A NEW SIMILARITY BETWEEN THE CRITICAL AND ZENO-LINE PARAMETERS

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We set new regularities between the critical and Zeno-line parameters. The most important one has the form $T_c/T_{\rm B}+\rho_c/\rho_{\rm B}=S(\beta)$, where T_c and ρ_c are the critical temperature and density. The parameters $T_{\rm B}$ and $\rho_{\rm B}$ determine the position of the straight line along which the compressibility factor is equal to 1 on the density-temperature plane. The quantity $S(\beta)$ is weekly dependent on the critical exponent β: $S(\beta)=0.64$ for the classical value $\beta=0.5$ and 0.67 for $\beta=1/3$. We show that this similarity faithfully describes both the numerical simulation data and experimental data for a wide class of real materials.

1. Introduction

The similarity relations in the theory of liquid state are known more than a century since the 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 [1, 2]. Presently, there is a considerable experimental evidence confirming one more relation besides the two described above. This feature characterizes the states where the compressibility factor is one (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 systems [3]. But it is appeared to be straight for many real substances [2, 4–8] and model systems [9, 10] too. Moreover, this phenomenon (ZL straightness) has a wider applicability than other similarity laws. For example, ZL is straight for noble gases [11], organic materials [2], and even some metals like Cs and Hg [7]. Recently, we have investigated the properties of different models and real substances connected with ZL [4–10]. We have found that there is a possible new similarity which is based upon the relation between the critical point and the Zeno-line. In the present work, we review our findings. 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 domains. This fact together with the three-term Guggenheim equation allows us to construct the relation for the liquid binodal branch (for arbitrary substance or model system). We have also found a simple relation between the critical point (CP) coordinates and ZL parameters. We have checked both relations (for binodal and for CP coordinates) for real substances. We have shown that our similarity faithfully describes both the numerical simulation data and experimental data for a wide class of real materials. We have also made the investigation of several model interatomic potentials to confirm our similarity and to find possible deviations. The deviations from our similarity relations take place for two cases: the numerically calculated coexistence curve gets into a domain corresponding to solidification; the liquid-vapor transition becomes metastable with respect to freezing. Finally, we make some predictions for metals which have critical parameters in the phase diagram domain still inaccessible for experiment. The article is organized as follows. The next section is devoted to theoretical relations concerning ZL. There, our relations for CP coordinates and for the binodal will be also presented. The behavior of ZL and the analysis of experimental data on real substances are presented in Section 3. Several systems with model potentials are considered in Section 4, where we establish the validity of similarities based on ZL. The conclusions are presented in the final section.

2. Theoretical Relations

In 1906, Bachinskii [3] rewrote the famous van der Waals equation in the form

$$Z = \frac{P}{nT} = 1 + \frac{27n(n/3 + 8T/27 - 1)}{8(3-n)T}. \tag{1}$$

Here, P, n, and T are reduced to the critical values P_c, n_c, and T_c (the subscript "c" refers to the critical point; here and below, we also set the Boltzmann constant $k_\mathrm{B} = 1$). Equation (1) states that the density-versus-temperature curve is a straight line for $Z = 1$. It intersects the temperature axis at the Boyle point $T = T_\mathrm{B} = 27/8$ and the density axis at the point $n_\mathrm{B} = 3$. It is possible to show for an arbitrary system [6] that if ZL is a straight line, then its equation is

$$\frac{T}{T_\mathrm{B}} + \frac{n}{n_\mathrm{B}} = 1. \tag{2}$$

The analysis of ZL with the use of the virial expansion gives us the general formulas for "B"-scripted values. According to the virial expansion for the pressure at small densities, we have

$$Z = \frac{P}{nT} = 1 + B(T)n + C(T)n^2 + ..., \tag{3}$$

where $B(T)$ and $C(T)$ are the second and third virial coefficients, respectively. Equations (2) and (3) show that T_B is the well-known Boyle temperature, where $B(T_\mathrm{B}) = 0$. The parameter n_B, which is referred below to as the Boyle density, can be also defined in terms of $B(T)$ and $C(T)$. (We will call T_B and n_B below as the Boyle and ZL parameters). For the systems with pair-additive interaction (with pair potential $\Phi(r)$), expansion (3) gives the following equations [2, 6]:

$$T_\mathrm{B} : \int\limits_0^\infty \left[\exp\left(\Phi(r)/T\right) - 1\right] r^2 dr = 0,$$

$$n_\mathrm{B} = \left(\frac{dB(T}{dT}\right)_{T_\mathrm{B}} \frac{T_\mathrm{B}}{C(T_\mathrm{B})}. \tag{4}$$

For model systems with known interactions $\Phi(r)$, the formulas (4) can be applied directly. For real substances, the values of T_B and n_B can be defined on the basis of experimental data. Now let us consider how the position of ZL correlates with the liquid-vapor coexistence curve. Formulas (4) were obtained by the expansion as $n \to 0$ and $T \to T_\mathrm{B}$. It is the "small-density" end of ZL. In [5], it was shown that, at another "high-density" end, the Zeno-line is an asymptote for the liquid branch of the binodal as $T \to 0$ (irrespective of whether the Zeno-line is straight or not). Strictly speaking, the liquid binodal branch should be completed at the triple point (TP), so ZL is an asymptote to the continuation of the binodal beyond TP. This fact connects ZL and the liquid binodal branch. As a result, the binodal in the $n - T$ plane appears to be inscribed into the triangle created by ZL and two axes as it is shown in Fig. 1. This geometric construction allows us to find the equation for the liquid binodal branch and relations for CP coordinates. It is well known that the binodal branches (n_Liq – liquid branch, n_Gas – gas branch) can be described by the so-called three-term Guggenheim equation [1]

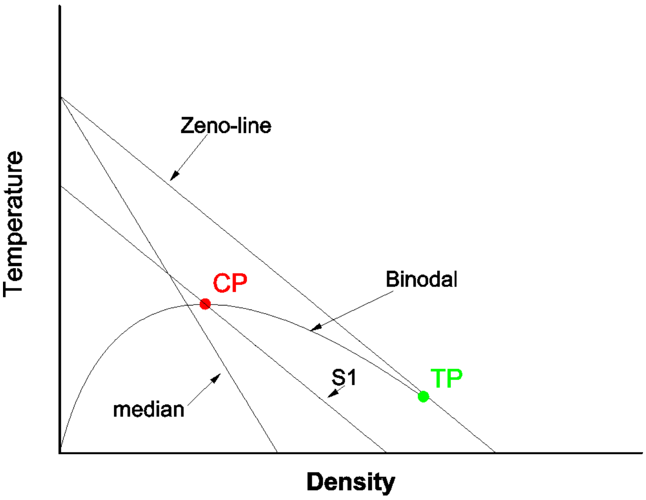

Fig. 1. Diagram of mutual disposition of the Zeno-line (ZL) and the gas-liquid binodal. CP is the critical point, TP is the triple point, and S_1 is the similarity line (2)

$$n_\mathrm{Liq} = n_c + A_\mathrm{Liq}\tau + D_\mathrm{Liq}\tau^\beta,$$

$$n_\mathrm{Gas} = n_c + A_\mathrm{Gas}\tau + D_\mathrm{Gas}\tau^\beta,$$

$$\tau = 1 - t/T_c, \;\; T \le T_c. \tag{5}$$

Here, A and D are some constants with the subscripts relating to the corresponding binodal branches. "β" is the critical index. For real substances in 3D with the scalar parameter of order $\beta = 0.326$ [12]. But it can be different for models (for the van der Waals system, it is 0.5, for a 2D Ising lattice gas, it is 1/8; for some other model systems, see [10]). The binodals are supposed very often to be symmetric relative to their diameters,

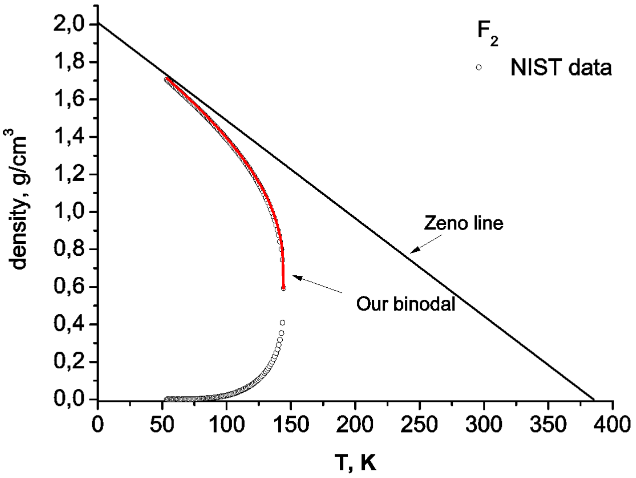

Fig. 2. The binodal for F_2. Points – NIST data [15], lines – our calculations according to Eqs. (5) and (6)

i.e. relative to the line $n(T) = 0.5[n_{\mathrm{Liq}}(T)+n_{\mathrm{Gas}}(T)]$. In this case, $A_{\mathrm{Gas}} = A_{\mathrm{Liq}}$ and $D_{\mathrm{Gas}} = -D_{\mathrm{Liq}}$. Equation (5) was used many times with different A and D [13, 14]. In the recent work [14], Eq. (5) was applied to 108 materials (supposing the symmetry of binodals), with the least-squares fitting of A and D to the known experimental data. The resulting error was within several percents. So Eq. (5) can be a reliable ground for the construction of binodal equations. In [6–8, 10], we used the condition of ZL asymptote to define the coefficients A and D in (5) for the liquid binodal branch. We did not suppose the symmetry of the binodal, as far as we are going to consider metals, where there is no such symmetry. As a result, we have [10] the following expressions:

$$n_{\mathrm{Liq}}(T \to 0) \to n_{\mathrm{Zeno-line}}(T) = n_{\mathrm{B}}(1 - T/T_{\mathrm{B}})$$

$$\Downarrow$$

$$A_{\mathrm{Liq}} = \frac{\frac{T_c}{T_{\mathrm{B}}} n_{\mathrm{B}} - \beta n_{\mathrm{B}} + \beta n_c}{1-\beta}, \quad D_{\mathrm{Liq}} = \frac{\left(1 - \frac{T_c}{T_{\mathrm{B}}}\right) n_{\mathrm{B}} - n_c}{1-\beta}. \tag{6}$$

The presence of ZL parameters and CP coordinates in (6) allows one to suppose that there is some simple relation between these values. The simplest hypothesis for this relation is also a linear dependence. In other words, the critical points of various substances can be located at some straight line on the $n - T$ plane. Initially, we supposed that this line should be the median of the triangle mentioned above [5] (median line in Fig. 1). This median is defined by the equation $\frac{T_c}{T_{\mathrm{B}}} + 2\frac{n_c}{n_{\mathrm{B}}} = 1$. But the detailed analysis [6–8] showed that the line parallel to ZL is more exact. In Fig. 1, this line is denoted as S_1. Then the corresponding equation for CP coordinates is

$$\frac{T_c}{T_{\mathrm{B}}} + \frac{n_c}{n_{\mathrm{B}}} = S_1(\beta), \quad S_1(\beta = 0.326) \approx 0.67. \tag{7}$$

In (7), we introduced the dependence of value S_1 on the critical index β. The value $S_1 = 0.67$ is exact for the Lennard–Jones (LJ) system, which belongs to the so-called "Ising" class of criticality with $\beta = 0.326$. The real substances in 3D also belong to this class [12]. So we can expect that Eq. (7) can also be true in these cases. For model systems (with known potentials), the index β can be different [10]. Equation (7) gives CP coordinates, but not the critical pressure. Unfortunately, the ZL equation (2) does not contain any pressure. But the products $n_{\mathrm{B}}T_{\mathrm{B}}$ and n_cT_c have the dimension of pressure. So it is possible to look for some connection between these products. In [8], the corresponding formula was presented in the form

$$\frac{n_cT_c - P_c}{n_{\mathrm{B}}T_{\mathrm{B}}} = S_2(\beta), \quad S_2(\beta = 0.326) \approx 0.076. \tag{8}$$

Here just like in (7), the parameter S_2 is dependent on the critical index. The value 0.076 again corresponds to LJ. But as we will see below, Eq. (8) is less exact than Eq. (7).

3. Real Substances and ZL Similarities

To check how accurate Eqs. (5)–(8) describe the binodals and CP coordinates of real substances, we made comparison of the calculated binodals with known experimental data [6, 8]. For many gases and liquids, the results of measurements are presented in the NIST databases [15]. We used it. As far as the liquid branch of the binodal is known, we can find Boyle parameters by means of least-square techniques. The corresponding procedure was proposed in [6], where one can find calculation details. We have found that, for noble gases, various molecular gases, and hydrocarbons, our liquid branches of the binodal are in agreement with experiments within several percents. As an example, we have drawn (Fig. 2) ZL and binodals for fluorine (F_2), which was not presented in our earlier articles. The maximum relative error of our calculations for F_2 is ∼ 3%. The ZL parameters for fluorine are $T_{\mathrm{B}} = 385.06$ K, $n_{\mathrm{B}} = 2.01$ g/cm^3, the critical parameters [15] are $T_c = 144.414$ K, $n_c = 0.593$ g/cm^3, $P_c = 5.1724$ MPa. The similarity parameters for fluorine are $S_1 = 0.67$ and $S_2 = 0.08$. For metals, we have the measurements data only for Cs and Hg (see [8] for references). For Hg, the maximum error can be greater ∼5–7%. In Fig. 3, we present a part of the Hg binodal to show this difference. The parameter $S_2 = 0.065$ for Hg, which deviates by 14% from LJ $S_2 = 0.076$. But $S_1(\mathrm{F}_2) = 0.67$, and it coincides with the exact LJ value. Using our relations (7) and (8), we can also estimate the critical parameters for metals, which are inaccessible in measurements. To do it, one can use the data of measurements at relatively low temperatures in metals. The corresponding technique was developed in [6–8]. The following results were obtained for 5 metals: for Al, $T_c = 6380$ K, $\rho_c = 0.45$ g/cm^3, $P_c = 1070$ Bar; for Cu, $T_c = 7090$ K, $\rho_c = 1.95$ g/cm^3, $P_c = 4500$ Bar; for W, $T_c = 12400$ K, $\rho_c = 4.92$ g/cm^3, $P_c = 7450$ Bar; for U, $T_c = 7000$ K, $\rho_c = 3.30$ g/cm^3, $P_c = 1710$ Bar; and, for Zr, $T_c = 15200$ K, $\rho_c = 1.00$ g/cm^3, $P_c = 421$ Bar. The general picture for binodals and ZL of different substances was published earlier in [6, 8]. So we present two new diagrams for S_1 and S_2, where one can see how accurate these criteria are. The diagram for S_1 presents the positions of CP for various substances reduced to Boyle parameters. If S_1 is constant, then all CP should be located at the corresponding straight line. One can see that only water has a pronounced deviation from the value S_1=0.67. Even for complex organic molecules like R13 (CClF$_3$), R22 (CClFV$_2$), R32 (CH$_2$F$_2$), as well as for quantum liquid He$_3$, the parameter S_1 corresponds to the LJ value. For S_2, the agreement is much worse. The corresponding diagram is S_2 versus the compressibility factor at CP. Here, the points should be located along the horizontal line, if this criterion is true. But only several substances have S_2 located within the interval 0.07–0.08. So this criterion needs in correction.

4. Model Systems and ZL Similarities

The model systems with known interaction potentials (as a rule, pairwise) are the best objects for investigation of their various properties. It is the case because all powerful techniques of the modern theory of liquids are applicable to model systems directly, as far as the potential is known. Consequently, it was interesting to apply our similarities to several popular model systems. This work has been done in [10]. There we took into account such model system as LJ, van der Waals, generalized LJ m-n (or Mie m-n) potential, square-well potentials, Stillinger–Weber, Sutherland potentials (or hard-sphere potential plus power tail), hard-sphere potential plus Yukawa attraction potential, Buckingham or Exp-6 potential, and one of the Morse potentials. The phase diagrams are known for these systems, and the Boyle parameters can be calculated directly by means of Eq. (4). So we can analyze our similarity directly and establish the limits of their applicability. We should note that the model systems have several interesting properties which influence greatly our relations. It is difficult to find these properties in real substances, but they are very evident in models. At first, the critical index β can have different values. That is why we have introduced the dependence on β for S_1 and S_2. It is well known that $\beta = 1/2$ in “mean-field” or “classical” 3D systems, while it is 0.326 (“Ising” value) in real substances [12]. The most known example is van der Waals model. Here $S_1(\beta = 0.5) = 17/27$ and $S_2(\beta = 0.5) = 5/81 = 0.062$. But there are model systems such that the index β can vary between classical and “Ising” values (see [10]). The Sutherland potential is a bright example. It has form

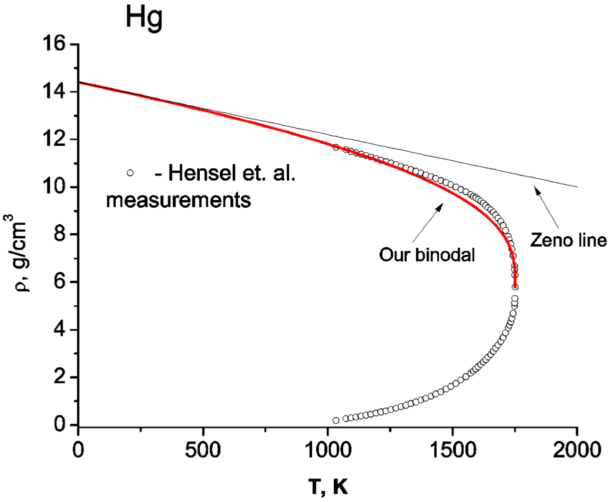

Fig. 3. The binodal for Hg. Hensel *et al.* – are the measurements from [16], lines – our calculations according to Eqs. (5) and (6)

$$\Phi(r) = \begin{cases} +\infty, & r < \sigma, \\ -\varepsilon\left(\frac{\sigma}{r}\right)^m, & r \geq \sigma. \end{cases} \tag{9}$$

If the power $m > 5 - \eta$, then the system belongs to the “Ising” class (η is the Fisher critical index [12], $\eta = 0.0335$). If $5 - \eta \geq m \geq 4.5$, then “...the exponents should be functions of m that interpolate between the Ising and classical values” [17]. At last, if $m < 4.5$, then the system possesses the classical (van der Waals) exponents, i.e., $\beta = 0.5$. So it is evident that the properties of a model system can change profoundly if the attraction range changes. Another property concerns the range of attraction itself. It is a well-known fact that

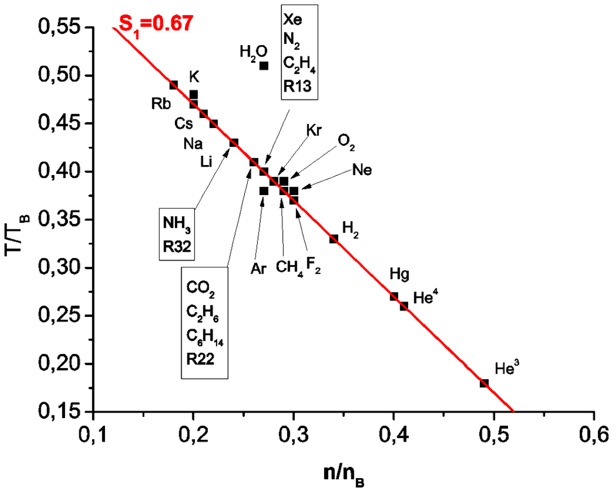

Fig. 4. Diagram for the S_1 criterion for different substances

the existence of the liquid-vapor transition is governed by the attraction part of interaction. A system with only the repulsive force has no this transition (there are only crystal - non-crystal transitions). But if the range of attraction is too small, then the region of liquid-vapor coexistence can be metastable with respect to the liquid-solid transition. In this case, the two-phase binodals are shifted entirely inside the melting region. For details, one can see our work [10]. Of course, our similarities are not applicable in this case. This gives us one limit of applicability. For example, for Sutherland potentials, the metastability holds for $m > 6$. One more important property manifests itself in the opposite case where the range of attraction is too long. Under these circumstances, the triple point temperature can increase up to the CP value. As a consequence, ZL is not a straight line (although it is still tangent to the continuation of the binodal beyond the triple point). In this case, our similarities are inapplicable as well. So here we have one more limitation. For the Sutherland potential, this limitation can be seen already at $m = 3.1$ [10]. The model systems allowed us to find the dependence of our similarities of the critical index β and to find their limits. In [10], we have presented the corresponding analysis with diagrams for S_1 and S_2 analogous to Figs. 4 and 5 of the present article. To demonstrate our findings here, we do not repeat these diagrams, but instead we have calculated S_1 and S_2 for only one potential – square-well one (SW). Its form is

$$\Phi(r) = \begin{cases} +\infty, & r < \sigma, \\ -\varepsilon, & \sigma \le r \le \lambda\sigma, \\ 0, & \sigma < r. \end{cases} \tag{10}$$

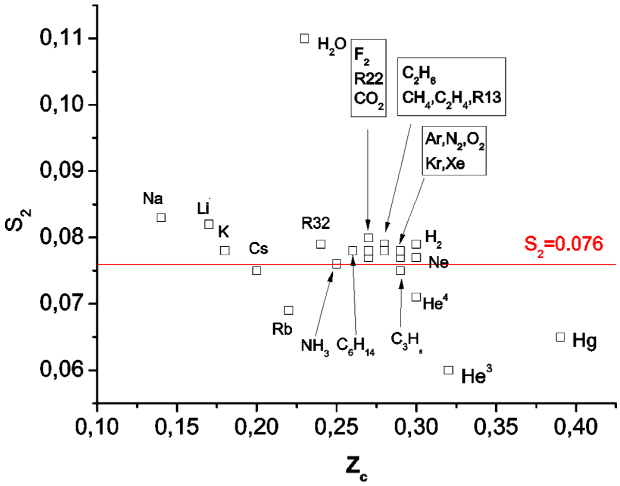

Fig. 5. Diagram for S_2 against $Z_c = P_c/(n_c T_c)$ for different substances. The line $S_2 = 0.076$ marks the LJ value

This potential is possibly the most studied one among all other model systems. In addition, we have the very simple formula for Boyle parameters of SW:

$$T_b(\lambda) = \left[\ln\left(\frac{\lambda^3}{\lambda^3 - 1}\right)\right]^{-1},$$

$$n_{\rm B}(\lambda) = \frac{2\pi\lambda^3}{3C(T_{\rm B}(\lambda))}\ln\left(\frac{\lambda^3}{\lambda^3 - 1}\right). \tag{11}$$

The properties of SW are greatly influenced by the attraction range, i.e. by λ. At present, we have abundant data of numerical simulations in the range $\lambda = 1.05$–3.0 made by different scientific groups (see our work [10] and references therein). The liquid-vapor transition becomes stable when $\lambda \ge 1.25$. We have also found that ZL is not straight already at $\lambda \sim 1.75$–2. So one can await that the LJ-like value $S_1 = 0.67$ would be valid for $\lambda \cong 1.25$–2. We should also note that, while the Boyle parameters can be calculated exactly, CP coordinates in various simulations have some scattering. The critical index β is usually supposed to be equal to 0.326 for $\lambda < 1.75$. But, at $\lambda = 2$, the value $\beta = 0.5$ is much better describes the SW binodal than the "Ising"-type universal exponent [18]. In Figs. 6 and 7, we present the dependence of S_1 and S_2 on the attraction parameter λ, respectively. The vertical dashed line $L1$ at $\lambda = 1.25$ and $L2$ at $\lambda = 2.0$ are the limits of applicability just discussed. The continuous horizontal line marks LJ-like values for these criteria. The dotted horizontal lines cut the 5% corridor around LJ values, i.e. $S_1 \pm 5\%$. Figures 6 and 7 demonstrate clearly that, for a SW system just like in the case of real substances, the value $S_1 = 0.67$

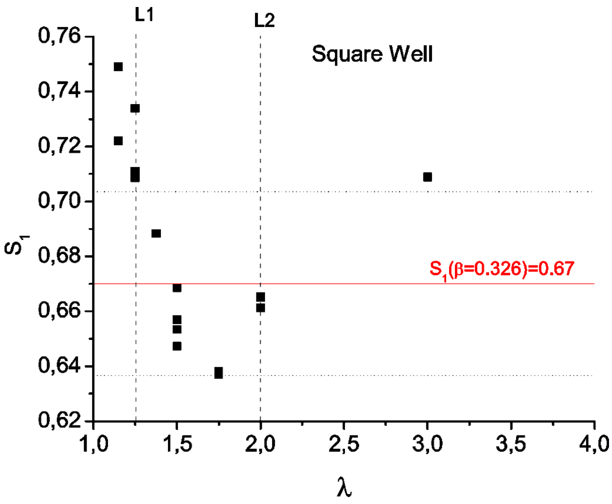

Fig. 6. Dependence of S_1 on λ for the square-well potential. Dotted, dashed, and continuous lines are explained in the text

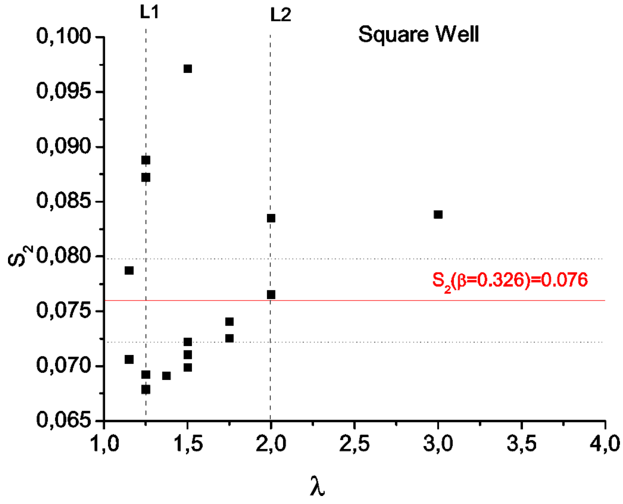

Fig. 7. The same as Fig. 6, but for S_2

is accurate enough, while $S_2 = 0.076$ is failed for some λ even within the 5% corridor. The references to different numerical simulations of SW binodals and CP are not presented here to keep space. One can find them in [10].

5. Conclusions

We have shown that the idea of the construction of a new similarity based on the correspondence of the critical and ZL parameters turns out to be highly fruitful. It is applied to a wider group of substances in comparison with those satisfying the corresponding states principle. The condition that the ZL must be tangential to the extension of the binodal liquid branch at $T > 0$ allows us to avoid difficulties related 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 experiments.

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НОВА ПОДІБНІСТЬ МІЖ КРИТИЧНИМИ ПАРАМЕТРАМИ І ПАРАМЕТРАМИ ЛІНІЇ $Z = 1$

Е.М. Апфельбаум, В.С. Воробйов

Резюме

Знайдено нові відносини між критичними параметрами лінії $Z = 1$. Найбільш значні серед них мають вигляд $T_e/T_{\mathrm{B}} + \rho_c/\rho_{\mathrm{B}} = S(\beta)$, де T_e і ρ_c – критичні температура і щільність. Параметри T_{B} і ρ_{B} визначають положення прямої лінії, вздовж якої коефіцієнт стискання на площині щільність–температура дорівнює 1. $S(\beta)$ слабо залежить від критичного індекса β: $S(\beta) = 0{,}64$ для класичного значення $\beta = 0{,}5$ і дорівнює 0,67 для $\beta = 1/3$. Показано, що це співвідношення позитивно описує як результати числового моделювання, так і експериментальні дані для широкого класу реальних речовин.