Correspondence between the Critical and the Zeno-Line Parameters for Classical and Quantum Liquids

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We set new regularities between the effective compressibility factor at the critical point (Z^*) and unit compressibility line (Zeno-line) parameters. For classical liquids, Z^* is the ordinary compressibility factor Z_c , but for quantum liquids Z^* depends on the de Boer parameters. As a result, we show that a wide group of real substances with the classical thermodynamical properties has $Z_c < 0.32$. Classical mercury and quantum H_2 , He^4 , and He^3 have H_2 0 or H_2 1. Using the low temperature part of the liquid—gas coexistence curve obtained from experiment, we can find the critical parameters for metals (Al, Cu, W, U, and Zr) for which these parameters are unknown in advance and lie in the domain of parameters still inaccessible for experiment.

1. Introduction

The similarity laws are regular and scalable volumetric features observed in a wide class of liquid—gas systems. The principle of corresponding states or the law of rectilinear diameter^{1,2} are the most well-known example of these features. Presently, there is considerable experimental evidence confirming one more similarity law. It characterizes the states where the compressibility factor is unity. These states form a straight line on the density-temperature plane. Let us denote the compressibility factor as $Z = Pm/\rho kT$. Here P is the pressure, ρ is the mass density, T is the temperature in K, m is the mass of an atom or molecule, and k is the Boltzmann constant. The states where the compressibility factor is unity are described by the solution of equation $Z(\rho(T),T) = 1$.

This empirical regularity is referred to as the Zeno-line. Corresponding data are presented for noble gases, hydrocarbons, water, and other nonmetallic materials. 4.5 We studied the experimental data for mercury and cesium and showed that Zeno-line is a straight line for these metals as well^{6,7} and recently showed⁸ that this empirical regularity has a theoretical verification at least for Lennard-Jones (L-J) liquid. An important point is that the Zeno-line tends asymptotically to the liquid branch of the binodal at low temperatures. This statement was proven in ref 7 and was confirmed for model systems and for a great totality of real substances (including metals: Hg, Cs, and Cu).

In the present paper, we use the universal expression suggested earlier in refs 9 and 10 for the description of the liquid branch of the binodal line for a wide group of real substances. In addition the extension of this line in $T \rightarrow 0$ domain has to tend to the Zeno-line asymptotically, that is, the Zeno-line becomes the tangent to the liquid binodal at $T \rightarrow 0$. The Zeno-line parameters were determined from the condition that the binodal, thusly constructed, deviates from experimental binodal data (or their low temperature part) minimally. In comparison with refs 9 and 10, we have added some more substances with known critical parameters. This addition includes alkaline metals Na, K, Li and Rb and nonmetallic substances H_2 , He^4 , and He^3 with quantum properties. The analysis of the correspondence between the critical and Zeno-line parameters for this wide group

2. Determination of the Zeno-line Parameters and Similarity Factors

The equation for the Zeno-line is (see refs 6-10)

$$\rho/\rho_{\rm B} + T/T_{\rm B} = 1 \tag{1}$$

where $T_{\rm B}$ is the Boyle point temperature (the second virial coefficient equals zero when $T \to T_{\rm B}$), and $\rho_{\rm B}$ is the density along the Zeno line at $T \to 0$. It should be noted that the Boyle temperature is determined by the intermolecular potential and depends significantly on its form. For example, for the L-J potential $T_{\rm B} = 3.418$ and $\rho_{\rm B} = 1.14$ (ref 9).

The expression that we will use to describe the liquid branch of the binodal has been suggested earlier⁹ on the basis of the analysis of experimental and model data. It has the form

of materials shows the existence of some regularities. One of them describes the dependence between the critical and Zenoline parameters and forms the straight line at the densitytemperature plane, which is parallel to the Zeno-line. The other reflects the dependence of binodal opening (we shall refer thus to the values $\rho_{\rm B}/\rho_c$ and $Z_{\rm c}$; see more discussion of the term in Section 3) on the compressibility factor at the critical point. The smaller is Z_c, the greater is the binodal opening. The overwhelming majority of classical substances form one group of materials with Z_c < 0.32. Classical mercury and quantum H_2 , He^4 , and He^3 form another group of materials with Z_c (or Z^*) > 0.37. We introduce some effective value of Z^* which characterizes the binodal opening for the quantum liquids. The latter quantity depends on the de Boer parameter and grows with increase of this parameter. The found regularities allow to set the critical parameters for several metals (Al, Cu, W, U, and Zr). 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.

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$$\rho(T) = \rho_{c} + \frac{1}{2} \left[\rho_{c} - \rho_{B} + 3\rho_{B} \frac{T_{c}}{T_{B}} \right] \tau + \frac{3}{2} \left[\rho_{B} - \rho_{c} - \rho_{B} \frac{T_{c}}{T_{B}} \right] \tau^{1/3}$$
 (2)

where $\tau=1-T/T_c$ and the subscripts B and c are related to the Zeno-line and critical point, respectively. Thus, if $T/T_c \to 1$ (critical point), then $\rho \to \rho_c$, and if $T \to 0$, then $\rho \to \rho_B$. Besides, eq 2 transforms into eq 1 if $T/T_c \ll 1$ and the critical and Zeno-line parameters are also connected by a simple similarity relation

$$T_c/T_B + \rho_c/\rho_B = S_1 = 0.67$$
 (3)

At first, we consider the substances with the known critical parameters. The parameters $\rho_{\rm B}$ and $T_{\rm B}$ will be found from the condition that the deviations of the binodal thus constructed from the experimental part of the binodal must be minimized. Consequently we can use the least-squares method in our calculations. Such a procedure was applied earlier for 17 gases and two metals (Hg, Cs) and was always successful. Here we include into our consideration alkaline metals Na, K, Li, and Rb and also substances H_2 , He^4 , and He^3 with quantum properties. The critical parameters of all these materials are known from experiments. In Figure 1, we present the results of the binodal calculation for H_2 . Although these substances display quantum properties, the agreement between experimental and calculated data is quite satisfactory. Analogously good agreement for other substances was demonstrated.

Let us discuss He⁴ and He³ with strong quantum properties. It should be noted that linearity of the Zeno-line for He⁴ was discovered in ref 3. Our calculations show that the three-term equation for binodal (2) describes experimental data only approximately. The deviation between experimental and calculated data is much greater in comparison with other substances considered here. However the critical parameters and coexistence curves are known for these liquids from experiment and we need to find the Zeno-line parameters for these substances only. Therefore we decided to include these quantum substances into our consideration since they play an important role in our further classification of substances.

The critical and Zeno-line parameters for substances considered earlier in ref 9 and added here are presented in Table 1. All values in Table 1 are presented within the accuracy 1%, excluding for the L-J and van der Waals (vdW) models.

The first four columns in this table give the values of the critical parameters and compressibility factor at the critical point Z_c . The latter is determined as

$$Z_{\rm c} = \frac{P_{\rm c}m}{\rho_{\rm c}kT_{\rm c}} \tag{4}$$

where P_c is the critical pressure. The references to the data of the critical point parameters are given in square brackets in the first column. The fifth and sixth columns give the Zeno-line parameters. The way of their determination is described in detail earlier. Finally, the last five columns show the values of similarity factors, which will be discussed below.

3. The Parameter Determining the "Opening" of the Binodal Curves

Let us build the binodals and Zeno-lines for different substances in coordinates reduced to the critical point, that is,

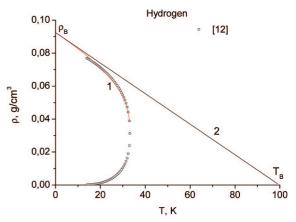


Figure 1. The phase coexistence curves and Zeno-line for H_2 . The symbol is experimental data on the binodal (ref 12). Line 1 is the results of our calculations of the liquid branch of binodal according to eqs 2 and 3. Straight line 2 is the Zeno-line of the present work. T_B and ρ_B are the Zeno-line parameters.

 ρ/ρ_c and T/T_c . The corresponding picture is presented in Figure 2 According to the relation 3 all Zeno-lines in these reduced coordinates intersect at one point when $\rho_B/\rho_c = T_B/T_c \approx 1.5$. The values ρ_B/ρ_c and Z_c can be characterized so-called the binodal "opening". The smaller values of the compressibility factor Z_c and greater ones of the ρ_B/ρ_c correspond to the widest binodal curves. We will say in this case that the corresponding binodals have the greatest opening. For example, the compressibility factor for sodium is equal to $Z_c = 0.137$ and $\rho_B/\rho_c = 5$. The corresponding binodal is the widest and has the greatest opening. Mercury has the greatest and least values of the compressibility factor and relation ρ_B/ρ_c correspondingly among the classical substances. Its binodal curve is the most narrow (opening is the smallest). Argon is located at an intermediate position.

The quantum liquids violate this order. Thus, He⁴ has $Z_c = 0.3$ and the opening of its binodal has to correspond to argon. Actually the binodal curves for He⁴ with $Z_c = 0.3$ and mercury with $Z_c = 0.387$ practically coincide. It also follows from Figure 2 that the binodal for quantum H₂ with $Z_c = 0.3$ is very close to the binodal for the van der Waals model system with $Z_c = 0.375$. This circumstance induces a suggestion that the Z_c for the quantum liquids, characterizing a binodal opening, has to differ from the classical one. The de Boer parameter $B = h/\sigma(2\pi mD)^{1/2}$ (where σ is the "diameter" corresponding to the distance at which the potential is equal to zero and D is the depth of the intermolecular potential) distinguishes a quantum liquid from the classical one. Below in Table 2, we give the values of the de Boer parameters for quantum liquids.

We see that the substances in Table 2 have approximately equal values of Z_c . The opening of the quantum liquids decreases with increasing the de Boer parameter. Thus the binodal opening for hydrogen is greater than the binodal opening for He⁴ and even greater than one for He³. So the liquids with strong quantum properties have the "narrowest" binodal curves. In order to take into account these peculiarities of the quantum liquids, we suggest that the factor characterizing the binodal opening for a quantum liquid Z^* can be presented as

$$Z^* = Z_{\rm c}(1 + aB) \tag{5}$$

where a is a coefficient. The value of this coefficient we find from the condition that Z^* for the quantum liquid has to coincide

TABLE 1: The Critical and Zeno-Line Parameters

	critical parameters				Zeno-line pa	arameters	similarity parameters			
model, subs	T _c , K	ρ_c , g/cm ³	P _c , atm	$Z_{\rm c} = P_{\rm c} m / \rho_{\rm c} k T_{\rm c}$	$T_{\mathrm{B}},\mathrm{K}$	$\rho_{\rm B}$, g/cm ³	S_2	$P_{\rm c}m/ ho_{\rm B}kT_{\rm B}$	$T_{\rm c}/T_{\rm B}$	$\rho_{\rm c}/\rho_{\rm B}$
L- J ^{9a}	1.305	0.314	0.127	0.308	3.418	1.14	0.076	0.033	0.38	0.285
vdW^a	1	1	1	3/8 = 0.375	27/8 = 3.375	3	5/81 = 0.061	1/27 = 0.037	0.296	0.333
Ar^{12}	1.51×10^{2}	0.54	48.63	0.29	3.93×10^{2}	1.87	0.078	0.031	0.38	0.27
Ne^{12}	44.49	0.48	26.79	$0.30, 0.34*^{b}$	1.19×10^{2}	1.63	0.077	0.033	0.37	0.30
Kr^{12}	2.01×10^{2}	0.91	55.25	0.29	5.38×10^{2}	3.24	0.077	0.032	0.39	0.28
Xe^{12}	2.90×10^{2}	1.10	58.42	0.29	7.40×10^{2}	3.95	0.077	0.031	0.39	0.27
NH_3^{12}	4.05×10^{2}	0.23	1.13×10^{2}	0.25	9.36×10^{2}	0.95	0.076	0.026	0.43	0.24
CO_2^{12}	3.04×10^{2}	0.47	73.77	0.27	7.41×10^2	1.80	0.077	0.029	0.41	0.26
ethane ¹²	3.05×10^{2}	0.21	48.72	0.28	7.79×10^{2}	0.74	0.079	0.030	0.39	0.28
ethene ¹²	2.82×10^{2}	0.21	50.42	0.28	7.14×10^{2}	0.78	0.078	0.030	0.40	0.27
F_2^{12}	1.44×10^{2}	0.59	51.72	0.27	3.85×10^{2}	2.01	0.080	0.030	0.38	0.30
hexane ¹²	5.08×10^{2}	0.23	30.34	0.26	1.24×10^{3}	0.90	0.078	0.028	0.41	0.26
CH_4^{12}	1.91×10^{2}	0.16	45.99	0.28	4.98×10^{2}	0.57	0.078	0.031	0.38	0.29
N_2^{12}	1.26×10^{2}	0.31	33.96	0.29	3.28×10^{2}	1.10	0.078	0.031	0.39	0.28
O_2^{12}	1.55×10^{2}	0.44	50.43	0.29	4.01×10^{2}	1.53	0.078	0.031	0.39	0.29
propene ¹²	3.66×10^{2}	0.22	46.65	0.29	8.94×10^{2}	0.86	0.075	0.032	0.41	0.26
R13 ¹²	3.02×10^{2}	0.58	38.79	0.28	7.63×10^{2}	2.13	0.078	0.030	0.40	0.27
R22 ¹²	3.69×10^{2}	0.52	49.90	0.27	9.08×10^{2}	1.99	0.078	0.029	0.41	0.26
$R32^{12}$	3.51×10^{2}	0.42	57.82	0.24	8.24×10^{2}	1.74	0.079	0.025	0.43	0.24
Cs^{13}	1.93×10^{3}	0.39	94.00	0.20	4.12×10^{3}	1.96	0.075	0.018	0.47	0.20
Li ¹⁵	3.22×10^{3}	0.12	6.89×10^{2}	0.17	7.17×10^3	0.55	0.082	0.017	0.45	0.22
Rb ¹⁵	2.02×10^{3}	0.29	1.25×10^{2}	0.22	4.13×10^{3}	1.60	0.069	0.019	0.49	0.18
K^{16}	2.18×10^{3}	0.18	1.48×10^{2}	0.18	4.66×10^{3}	0.89	0.078	0.017	0.48	0.20
Na ¹⁵	2.50×10^{3}	0.21	2.56×10^{2}	0.14	5.39×10^{3}	1.00	0.083	0.013	0.46	0.21
Hg^{17}	1.75×10^{3}	5.80	1.65×10^{3}	0.39	6.55×10^{3}	14.40	0.065	0.042	0.27	0.40
water ^{18,19}	6.47×10^2	0.32	2.21×10^{2}	0.23	1.27×10^{3}	1.20	0.11	0.030	0.51	0.27
H_2^{12}	33.15	0.031	12.96	0.30, 0.37*	99.84	0.093	0.079	0.041	0.33	0.34
$(He^4)^{12}$	5.20	0.070	2.27	0.30, 0.39*	19.46	0.17	0.071	0.030	0.26	0.41
$(He^3)^{12}$	3.34	0.039	1.15	0.32, 0.47*	18.55	0.078	0.060	0.028	0.18	0.49

^a All values in these lines are given in dimensionless units. ^b The asterisk denotes the Z* for the quantum liquids recalculated according to eq 5.

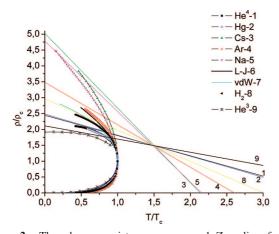


Figure 2. The phase coexistence curves and Zeno-line for the substances in the coordinates reduced to the critical point. The lines with symbols (marked by numbers) correspond to experimental data on the binodal for different substances. The straight lines with numbers are the Zeno-lines. Each number replays the corresponding symbol.

TABLE 2: The de Boer Parameters Values *B* for Quantum Liquids^{22,23}

	Ar	Ne	D_2	H_2	He ⁴	He ³
В	0.069	0.217	0.452	0.78	0.99	1.76
$Z_{\rm c}$	0.289	0.3	0.3	0.3	0.3	0.321
Z^*	0.293	0.319	0.34	0.37	0.386	0.48

with Z_c for the classical one with the similar thermodynamical properties. In our case, it is evidently from Figure 2 that the binodal curves for the quantum He⁴ practically coincide with the classical Hg, that is, $Z_c(Hg) = Z^*(He^4)$. This procedure allows to find the value of a, which is equal to $a \approx 0.29$. The values of Z* thusly calculated are presented in Table 2. We see also that $Z^*(H_2) = 0.37$ is very close to Z_c corresponding to the classical van der Waals model ($Z_c = 0.375$), that is, the binodal curves for H2 and van der Waals model are close. Figure 2 confirms this fact. Now relation 5 can be considered as a purely empirical one. The problem of its theoretical basis deserves a separate investigation.

Besides the derivative $d\rho/dT$ along the binodal contour for quantum liquids in the domain $T \rightarrow 0$ can change sign. This tendency is amplified with increase of the de Boer parameter. If for hydrogen the change of the derivative sign is practically unnoticeable, then for He³ this one is marked (see Figure 2). Therefore the Zeno-line parameters for He³ were constructed as a straight line touching the He³ binodal contour at some point with T > 0 passing over the intersection point of all Zeno-lines. Such procedure gives the possibility to estimate the Zeno-line parameters for He³.

4. Similarity Factors

From the parameters characterizing the critical point position and Zeno-line we can form several dimensionless combinations. First of them is eq 3. The others can be written as

$$S_2 = \frac{\rho_{\rm c} T_{\rm c} - P_{\rm c}}{\rho_{\rm B} T_{\rm B}}; \quad S_3 = \frac{P_{\rm c}}{\rho_{\rm B} T_{\rm B}}$$
 (6)

where S_2 , S_3 depend weakly on the sort of materials. The values of these similarity parameters are presented in Table 1. For most substances considered here, these factors have rather close values deviating weakly from some general constant value. Dispersion of the values is evidently greater for mercury and alkaline metals and it especially large for water. Now it is very difficult to identify for the noticeable deviations for these substances. On one hand, there can be inaccuracies connected with the experimental measurements of the corresponding critical parameters (especially for Na, K, and Rb). On the other hand, there can be substance specific features, which we cannot take into account in the frame of our consideration.

Let us introduce the dimensionless variables $x = \rho_c / \rho_B$ and $y = T_c / T_B$. Then the similarity relations 3 and 5 can be rewritten as

$$x + y = S_1$$
; $xy(1 - Z_c) = S_2$; $xyZ_c = S_3$ (7)

Let us consider the first and second parts of eq 7 and then the first and third parts. The solutions of the corresponding equations can be written as

$$(x_1, y_1) = \frac{S_1}{2} \left[1 \pm \sqrt{1 - \frac{4S_2}{S_1^2 (1 - Z_c)}} \right]$$
 (8)

$$(x_2, y_2) = \frac{S_1}{2} \left[1 \pm \sqrt{1 - \frac{4S_3}{S_1^2 Z_c}} \right]$$
 (9)

where the pair of the solutions (x_1,y_1) corresponds to the first and second parts of eq 7 and (x_2,y_2) corresponds to the first and third parts. We apply the plus sign to find x and minus to find y. Equation 8 is valid for the restricted values of Z_c when there is an inequality

$$Z_c \le 1 - 4S_2/S_1^2 \tag{10}$$

If we take $S_2 = 0.076$ (as for L-J liquid), then we find $Z_c \le 0.32$. The latter inequality is fulfilled for the overwhelming majority of the classical liquids considered here. Only mercury has $Z_c = 0.387$. The value of the effective compressibility factor at the critical point Z^* for the quantum liquids also is greater than 0.32 (see Table 2). The solution of eq 10 is valid when

$$Z_c \text{ or } Z^* \ge 4S_3/S_1^2$$
 (11)

The value of $S_3 = 0.042$ for mercury, so the inequality 10 becomes Z_c or $Z^* \ge 0.37$. The latter inequality is valid for the mercury and quantum liquids. The dependences of ρ_c/ρ_B and T_c/T_B on Z_c are plotted in Figure 3 The dependencies corresponding to eqs 7 and 8 are also shown in this figure. One can see that the left branch of these dependencies described by equation 7 corresponds to the classical liquids. The right branch equation 8 describes mercury, the van der Waals model, and the quantum liquids. It should be noted that there is a gap in the Z_c values between these groups of materials. Besides, the inequality $\rho_c/\rho_B < T_c/T_B$ is valid for the classical liquids. For mercury and quantum liquids, the latter inequality turns into the inverse one. It should be noted that in data for H_2O , Rb noticebly deviates from the general block of the points.

5. The Determination of the Critical Parameters of Some Metals

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 Zeno-line

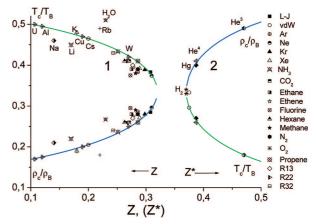


Figure 3. The dependence of ρ_c/ρ_B and T_c/T_B on Z_c . The symbols correspond to different substances. Lines: 1, eq 7; 2, eq 8.

parameters. This is the present state of knowledge for most of metals including uranium. Their critical parameters appear to be too high for precise experimental study (except heavy alkali and mercury). Below we will consider metals Al, Cu, W, U, and Zr. Parameters of the critical point of metallic uranium, for example, are in urgent need, first, to develop perspective powerful devices²⁴ and, second, as an important ingredient for the analysis of nuclear safety in hypothetical severe reactor accidents at nuclear plants exploited recently.²⁵ But, nowadays the critical parameters of these metals are known mostly from theoretical predictions.

The low temperature branches of binodals found on the basis of the experimental data for these substances are presented in Figure 4a–e.The Zeno-line parameters are unknown as well as the critical parameters. The procedure of finding the critical and Zeno-line parameters was described in details in refs 9 and 10. The main idea of this kind of calculation is that the deviation of the experimental liquid branch of binodal from the one calculated according to eqs 2 and 3 must be minimized. (In refs 9 and 10, the minimization criterion was that the relative deviation was less than 1%. This value was also used in present work.) After that the values of T_c , ρ_c and T_B , ρ_B are found and if the inequality $T_c/T_B > \rho_c\rho_B$ holds, we can use the similarly relation 7 to find the critical pressure. Our calculations show that this inequality is valid for all metals considered here.

It should be noted that the experimental data for Al, Cu, W, and Zr are really do not belong to the binodals, they belong to the part of isobar curves. It follows from thermodynamical considerations²⁶ that the isobar curves for the liquid state go very close to the binodals. This behavior of binodals can be explained by a very small compressibility of liquids far from their critical points. Therefore the measured binodals^{27–31} practically coincide with the corresponding binodals.

The results of our calculations of the critical and Zeno line 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 these results in Figure 4a-d 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 and U. Among them, we choose tungsten data from refs 28 and 31 since they give the most reasonable values of the critical parameters. Uranium is one of the less studied elements. The estimates of its critical parameters can vary two times in magnitude. 32 Nevertheless,

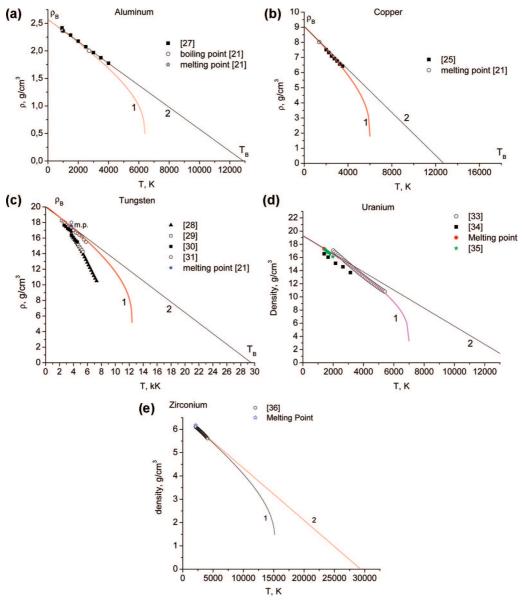


Figure 4. The phase coexistence curves, Zeno-line and critical parameters for metals Al (a), Cu (b), W (c), U (d), and Zr (e). The symbols are experimental data along the binodal. Line 1 shows the results of our calculations of the liquid branch of binodal according to eq 3. Straight line 2 is the Zeno-line.

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

metal	$T_{\rm c},~{ m K}$	$\rho_{\rm c},~{\rm g/cm^3}$	method	ref	$T_{\rm B},~{ m K}$	$\rho_{\rm B},~{\rm g/cm^3}$	$P_{\rm c}$, atm	Z_{c}
Al	6.38×10^{3}	0.45	this work		1.29×10^{4}	2.57	1.07×10^{3a}	0.12
	8.86×10^{3}	0.28	scaling	37			4.68×10^{3}	0.60
	8.00×10^{3}	0.64	extrapolation	14			4470	0.28
Cu	7.09×10^{3}	1.95	this work		1.56×10^{4}	8.60	4.50×10^{3a}	0.19
	7.62×10^{3}	1.40	scaling	37			5770	0.39
	8.39×10^{3}	2.40	extrapolation	14			7460	0.28
W	1.24×10^{4}	4.92	this work		2.91×10^{4}	20.1	7.45×10^{3a}	0.27
	1.25×10^{4}	4.52	estimate	38			1.10×10^{4}	0.43
	1.40×10^{4}	4.71	estimate	28			5.00×10^{3}	0.13
U	7.00×10^{3}	3.30	this work		1.40×10^{4}	19.3	1.71×10^{3a}	0.27
	9.00×10^{3}	2.60	estimate	37			5.00×10^{3}	0.60
	1.16×10^{4}	5.30	extrapolation	14			6.10×10^{3}	0.28
Zr	1.52×10^{4}	1.00	this work		2.93×10^{4}	6.58	4.21×10^{2a}	0.03

^a The critical pressure is determined according to eq 6.

there are sets of measurements of the properties of uranium in the liquid state. 33-35 We calculated the critical parameters of uranium relying on these measurements data and melting point data. One can see from Figure 4d, that the melting point for uranium lies on the binodal curve calculated here. The latter passes between the experimental data points of refs 33–35. The low temperature measurements of the Zr binodale have been recently carried out in ref 36. The experimental

data and our theoretical curve are presented in Figure 4e. According to our calculated data Zr has the lowest value of the compressibility factor at the critical point.

Thusly obtained data for Al, Cu, W, U, and Zr are added in Table 2.

Our findings connect the binodal opening with $Z_{\rm c}$ and use the experimentally measured slope of the binodal curve to determine the Zeno-line parameters. As a result if $T_{\rm c}/T_{\rm B} > \rho_{\rm c}/\rho_{\rm B}$ then $Z_{\rm c} < 0.32$. In this respect, data of ref 28 for tungsten with $Z_{\rm c} = 0.426$ and ref 31 for uranium with $Z_{\rm c} = 0.6$ seem to be questionable. Our analysis shows that such high values of $Z_{\rm c}$ are typical for the quantum liquids with a weak interparticle interaction. Moreover, our study corresponds to the theoretical and experimental information on the liquid—gas coexistence curves, critical and Zeno-line point parameters. This suggests that these findings are well justified.

6. Conclusion

We have shown that the idea of the construction of a new similarity based on the correspondence of the critical and Zenoline parameters turns out to be quite fruitful. It is applied to a wider group of substances in comparison with ones satisfying the corresponding states principle. The condition that the Zenoline must be tangential to the extension of the binodal liquid branch at $T \rightarrow 0$ allows us to avoid difficulties connected with the uncertainty of intermolecular potentials. Because of this new similarity, we can find the critical density, temperature, and pressure 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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