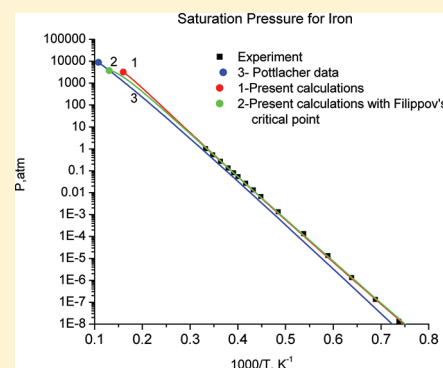


Application of the New Scaling Relations and Global Isomorphism to the Study of Liquid–Vapor Saturation Pressure

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ABSTRACT: We apply the new scaling relations and global isomorphism between continuous and discrete systems to find of saturation pressure. On this basis, we obtain the expression for the saturation pressure containing the critical, Z line parameters and two fitting parameters. First we calculate the saturation pressure for a number of model systems and real substances the critical parameters for which are known and verify that the accuracy is acceptable in a wide liquid–gas temperature domain. Then we discuss situation with the saturation pressure for metals (aluminum and iron), the critical parameters for which are unknown in advance and lie in the domain of parameters still inaccessible for experiments.



INTRODUCTION

Saturation pressure (SP) is one of the main thermodynamic substance characteristics needed for many technical and technological applications. In databases^{1,2} for example, there is a wealth of the most reliable experimental information on the SPs of different substances, which can serve as a test for theoretical models. As a rule, databases are constructed directly from the measurement data, and therefore, the information contained in the databases is the most accurate. However, the problem is that the measurement data do not necessarily cover all points of the phase plane. Moreover, the necessary measurements are not available for some substances.

A set of different interpolation expressions obtained by a great variety of methods are used for the SP calculations. These expressions as a rule are valid in a restricted temperature range. Some examples of such expressions can be found in ref 2. Numerical methods, which became widespread during the last years, enable one to compute thermodynamical functions of systems whose particles interact according to a certain law, for any densities and/or temperatures. These methods are diverse realizations of the Monte Carlo method or the method of molecular dynamics.³ Formally, various thermodynamical quantities are computed in these methods precisely, and the results are subjected to numerical error only. The calculations of the SP are carried out on the base of thermodynamical equilibrium condition leading to equality of pressures and chemical potentials of liquid and gas phases along phase equilibrium line. However, to apply these methods, one must know the interaction potential, which can be a pair or a multiparticle potential. At the same time, for the majority of substances, the very potential of interaction among the atoms or molecules forming the substance remains unknown. For this reason, we face another obstacle substantially interfering with the precise determination of thermodynamical properties.

Another direction of investigation is connected with the use of similarity laws. The similarity relations in the theory of liquid state are known more than a century since pioneering investigations of van der Waals. The principle of corresponding states and the law of rectilinear diameter are the well-known examples of such similarities.^{4–6} Presently there is considerable experimental evidence confirming an additional relation besides the two described above. This feature characterizes the states where the compressibility factor (CF) is unity (i.e., $Z = P/nT = 1$, where P is the pressure, n is the particle density, and T is the temperature). The contour $Z = 1$ is referred to as the Zeno-line (ZL). It is easy to show that ZL is a straight line on the density–temperature plane for van der Waals system.⁷ But it is appeared to be straight for many real substances^{8,9} and model systems¹⁰ too. Moreover, this phenomenon (ZL straightness) has a wider applicability than other similarity laws, because ZL is straight for noble gases,² organic materials,^{8,9} and even some metals like Cs, Hg, and others.¹¹

The similarity laws allow one to set a correspondence between different thermodynamic values without explicit use of the equation of state. Thus, the universal expression for the description of the liquid and gas branches of the binodal line for a group of real substances has been suggested in refs 4–6 and later in refs 10 and 11. The dependence of the gas density along the binodal line on temperature has a power-law behavior in all these works. This is contradictory to the Clapeyron–Clausius law according to which the gas density has to decrease exponentially with temperature decrease. So all methods of calculation of SP based on the similarity laws are not valid in the domain of low temperatures.

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To remove this shortcoming, here we use a different method of construction for the gas branch of the binodal curve. It is well-known that the connection between continuous and discrete systems in statistical physics is the source of new methods and fruitful applications. The lattice models (LM) are usually considered as the simplified pictures of the real ones. Due to their numerical and analytical tractability, they serve as the main sources of the rigorous results. The famous Onsager's solution of the two-dimensional Ising model is a well-known example which provided new insight for the theory of critical phenomena.¹² In the modern theory of critical phenomena, the ideology of the isomorphism classes of critical behavior provides the description of real systems using the results obtained for the model systems among which the lattice models play an important role.¹³

In recent works^{14,15} the geometrical relations between ZL and binodals have been used to consider possible global isomorphism between the phase diagram of the lattice gas (LG or equivalently the Ising model) and the liquid–gas part of the diagram of a simple continuous fluid. Using a certain symmetrical binodal for a lattice model, we transition to the binodal of the real substance. This transition requires the use of a corresponding projective transformation (PT). Such PT has been suggested in ref 14. In this work, we use a somewhat more complicated transformation proposed in ref 15. The latter rigorously speaking is not at all a projective one since it includes nonalgebraic function of the lattice gas density (x ; see below).

The transformation allows a match to be found between the lattice variables (density (x) and temperature (t)) and real liquid variables (density (n) and temperature (T)). The character of this transformation depends on the critical point and Z-line parameters.

Here we use the similarity laws and the ideology of the isomorphism for calculation of the saturation pressure. We construct the approximation expression for the saturation pressure which depends on the critical and Z-line parameters. It also includes two fitting parameters α and β . These parameters determine behavior of the saturation pressure both at low and near critical temperatures.

The values of these parameters are found from the condition of minimization of a mean deviation of the calculated pressure from experimental (or tabulated) value. First we check the validity of the approximation for model systems and substances the critical parameters of which are known from experimental or table data. We consider two model systems (describing by the Lennard-Jones and square-well potentials) and three real substances—argon, mercury, and cesium. The consideration is being given to a wide temperature range enveloping the triple and critical points. The mean error is little less than 4% for all these model systems and substances.

Then, we calculate the saturation pressure for aluminum and iron for which the low temperature parts of the saturation pressure are known from experiments. There are estimations of the critical parameters for these metals only. We carried out the calculations for the different values of the critical parameters and find a corresponding mean error. That enables us to choose more plausible values of the critical point parameters.

LATTICE BINODAL AND TRANSFORMATION RELATIONS

Let us start from the symmetric expression for the binodal of LG as suggested in ref 15. Here we somewhat modify it

introducing an additional parameter α (in ref 15 we used the condition $\beta = \alpha$). The lattice binodal we present as

$$x_{1g}(t, \alpha, \beta) = \frac{1}{2}(1 \pm (1 - e^{-(1-t)^{1/\beta}/\alpha t})^\beta) \quad (1)$$

where α and β are determined by the shape of LG binodal. The signs plus or minus correspond to the liquid or gas branch of the binodal. The t and x terms are the reduced temperature ($0 < t < 1$) and density ($0 < x < 1$) of the LG. Near the critical point, eq 1 has a nonanalytical peculiarity. To find the behavior of x near the critical point, we can present t as $t = 1 - \delta$, where $\delta \ll 1$. Substituting the latter expression in eq 1 and using the smallness of δ , we obtain $|x - 1/2| \sim (1 - t)^\beta$. In this sense the parameter β describes the near-critical behavior for the lattice density and plays a role analogous to the density critical exponent. Therefore, if we want to accurately describe the neighborhood of the critical point, the value of β should be used, consistent with the isomorphism classes of critical behavior. For example, the van der Waals equation of state is classical and corresponds to the Landau mean-field theory where $\beta = 1/2$. Meanwhile, the 3D Ising model gives $\beta = 0.33$ – 0.34 . On the other hand, when we want with the help of eq 1 to describe the binodal in a wide range of temperatures, not only in near-critical point region, the parameters β and α must be the condition best fit the calculated curve to the experimental or table data. In this case, we will consider this parameter as a fitting one outside the context of critical phenomena.

From eq 1 it follows also that the gas density along the binodal at $t \rightarrow 0$ changes as

$$x_g = 0.5\beta \exp\left(-\frac{1}{\alpha t}\right) \quad (2)$$

We see that the latter decreases exponentially with temperature. The parameter α determines the rate of this decrease. The asymptotic form of eq 2 corresponds to the general dependence on temperature of a gas density along the binodal at $t \rightarrow 0$ for an arbitrary system. The parameter α allows changing the gas density at low temperatures. This characteristic behavior of the gas branch of the binodal lattice provides an exponential decrease of density (pressure) of real gases at low temperatures.

Our future task is to describe the dependence of the saturation density and pressure on temperature in a wide range of variation of the latter and not only in the vicinity of the critical point. Therefore the parameters β and α will play the role of fitting parameters. Their values will be found from the condition of a mean deviation minimization of the calculated pressure from experimental (or tabulated) one.

The ability to use eq 1 for different lattice models has been established earlier in work.¹⁵ Comparison of the binodal curves, calculated by a corresponding choice of a parameter $\beta = \alpha$ gave good agreement with analytical results¹⁶ and simulations.^{17,18}

It has been shown in ref 14, that a projective transformation exists, which allows the mapping binodal of LG onto a binodal of real fluid. Here we use a somewhat more complicated transformation suggested in ref 15. This transformation has the form

$$\rho = \rho_B(1 - T/T_B)x_{1g}(t, \beta, \alpha)^{\gamma}; \quad t = \frac{T}{T_c} \frac{1 - T_c/T_B}{1 - T/T_B} \quad (3)$$

The parameters γ are determined as

$$\gamma = \frac{\ln \left[\frac{\rho_c}{\rho_B} \frac{T_B}{T_B - T_c} \right]}{\ln(1/2)} \quad (4)$$

This transformation sets the correspondence between two triplets of nonconcurrent lines in the plane (ρ, t) for LM and plane (n, T) for the real fluid. These two triplets are

$$t = 1 \Leftrightarrow T = T_c; x = 1/2 \Leftrightarrow \rho = \rho_c; x = 1 \Leftrightarrow \rho/\rho_B + T/T_B = 1 \quad (5)$$

We can see that the critical point ($x = 1/2, t = 1$) and Zeno-line of LM transform into the critical point (n_c, T_c) and the corresponding Zeno-line.

Substituting eq 3 into eq 1, we obtain the expression for a substance binodal with the definite critical point and Z-line parameters, depending on two arbitrary parameter β and α .

SATURATION PRESSURE

The saturation pressure will be calculated based on the equation

$$P = \rho T Z(\rho, T) \quad (6)$$

where P , ρ , T , and $Z(\rho, T)$ are the pressure, density, temperature, and CF along the binodal. Equation 6 is valid both for gas and liquid branches of the binodal. Below it will be used for the gas branch along which the gas density varies within several orders of magnitude when the temperature changes from the critical point up to the triple point. The gas compressibility factor varies from unity when $T \rightarrow 0$ until 0.2–0.4, depending on the substance. For example, the value of the critical density at the critical point ($T_c = 150.9$ K) for argon equals $\rho_c = 0.536$ g/cm³, whereas at the triple point ($T_t = 83.8$ K), this value equals $\rho_t = 0.0041$ g/cm³. The value of the gas CF in the same temperature range changes from $Z_c = 0.29$ until $Z_t = 1$.

Now we express the gas density and CF in eq 6 by means of corresponding values of LG. For that we use eq 3 for the gas density. The issue connected with the transformation of the CF deserves a special discussion.

TRANSFORMATION OF THE CF

First we calculated the dependence of the compressibility factor along the binodal on temperature reduced to the critical value for the van der Waals equation. This asymmetric dependence is presented in Figure 1 at the Z – T plane. The critical value of the CF equal to $Z_c = 3/8$ corresponds to the critical temperature $T = 1$. The left branch of this curve describes liquid. The CF falls from the critical value $3/8$ until zero along this line. The right branch corresponds to gas. The CF increases from $3/8$ to unity along this line. The middle line is diameter $Z = (Z_g + Z_l)/2$. We see that, in comparison with the ordinary phase diagram of the density–temperature, the gas and liquid branches are reversed. Despite the fact that the dependence $Z(T)$ is asymmetric, the Z-line in these coordinates is the straight vertical line $Z = 1$ just as in lattice models and this line is tangent to the gas (not liquid as at the density–temperature plane) branch of the CF at low temperatures. With the help of transformation (3–4), we can symmetrize the dependence

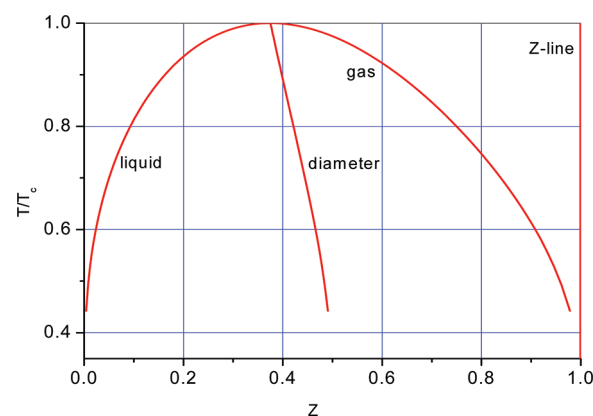


Figure 1. CF along the binodal for the van der Waals equation at the Z – T plane.

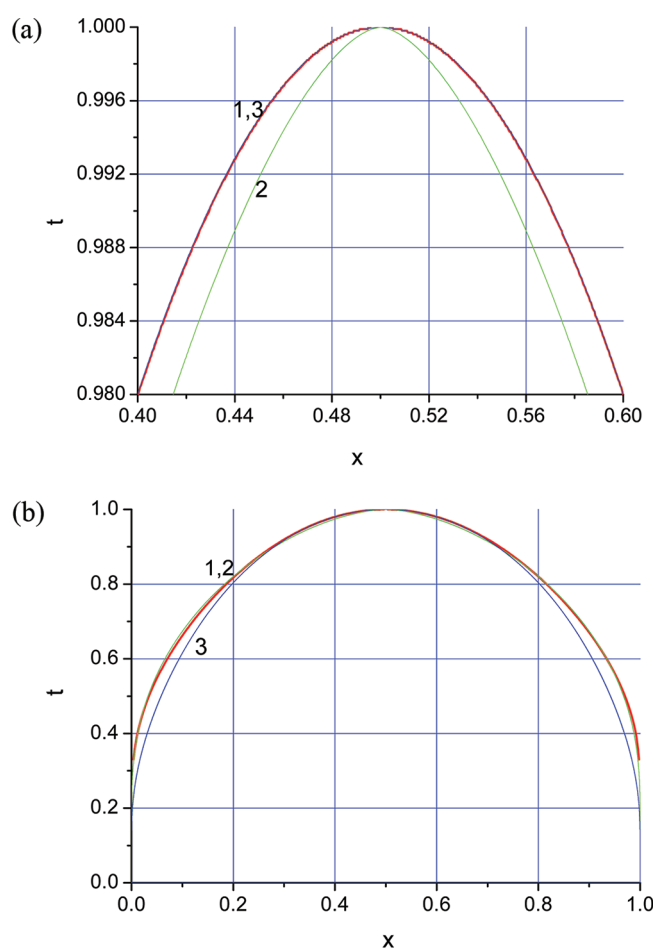


Figure 2. Dependence of $t(x)$: (a) near-critical region, (b) entire temperature range. Curve 1 is the calculation according to eq 9 using the exact van der Waals values of the CF along the binodal; curves 2 and 3 are the calculations according to eq 1 with $\alpha = \beta = 0.605$ and $\alpha = 0.988$ and $\beta = 0.5$, respectively.

$Z(T)$, assuming $T_B \rightarrow \infty$, since the Z-line must be vertical. In this case instead of eq 3, we obtain

$$\frac{\rho_l}{\rho_B} = x_l(t) \ln(\rho_c/\rho_B)/\ln(1/2); t = T/T_c \quad (7)$$

Table 1. Experimental and Calculated Values of the Saturated Pressure

LJ system $\beta = 0.545$; $\alpha = 0.5$; $\epsilon = 3.4\%$ ²⁰			Ar; $\beta = 0.55$; $\alpha = 0.485$; $\epsilon = 2.7\%$ ²		
T	P_c	P	T, K	P_c, atm	P_c, atm
0.7	0.00131	0.00148	83.78	0.687	0.7162
0.75	0.00264	0.00269	84	0.705	0.7332
0.8	0.0047	0.00458	85	0.79	0.8146
0.85	0.00769	0.00738	87	0.983	0.9992
0.9	0.01168	0.01139	91	1.476	1.469
0.95	0.01741	0.01692	96	2.33	2.289
1	0.02505	0.02433	101	3.513	3.436
1.05	0.03384	0.034	106	5.083	4.994
1.1	0.04511	0.04631	111	7.111	7.056
1.15	0.05974	0.06161	116	9.66	9.724
1.2	0.07718	0.08011	121	12.81	13.1
1.25	0.0973	0.1016	126	16.63	17.29
1.3	0.1204	0.1239	131	21.21	22.39
1.314	0.126	0.1271	136	26.64	28.44
SW; $\lambda = 1.5$; $\beta = 0.475$; $\alpha = 0.67$; $\epsilon = 1.2\%$ ²¹			141	33.04	35.41
0.8533	0.0075	0.00757	146	40.52	43
1	0.0251	0.02439	150	47.39	48.4
1.05	0.03526	0.03455	150.9	48.98	48.41
1.08	0.04277	0.04218	Mercury $\beta = 0.435$; $\alpha = 0.44$; $\epsilon = 2.4\%$ ²²		
1.1	0.04843	0.04799	1033	83.9	92.48
1.12	0.05461	0.05445	1073	108.7	115.8
1.15	0.065	0.06545	1093	122.9	129
1.18	0.07707	0.07807	1113	138.3	143.3
1.2	0.08622	0.08719	1133	155	158.9
1.217	0.0931	0.093	1153	173.2	175.6
SW; $\lambda = 1.75$; $\beta = 0.48$; $\alpha = 0.57$; $\epsilon = 2.8\%$ ²¹			1173	192.8	193.7
1	0.0019	0.00217	1193	213.8	213.3
1.2	0.00894	0.00878	1213	236.5	234.3
1.268	0.01357	0.01305	1233	260.7	256.9
1.3	0.0161	0.01555	1253	286.6	281.1
1.5	0.04236	0.04127	1273	314.2	307.1
1.55	0.0519	0.05125	1293	343.7	335
1.57	0.0561	0.05574	1313	374.9	364.8
1.6	0.06299	0.06304	1333	408.1	396.7
1.62	0.06786	0.0683	1353	443.3	430.8
1.65	0.0757	0.07683	1373	480.5	467.1
1.68	0.08419	0.08611	1393	519.7	505.9
1.7	0.09018	0.09271	1413	561.2	547.2
1.72	0.0967	0.09962	1433	604.9	591.1
1.73	0.1	0.1032	1453	650.9	637.9
1.75	0.1071	0.1105	1473	699.3	687.6
1.8	0.1259	0.1275	1493	750.2	740.4
1.809	0.1263	0.1261	1513	803.6	796.4
SW; $\lambda = 2$; $\beta = 0.405$; $\alpha = 0.6$; $\epsilon = 3\%$ ²¹			1533	859.7	855.8
1.897	0.0192	0.02248	1553	918.5	918.8
2.1	0.0432	0.04263	1573	980.1	985.4
2.2	0.05992	0.05717	1583	1012	1020
2.35	0.09101	0.08717	1593	1045	1056
2.45	0.1168	0.1145	1603	1078	1092
2.5	0.1315	0.1309	1613	1112	1130
2.52	0.1378	0.1381	1623	1147	1169
2.53	0.1408	0.1418	1633	1183	1208
2.54	0.1442	0.1456	1643	1220	1249
2.56	0.1508	0.1535	1653	1257	1290
2.57	0.1541	0.1576	1663	1296	1333
2.68	0.1975	0.1978	1673	1335	1376
			1683	1375	1420
			1693	1416	1465
			1703	1458	1510

Table 1. continued

Mercury $\beta = 0.435$; $\alpha = 0.44$; $\varepsilon = 2.4\%$ ²²				Cs; $\beta = 0.555$; $\alpha = 0.756$; $\varepsilon = 2.8\%$ ²³			
1033	83.9	92.48		900	0.67	0.6929	
1713	1501	1555		1000	1.7	1.7	
1723	1545	1599		1100	3.6	3.583	
1728	1567	1620		1200	6.9	6.733	
1733	1588	1641		1300	11.8	11.57	
1738	1613	1659		1400	18.6	18.53	
1743	1636	1674		1500	27.6	27.98	
1748	1659	1679		1600	38.8	40.24	
1749	1664	1677		1700	52.2	55.39	
1750	1669	1671		1800	67.8	73.08	
1751	1673	1671		1900	85.8	91.11	
				1938	94	93.92	

Table 2. Values of the Calculated Parameters^a

	model				substances		
	L-J	SW			Ar	Hg	Cs
		$\lambda = 1.5$	1.75	2			
T_c	1.314	1.217	1.809	2.68	150.86	1751	1938
ρ_c	0.314	0.308	0.265	0.251	0.536	5.8	0.39
Z_c	0.308	0.248	0.263	0.294	0.29	0.39	0.2
T_B	3.418	2.846	4.842	7.484	393	6650	4120
ρ_B	1.14	1.375	1.0	0.844	1.97	14.4	1.96
α	0.5	0.67	0.57	0.6	0.485	0.49	0.756
β	0.545	0.435	0.48	0.405	0.55	0.435	0.555
ε , %	3.4	1.2	2.8	3	2.7	2.4	2.8

^aTemperature and density for the model system are given in dimensionless Lennard-Jones units. For substances, they are presented in kelvin and grams per cubic centimeter.

This equation turns into the identity at the critical point since the value $x = 1/2$ at $T = T_c$. The liquid density tends to $\rho \rightarrow \rho_B$ along the binodal at $T \rightarrow 0$.

Let us change in eq 7 the value ρ_l/ρ_B by Z_g and ρ_c/ρ_B by Z_c . Then instead of eq 7, we have

$$Z_g = x_l(t)^{\ln(Z_c)/\ln(1/2)} \quad (8)$$

Equation 8 can be considered as an interpolation equation for the gas branch of CF along the binodal because it has correct asymptotic behavior both at $T \rightarrow T_c$ ($Z_g \rightarrow Z_c$) and $T \rightarrow 0$ ($Z_g \rightarrow 1$). It should be noted that the equality $Z_c = \rho_c/\rho_B$ is nothing else than Timmerman's relation.⁵ The inverse transformation

$$x_{g,l}(t) = Z_{l,g}^{\ln(1/2)/\ln(Z_c)} \quad (9)$$

converts the asymmetric CF of a real substance into some symmetric function for a lattice model.

Now we can build the function $x_{g,l}(t)$ taking as $Z_{l,g}$ the exact values of the CF according to the solution of the van der Waals equation, presented in Figure 1. Thusly obtained functions (curve 1) are presented in Figure 2 for the near-critical region (a) and for the full temperature range (b). These curves are symmetrical with respect to the line $x = 1/2$. Now we will try to describe these lines using eq 1. Curve 3 is calculated with $\beta = 0.5$ and $\alpha = 0.988$. This value of β corresponds to the classical Landau mean-field theory. Curves 1 and 3 in Figure 2a are practical indistinguishable. But if we turn now to Figure 2b, curve 3 begins to significantly deviate at low temperatures from the exact solution. Here we go on a conscious reduction in

accuracy in the near-critical region due to its increase with respect to the curve as a whole. The smallest deviation in the whole temperature range between the curve calculated from eq 1 and curve corresponding to the exact solution is obtained when $\alpha = \beta = 0.605$. Curve 2 in Figure 2 corresponds to this case. It describes a somewhat worse near critical region, but more accurately at low temperatures. Of course the parameters β and α become simply fitting.

Solid lines (1) in Figure 2 are the calculations according to eq 9 with using the values of CF from the solution of the van der Waals equation.

This comparison shows that we can use eq 8 for calculation of the gas CF for different substances fitting the corresponding values of α and β parameters.

■ SATURATION PRESSURE AFTER TRANSFORMATION

After the transformation, the saturation pressure can be presented as

$$P(T, \beta, \alpha) = T\rho_B(1 - T/T_B)x_g(t, \beta, \alpha)^Y x_l \\ (T/T_c, \beta, \alpha)^{\ln Z_c/\ln(1/2)} \quad (10)$$

According to this expression the saturation pressure depends on the critical and Z-line parameters and also two fitting parameters α and β . The values of these parameters are found from the condition of a mean deviation minimization of the

calculated pressure from experimental (or tabulated) one. The mean deviation is found as

$$\varepsilon(\beta, \alpha) = \frac{\sum_{i=1}^n \left| \frac{P(\beta, \alpha)}{P_e} - 1 \right|}{n} \times 100\% \quad (11)$$

where P_e is the experimental or table saturation pressure. The sum in eq 11 is taken over entire massive of the experimental (table) data along the liquid–gas coexisting line.

First we calculate the saturation pressure using eq 10 for the same model systems or substances for which there is a wealth of experimental (table) information on the saturation pressure. The calculated (P) and table (P_e) values of the saturation pressure are given in Table 1 below for two model systems (the Lennard-Jones (LJ) system and the system described by the square-well potential (SW) with three different potential ranges λ) and three real substances (argon, mercury, and cesium). For every substance or model system, the values of α and β are given in Table 1. The parameters needed for calculation are collected in Table 2.

The data given in Tables 1 and 2 show that the method suggested above facilitates a unified way to calculate the saturation pressure in a wide temperature range for the different model systems and substances. Moreover the mean deviation of the calculated and experimental saturated pressures for all this wealth of model systems and substances does not exceed 3.5%. In addition, it covers a wide temperature range, which could not be described with such accuracy by methods known earlier. The calculation procedure is determined by the critical point and Z-line parameters and two fitting parameters.

SATURATION PRESSURE FOR ALUMINUM AND IRON

It is a challenge to use the method suggested above when we know the low-temperature branch of the saturation pressure only. The experimental data describing the critical parameters are absent due to experimental challenges such as high temperatures and pressures. This is the present state of knowledge for many metals, which have the critical parameters in the phase diagram domain still inaccessible for experiments. Information regarding the critical and Zeno-line parameters was obtained by several authors using various approaches. Let us consider, for example, metals Al^{5,11,26–28} and Fe.^{5,29,30} The low-temperature branches of the saturation pressure found on the basis of the experimental data^{24,25} for these substances are presented in Figures 3 and 4. Z-line parameters are determined with these data according to the method described earlier in ref 10. The critical,

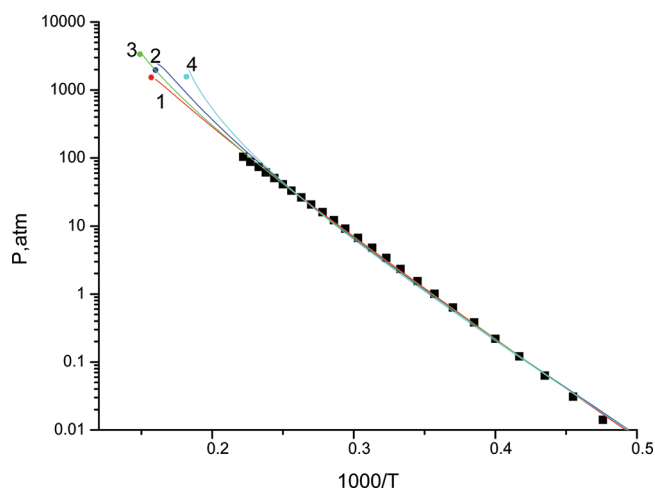


Figure 3. Dependence of the SP upon temperature for Al. The symbols are experimental data.²⁴ Lines 1–4 are our calculations with the critical parameters in accordance with refs shown in Table 3.

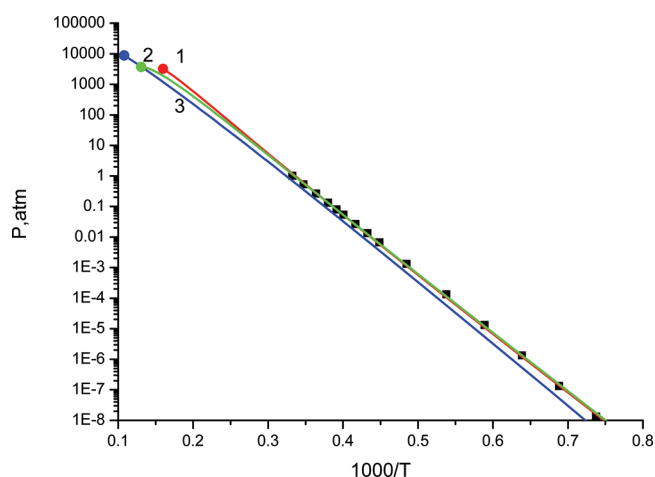


Figure 4. Dependence of SP upon temperature for Fe. The symbols are experimental data.²⁵ Lines 1–4 are our calculations with the critical parameters in accordance with the references shown in Table 3.

Z-line, and other calculated parameters for these metals are collected in Table 3.

The results of calculations according to eq 10 of the saturation pressure for the critical parameters collected in Table 3 are given in Figures 3 and 4. The range of variation of the temperature and pressure for Al and Fe is shown in the first column of Table 3 as well.

Table 3. Critical and Other Calculated Parameters for Al and Fe

metal	ref	T_c , K	ρ_c , g/cm ³	P_c , atm	Z_c	T_B , K	ρ_B , g/cm ³	α	β	ε , %	line figure
Al, Figure 3; $T = 2000$ – 7000 K; $P = 0.006$ – 5000 atm	11	6680	0.45	1563	0.175	12890	2.57	0.635	0.525	7.6	1
	26	6250	0.7	1970	0.15	15500	2.57	0.405	0.395	12.1	2
	27	5520	1680								
	28	6700	0.56	3730	0.33	14800	2.57	0.49	0.55	9.2	3
	5	5500	0.49	1525	0.19	11500	2.57	0.525	0.37	15	4
Fe, Figure 4; $T = 2000$ – $10\,000$ K; $P = .001$ – $10\,000$ atm	a	6500	1.36	2662	0.2	15000	8	0.78	0.48	6.4	1
	5	7650	1.63	1534	0.2	15000	8	0.86	0.47	5.8	2
	29	9250	1.21	8856	0.2					33	3

^aHere, we calculate the Fe critical and Z-line parameters by a method described in ref 11.

From Figures 3 and 4 and Table 3, it is difficult to make a definite conclusion about the choice of the critical values, since all curves quit adequately describe the low temperature experimental data. Nevertheless the minimal deviations of the calculated data from experimental ones for Al and Fe equal to ~8 and ~6%, respectively. These deviations take place with the use of the critical parameters suggested in ref 11 for Al and ref 5 for Fe. The other critical values given in Table 3 leads to a greater error.

CONCLUSIONS

In this work, a new step is made toward the better understanding of the similarity laws and global isomorphism between continuous and discrete systems in thermodynamics of real liquids. Using new scaling relations and global isomorphism, we construct an expression for the saturation pressure along binodal, containing two fitting parameters. The latter are found by force of the minimization of the mean deviation of the calculated values of the SP from experimental values. This way of the SP calculation shows an acceptable accuracy for a number model systems and substances, the critical parameters of which are known. The application of this method for substances whose critical parameters can only be estimated allows a more credible value of the latter to be predicted.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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