-line, and critical parameters for metals Al (a), Cu (b), and W (c). The symbols are experimental data on the binodal. Line 1 is the results of our calculations of the liquid branch of the binodal according to eq 3. Straight line 2 is the Zeno-line.

TABLE 3: Critical and Zeno-Line Parameters for Metal Liquids Al, Cu, and W

metal	T_c , K	ρ_c , g/cm ³	method	ref	T_B , K	ρ_B , g/cm ³
Al	6378	0.45	this work		12888	2.57
	8860	0.28	scaling	22		
	8000	0.64	extrapolation	23		
Cu	7093	1.95	this work		15593	8.6
	7620	1.4	scaling	22		
	8390	2.4	extrapolation	23		
W	12387	4.92	this work		29131	20.1
	12500	4.52		26		

for Al, Cu, and W really do not belong to the binodals, they belong to part of the isobar curves. It is followed from thermodynamical consideration²⁷ that the isobar curves for the liquid state go very close to the binodals. Therefore, the measured isobars^{17–21} practically coincide with the corresponding binodals. However, it is also possible that the experimental

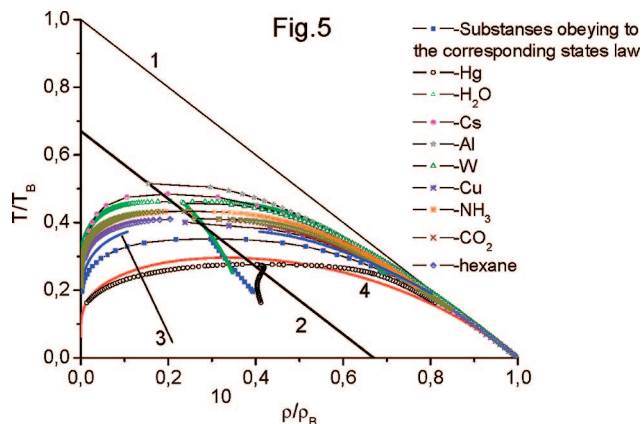


Figure 5. Dependence of the temperature and density along the phase coexistence curves on parameters reduced to the Zeno-line parameters for the different model systems and substances: (line 1) $Z = 1$ line, (line 2) critical points line, (line 3) Lennard-Jones numerical modeling of ref 11, (line 4) according to the van der Waals equation. The symbols correspond to the different substances. We have added the average diameter for Hg, water, and substances satisfying the corresponding states law.

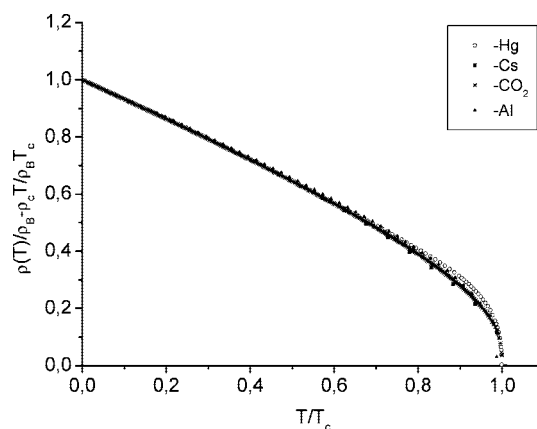


Figure 6. Dependence of the modified density (eq 7) along the liquid branch of the binodal via T/T_c for Hg, Cs, CO₂, and Al.

points can lie at the Zeno-line, as takes place for Al. To take into account the possible difference, we somewhat increase the value of the criterion δ , i.e. $\delta < 0.01$.

The results of our calculations of the critical and Boyle point parameters are collected in Table 3. Besides, in this table, one can find the values of the critical parameters as obtained by other authors. We also present the corresponding Figure 4 with the binodals and the Zeno-lines for these substances. It should be noted that there is substantial scatter in the experimental data for W. Among them, we choose data from refs 18 and 21 since they give the most reasonable values of the critical parameters.

Our findings are consistent with earlier known results. Moreover, they correspond to the theoretical and experimental information on the phase coexistence curves and critical and Boyle point parameters. This suggests that these findings are well justified.

Universal Triangle of States and Liquid Branch of the Binodal

Similarly to earlier work,⁷ let us present the binodals of all model systems and real substances considered above on the density–temperature plane using the coordinates reduced to the Zeno-line parameters, $\rho' = \rho/\rho_B$ and $T' = T/T_B$. In these coordinates, the Zeno-line is a straight line, universal for all

substances, and this line cuts off unit segments on the temperature and density axes. The corresponding picture is shown in Figure 5. We have added the water data following refs 24 and 25 to this figure.

One can see that the binodals of all substances are inscribed into a triangle, formed by the $Z = 1$ line and axes. The critical parameters lie close to the line defined by eq 7, which is parallel to the $Z = 1$ line. It is significant that the critical temperature and density reduced to the Boyle point parameters lie in a sufficiently restricted area and differ by less than a factor of 2 in value. This range is determined by extreme points located near the line of critical points. One extreme point has a maximum value $\rho_c/\rho_B \approx 0.4$ and a minimum value $T_c/T_B \approx 0.278$ and corresponds to the mercury critical parameters. The other extreme point has minimum $\rho_c/\rho_B \approx 0.175$ and maximum $T_c/T_B \approx 0.51$ values and corresponds to another metal—aluminum. The critical parameters for the other substances, considered in this paper, lie between these extreme values.

Let us introduce the modified density along the liquid binodal, which follows from eq 4 and is defined as

$$\tilde{\rho}(T) = \rho(T)/\rho_B - \rho_c T/\rho_B T_c = F(T/T_c) \quad (8)$$

The similarity dictates that this is a universal function of T/T_c , namely, $F(x) = 1 - x - [1 - x - (1 - x)^{1/3}]/2$. The dependence shown in eq 8 is presented in Figure 6 for Al, Hg, CO₂, and Cs. Some of these substances have the extreme position of the binodals in Figure 5. Evidently the similarity provides a universal behavior of the liquid branches of the binodals for all substances considered in Figure 6.

Conclusion

We have shown that the idea of construction of a new similarity based on the correspondence of the critical and Z -line parameters turns out to be highly fruitful. It is applied to a more wide group of substances in comparison with those satisfying the corresponding states principle. The condition that the Zeno-line must be tangential to the extension of the binodal liquid branch at $T \rightarrow 0$ allows us to avoid difficulties connected to the uncertainty of intermolecular potentials. Due to this new similarity we can find the critical density and temperature using only the experimental data on the low-temperature part of the liquid binodal branch. Consequently, it is possible to find the critical parameters of the substances that have the critical point in the phase diagram domain still inaccessible for experiment.

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