

## Triangle of Liquid–Gas States

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We demonstrate for the first time that (a) the straight line of the unit compressibility factor (Zeno line) tends asymptotically to the liquid branch of binodal at low temperatures, (b) the straight line with a half density has to be close to the average of vapor–liquid densities along the binodal curve (rectilinear diameter), and (c) 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 on the axes. These statements are confirmed for model systems and for a wide group of real substances (for the first time including metals: Hg, Cs, and Cu). Critical parameters of all substances under study are located in the vicinity of the triangle median, drawn to the density axis, with a dispersion on the order of 2 in reduced units.

### 1. Introduction

For more than a century, researchers have recognized that liquid–gas systems exhibit several regular and scalable volumetric features including the following characteristics.

(a) The law of corresponding states claims that for many systems various thermodynamic functions coincide when expressed in a dimensionless form.<sup>1,2</sup> Thus, to determine the main thermodynamic characteristics of a substance with experimental accuracy, it is sufficient to know only two parameters related to the potential curve: depth  $D$  of the potential well and the equilibrium distance  $\sigma$  ( $\sigma$  is the “diameter” corresponding to the distance where the potential is equal to zero). These parameters determine in a natural manner the set of dimensionless variables, which in turn causes the similarity of thermodynamic functions. Thus, temperature dependence of the saturated vapor pressure  $p(T)$  for all substances of this group is expressed in a universal form:

$$p^* = p/p_0 = \phi(T/D) \quad (1)$$

Here,  $p_0 = D/\sigma^3$  is a natural (molecular) unit of pressure for the system under study. As the natural unit of density for such systems, one could use the expression  $\rho_0 = m/\sigma^3$ , where  $m$  is the mass of a particle. The critical parameters also can be applied to obtain dimensionless variables.

(b) The law of rectilinear diameter states that, for any species, the average of the sum of vapor ( $\rho_2$ ) and liquid ( $\rho_1$ ) densities is a linear function of temperature in the vapor–liquid coexistence region. In dimensionless units, this law has the form

$$\frac{\rho_1 + \rho_2}{2} = \rho_c + A(T_c - T) \quad (2)$$

where  $A$  is constant and the subscript “c” indicates the critical point.

(c) Another lesser known empirical regularity is the law of rectilinear Zeno line. Along the contour defined by  $Z = 1$  (Zeno

line), where the compressibility factor  $Z = p/\rho kT$  is the same as for an ideal gas, the density of many liquids has been found to be an almost linear function of temperature. The linearity of the  $Z = 1$  contour was discovered by Batschinski in 1906,<sup>3</sup> i.e.

$$\rho = A - BT \quad (3)$$

This straight line begins at the Boyle point  $T_B = A/B$ , in which the second virial coefficient is equal to zero, and intersects the density axis at the Boyle density  $\rho_B = A$ . The Zeno line together with the axes form Batschinski's triangle.

There are various fields of application of these laws. For example, for ethane, the law of rectilinear diameter is valid in the entire vapor–liquid region,<sup>4</sup> while noticeable deviations from eq 2 take place for a majority of other substances near the critical point. It is worth noting that these deviations tend to decrease with the temperature and the accuracy of this law increases.

The law of corresponding states is accurate to within a few percent for dense and condensed rare gases Ne, Ar, Kr, and Xe and also for substances such as N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, or others.<sup>1,2</sup> However, there are many other substances such as water and metals where this regularity does not work properly.

The law of rectilinear Zeno line (Batschinski's law), originally deduced for the van der Waals equation,<sup>5,6</sup> appeared to have the largest field of application, including that for substances disobeying the van der Waals equation (see below). Its validity is experimentally confirmed for all substances that obey the law of corresponding states<sup>7</sup> and also for hydrocarbons,<sup>8</sup> water, carbon dioxide, methane,<sup>5</sup> and for many others. As was shown earlier,<sup>9</sup> this regularity is valid also for metal–mercury as well. Deviations from this regularity, apparently, relate to the change in the vapor composition when the temperature varies (see below).

The variation range of critical parameters for different substances is very broad. For example, the critical temperatures of liquefied rare gases have negative values equal to several tens of kelvin, whereas the critical points for metals are in the range of several thousand kelvin.

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There are indications<sup>1,2,5</sup> that the similarity laws above are not independent, but to date, no specific relations between them have been found. So, in this paper, we show for the first time a relation between the Zeno line and the average liquid–gas diameter along the coexistence curve. To obtain this relation, we consider two models and a group of real substances obeying Batschinski's law (for the metals Cs and Cu of this group, the validity of this law is demonstrated in this paper). Further, we demonstrate that the straight line  $Z = 1$  is the asymptote for the liquid branch of the binodal at low temperatures. The binodals then are inscribed into Batschinski's triangle. Further, we show that a straight line with a half density ( $Z$ -median) is close to the average diameter and coincides with it at low temperatures. That means that at least for low temperatures the law of rectilinear diameter can be considered as the consequence of Batschinski's law. One more consequence is that the critical points are located near the  $Z$ -median. Therefore, it is possible to decrease significantly the quantitative variety of reduced critical parameters by a factor of less than 2, if the binodals are expressed in coordinates  $\rho/\rho_B$  and  $T/T_B$ .

This paper is organized as follows. We consider the van der Waals equation in the next section and show that all similarity laws and conclusions mentioned above follow from this equation. Section 3 describes the theoretical analysis demonstrating that the regularities have a general character. In section 4, we will apply our results to Lennard–Jones systems. In section 5, we consider how the real substances obey these laws. Conclusions and outlook are given in sections 6 and 7, correspondingly.

## 2. Van Der Waals Equation

In this section, we intend to show that all the above-listed regularities are the consequences of the van der Waals equation. The law of corresponding states straightforwardly follows from the van der Waals equation written in dimensionless units ( $\rho' = \rho/\rho_c$  and  $T' = T/T_c$ , where  $\rho$  is the density,  $T$  is the temperature, and the subscript “c” indicates the critical point). The expression for the pressure can be written as

$$p' = \frac{8T'\rho'}{3 - \rho'} - 3\rho'^2 \quad (4)$$

For the sake of clarity, all the primes in the equations given below are omitted.

To verify the rectilinear law, we use the expression for the chemical potential deduced from eq 4

$$\mu = \frac{8T}{3 - \rho} - 6\rho + \frac{8T}{3} \ln\left(\frac{3\rho}{3 - \rho}\right) + \varphi(T) \quad (5)$$

where  $\varphi(T)$  is an arbitrary function of temperature. Along the coexistence curve, the following relations are valid:  $p(\rho_1, T) = p(\rho_2, T)$  and  $\mu(\rho_1, T) = \mu(\rho_2, T)$ . Here,  $\rho_1$  and  $\rho_2$  are the densities of the coexistence phases. The two latter conditions and eqs 4 and 5 give rise to the parametric equations

$$T = \frac{1}{8}(\rho_1 + \rho_2)(3 - \rho_1)(3 - \rho_2) \quad (6)$$

$$p = \rho_1\rho_2(3 - \rho_1 - \rho_2) \quad (7)$$

$$\frac{8T}{3} \ln\left(\frac{\rho_1(3 - \rho_2)}{\rho_2(3 - \rho_1)}\right) - (\rho_1 - \rho_2)\left(6 - \frac{8T}{(3 - \rho_1)(3 - \rho_2)}\right) = 0 \quad (8)$$

By solving numerically the parametric system of eqs 6–8, we find  $\rho_1$  and  $\rho_2$ . The temperature and pressure along the coexistence curve can be easily defined using eqs 6 and 7. Using eq 1 and the definition for the compressibility factor  $Z = p/\rho T = (3p'/8\rho'T')$ , we obtain

$$Z = \frac{P}{\rho T} = 1 + \frac{27\rho(\rho/3 + 8T/27 - 1)}{8T(3 - \rho)} \quad (9)$$

The line  $Z = 1$  is defined as

$$\rho = 3 - 8T/9 \quad (10)$$

The binodal and the line  $Z = 1$  in accordance with eqs 6, 8, and 10 are drawn in Figure 1a. The straight line  $Z = 1$  is the asymptote for the liquid branch of the binodal when  $T \rightarrow 0$ . This statement has a simple proof. In the limiting case,  $T \rightarrow 0$  and  $\rho_2 \rightarrow 0$  and it follows from eq 6 that

$$\rho_1 = \frac{3}{2} + \sqrt{\frac{9}{4} - \frac{8T}{3}} \quad (11)$$

or  $\rho_1|_{T \rightarrow 0} = 3 - 8T/9$ . The latter coincides with eq 10.

The average diameter  $\rho_d = (\rho_1 + \rho_2)/2$  is shown in Figure 1 as line 2. It is practically a straight line. The density along the average diameter has to be close to the density along the line  $Z = 1$  divided by 2, i.e.

$$\rho = 3/2 - 4T/9 \quad (12)$$

The line corresponding to eq 12, shown in Figure 1, is dubbed as a  $Z$ -median (or Bachinskii's triangle median). In fact, the  $Z$ -median goes closely to the average diameter line. The value of the density at the critical point is equal to 19/18 according to eq 12. The corresponding value at the average diameter is equal to 1. It is easily to show from eqs 6–8 that at  $T \rightarrow 0$  the average diameter is described by eq 12, i.e., the average diameter and  $Z$ -median coincide. So, the rectilinear behavior of the diameter can be considered as the consequence of Bachinskii's law at  $T \rightarrow 0$ .

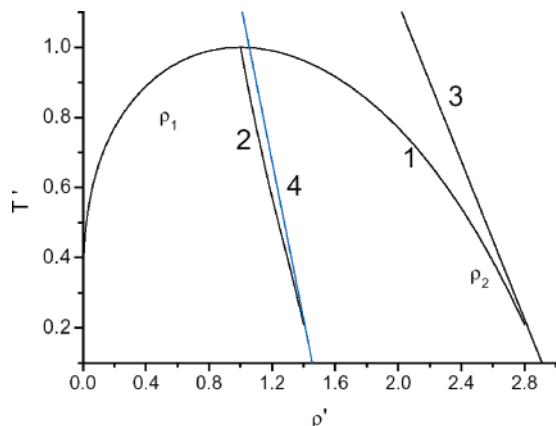
The analysis of van der Waals equation shows the following: (1) the line  $Z = 1$  is an asymptote to the liquid branch of the binodal for  $T \rightarrow 0$ ; (2) Bachinskii's triangle median has no detectable differences from the line of average diameter of a van der Waals system; (3) the law of rectilinear diameter is the consequence of Bachinskii's law at low temperatures.

In the following part of our paper, we will show that all these statements are not a simple consequences of the van der Waals equation, but they are valid also for a model system and for some real substances.

## 3. Analysis of the Correlation between the Position of the $Z = 1$ Line and the Liquid Branch of the Binodal and the Average Diameter

The condition of equilibrium between the liquid (1) and gas (2) phases can be written as

$$F_1 - F_2 + p(v_1 - v_2) = 0 \quad (13)$$



**Figure 1.** Dependence of temperature of the coexistence phases on the density along the equilibrium line according to the van der Waals equation: (1) binodal, (2) average diameter, (3)  $Z = 1$  line, (4)  $Z$ -median.

where  $F_1$  and  $F_2$  are the corresponding free energies and  $v_1 = 1/\rho_1$  and  $v_2 = 1/\rho_2$  are the specific volumes of the phases.

Let us consider in a formal way the case  $T \rightarrow 0$ , disregarding the solidification and considering the liquid state at this condition as a metastable state. Then, the equilibrium pressure diminishes  $p \rightarrow 0$  and  $v_2 \gg v_1$ . The vapor for these conditions is an ideal gas, and its free energy and pressure are given by the following equations

$$F_2 = \frac{kT}{m} \ln \left( \frac{\Lambda^3 \rho_2}{e g_a m} \right) \quad (14)$$

$$p = \frac{kT \rho_2}{m} \quad (15)$$

where  $\Lambda = h/[2\pi mkT]^{1/2}$  is the thermal wavelength and  $g_a$  is the inner statistical sum of an atom in vapor. Substituting eqs 14 and 15 into eq 13, we produce the expression for a specific volume of vapor and pressure along the coexistence line

$$1/\rho_2 = \frac{\Lambda^3}{m g_a} \exp \left( -\frac{m F_1}{kT} \right) \quad (16)$$

$$p_s = \frac{kT g_a}{\Lambda^3} \exp \left( \frac{m F_1}{kT} \right) \quad (17)$$

Equations 16 and 17 define the vapor specific volume and pressure along the coexistence line if the dependence of liquid free energy on the temperature is known. Hereafter,  $\rho$  denotes the number density, which is different from the mass density.

In the following, we can use a general expression for the liquid pressure

$$p = \rho kT - \frac{2\pi \rho^2}{3} \int_0^\infty r^3 \frac{d\Phi(r)}{dr} G(r, \rho, T) dr \quad (18)$$

In eq 18,  $\Phi$  is the interaction potential between two atoms of the substance under study and  $G$  is the pair correlation function. Without a significant loss of generality, the potential can be written as

$$\Phi = \Phi^+ - \Phi^- \quad (19)$$

where  $\Phi^+$  ( $\Phi^-$ ) corresponds to repulsive (attractive) forces. Substituting eq 19 in eq 18, we rewrite eq 18 as a difference of positive and negative parts

$$p = \rho kT + p^+ - p^- \quad (20)$$

where

$$p^\pm = \frac{2\pi \rho^2}{3} \int_0^\infty r^3 dr \left| \frac{d\Phi^\pm(r)}{dr} \right| G(r, \rho, T) \quad (21)$$

In eq 20, we took into account the fact that  $d\Phi^+/dr < 0$  and  $d\Phi^-/dr > 0$ . The equation for the unit compressibility factor  $Z = p/\rho kT = 1$ , following from eq 18, has a form

$$p^+ - p^- = 0 \quad (22)$$

The liquid pressure in the limit  $p \rightarrow 0$  is expressed as

$$p^+ + \rho kT - p^- = 0 \quad (23)$$

Let us compare eqs 22 and 23. This inequality is valid when  $T \rightarrow 0$

$$p^\pm \gg \rho kT \quad (24)$$

Note that a subtraction of two big quantities is contained in eqs 22 and 23. The solutions of these equations almost coincide. Moreover, if one takes into account the conditions  $p \rightarrow 0$  and  $T \rightarrow 0$  simultaneously, it is possible to show that the binodal and line  $Z = 1$  satisfy the same equation in these limits. In fact, the pressure along the liquid branch of the binodal for  $p \rightarrow 0$  is described by eq 23. But, eq 23 at  $T \rightarrow 0$  transforms into eq 22, describing the  $Z = 1$  line. Thus, the  $Z = 1$  line is an asymptote for the liquid branch of the binodal in the limit  $T \rightarrow 0$ .

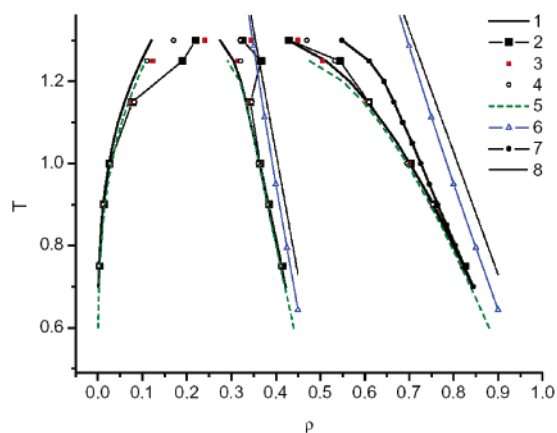
Our arguments still retain validity in the dense fluid region near the triple point where the intermolecular interaction becomes important. The attractive and repulsive contributions are in dynamic balance along the entire Zeno contour. These arguments are also valid in the solid region below the triple point. However, the issue of the behavior of the  $Z = 1$  line in the sublimation region deserves separate consideration.

We note that for metals and some other substances inequality 24 remains valid along the entire coexistence line up to the critical point. This means that eqs 22 and 23 have close solutions not only in the limit of low temperatures, but in a wide range of its variation as well. The relative contribution of the thermal (positive) part in reduced units is equal to  $p^+ = 4$  for the van der Waals equation at the critical point. The corresponding contribution to the negative part  $p^-$  is equal to 3. The difference of these two values gives the pressure at the critical point  $p_s = 1$ . According to data of the numerical modeling<sup>10</sup> for a Lennard–Jones system at the critical point ( $T_c = 1.35$ ,  $\rho_c = 0.35$ ), the value  $p^+ + \rho kT$  is equal to 109.42, whereas  $-p^- = 109.28$ . The difference of these two large values gives a relatively small quantity—the critical point pressure ( $p_c = 0.14$ ). In the latter case, all pressures are expressed in dimensionless molecular units.

Now, when the asymptotic behavior of the  $Z = 1$  line is proven, we can show that the law of rectilinear diameter is the consequence of Bachinskii's law at low temperatures. The asymptote for the gas branch of the binodal at  $T \rightarrow 0$  is line  $\rho = 0$ . So, the average diameter is described by the same equation as the  $Z$ -median in this limit. Therefore, if the  $Z = 1$  line is straight, then the  $Z$ -median is also straight and the same is true for the diameter at low temperatures.

#### 4. Model Lennard–Jones System

Let us consider a system in which particles interact via Lennard–Jones potentials. The Lennard–Jones (LJ) potential



**Figure 2.** Binodals and average diameters for a Lennard–Jones system, calculated by different authors: (1) ref 14, (2) ref 12, (3) ref 13 (first calculation), (4) ref 13 (second calculation), (5) ref 15, (6) ref 10 ( $Z = 1$  line), (7) this work ( $Z = 1$  line by our calculation according to the data of ref 14; see text), (8) this work (our calculation according to eq 26). The average diameter is also drawn for lines 6 and 8.

with the parameters  $D$  and  $\sigma$  is written as

$$U(r) = 4D \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right) \quad (25)$$

The thermodynamic properties of an LJ system in a two-phase domain were studied numerically via molecular dynamic simulation,<sup>10,11</sup> via grand canonical Monte Carlo simulation,<sup>12</sup> via the Monte Carlo simulation in the generalized ensemble,<sup>13,14</sup> and using the theory of integral equation.<sup>15</sup>

All the results of these simulations are presented in Figure 2 on the density–temperature plane with rescaled LJ parameters (temperature  $T \rightarrow T/D$ , density  $\rho \rightarrow \rho\sigma^3$ ). The gas and liquid branches of the binodals and the corresponding lines for the average diameters are created according to the data of different authors. All the obtained data for the binodal and the middle diameter are in good agreement with each other for the low-temperature regime. However, some deviations take place as the critical point is approached. These deviations can be a consequence of inaccuracies of numerical calculations. For example, two different simulations for the same model<sup>13</sup> give different results in the critical point domain (see Figure 2). Regarding another simulation result,<sup>12</sup> it should be emphasized that in the critical point domain one point evidently is outside the main data mass. This clearly demonstrates the fact that the system behavior in the vicinity of the critical point cannot be described numerically with enough accuracy. In our view, the simulation data<sup>14</sup> are the most up-to-date and accurate. It is in good agreement with others results.<sup>10,15</sup> Nevertheless, the law of rectilinear diameter is valid for all the above-listed models.<sup>15</sup> Let us consider whether the other regularities considered above will be valid for the Lennard–Jones system as well.

The equation of state was constructed<sup>10</sup> in the analytical form on the basis of molecular-dynamical modeling and virial expansions. We calculate the  $Z = 1$  line and the corresponding  $Z$ -median using this equation (line 6 in Figure 2). It is obvious that there is a close resemblance with the van der Waals equation: the  $Z = 1$  line approaches asymptotically to the liquid branch of the binodal. The median of the triangle formed by the  $Z = 1$  line is correlated with the average diameter in accordance with data,<sup>12–15</sup> while the diameter is rectilinear.

For the known interaction potential, the equation for the  $Z = 1$  line can be analytically written as<sup>16</sup>

$$\rho_{Z=1}(T) = \frac{dB(T)}{dT} \bigg|_{T=T_B} \frac{1}{C(T_B)} (T_B - T) \quad (26)$$

where  $B(T)$  and  $C(T)$  are the second and third virial coefficients,  $T_B$  is the Boyle temperature when  $B(T_B) = 0$ . Equation 26 was deduced from the virial expansion. The value  $T_B = 3.418$  (in molecular units) for the Lennard–Jones potential. The lines  $Z = 1$  and  $Z$ -median (line 8 in Figure 2) are constructed according to eq 26. They are in good agreement with the calculations<sup>10</sup> (line 6). Since the equations of state in an analytical form were absent in the works of others, it is impossible to construct the  $Z = 1$  line for them. On the other hand, with the approximation of the average diameter by a straight line one can find the value of the temperature ( $T^*$ ), where the  $Z = 1$  line intersects the temperature line. Then, we can compare it with the value of Boyle temperature (eq 26) for the Lennard–Jones potential. The value  $T^* = 3.24$  according to the data<sup>14</sup> is close to  $T_B = 3.418$ . We also multiply by two the densities that correspond to the average diameter,<sup>14</sup> keeping the temperature. This is line 7, presented in Figure 2. Although we cannot claim that line 7 is the  $Z = 1$  line, one can see that the former asymptotically approaches the binodal at low temperatures.

In the following section, we consider a group of real substances for which the phase equilibrium and equation of state are experimentally well established. First, we will consider substances that satisfy the law of corresponding states, then water, and finally metals, mercury and cesium, for which the critical parameters are known.

## 5. Experimental Binodals, Average Diameters, the Line $Z = 1$ , and the $Z$ -Median for Different Substances

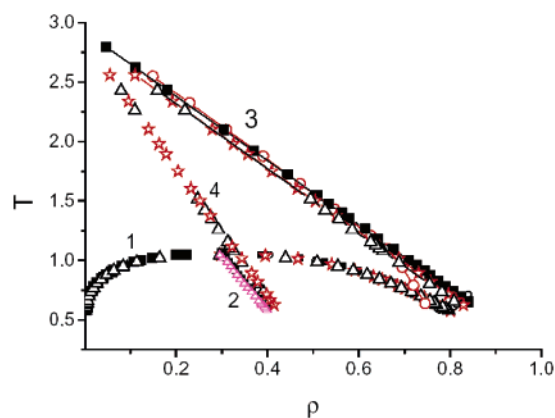
### Substances that Satisfy the Law of Corresponding States.

In Figure 3, the binodals (curves 1) and lines  $Z = 1$  (straight line 2) of rare gases are presented in the plane  $T-\rho$  in reduced molecular units. This picture is constructed according to experimental data.<sup>7</sup> Lines 3 and 4 are shown in this figure too. The first line corresponds to the  $Z$ -median for Xe. Line 4 is the average diameter for Xe. Lines 3 and 4 go close to each other. These lines have the same relative order for other elements obeying the law of corresponding states.

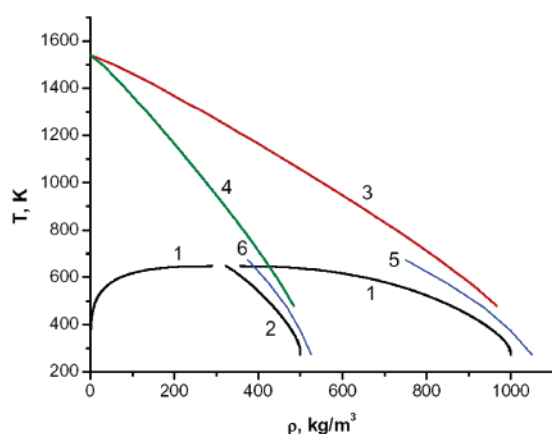
**Water.** The binodal (curve 1) and average diameter (curve 2) for water are drawn in Figure 4 according to data.<sup>17,18</sup> The dependence of the average diameter on temperature becomes rectilinear only as the critical point approaches. Lines 3 and 4 correspond to  $Z = 1$  and the  $Z$ -median, according to data.<sup>5</sup> These lines are slightly distorted. The density along line 4 exceeds the average density. An independent calculation of the line  $Z = 1$  was done using the data.<sup>18</sup> For this purpose, the water isotherms<sup>18</sup> were created in the pressure–temperature plane. The coordinates of the line  $Z = 1$  are determined at the points of intersection of these isotherms with the corresponding isotherms of the ideal gas. The dependences obtained by this approach for the  $Z = 1$  line and the  $Z$ -median are presented in Figure 4 as lines 5 and 6, correspondingly. In the latter case, the values of the density along the  $Z$ -median are in better agreement with the values of the density along the middle diameter. The situation for water is qualitatively the same as has been discussed above.

**Mercury.** The investigation of the  $Z = 1$  and  $Z$ -median lines for metals is of the most interest. The straight line  $Z = 1$  for mercury was defined<sup>9</sup> using the experimental data.<sup>19,20</sup> The results of this work are presented in Figure 5, where the binodal, curve 1, and the average diameter, 2, were obtained according to data.<sup>19,20</sup> The other lines are  $Z = 1$ , 3, and the  $Z$ -median, 4. The situation completely corresponds to the one obtained

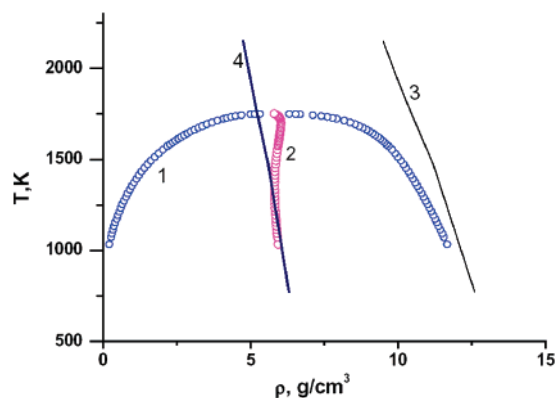




**Figure 3.** Dependence of temperature of the coexisting phases on the density along the equilibrium line for the substances that obey the law of corresponding states: (1) binodal, (2) average diameter, (3)  $Z = 1$  line, (4)  $Z$ -median for Xe. All dependencies are created using the data of ref 7.



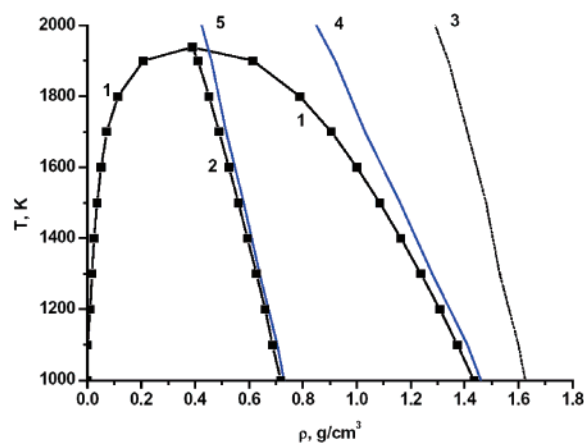
**Figure 4.** Dependence of temperature of the coexisting phases on the density along the equilibrium line for water: (1) binodal, (2) average diameter of ref 17, (3)  $Z = 1$  line of ref 5, (4)  $Z$ -median of ref 5, (5)  $Z = 1$  line calculated in this paper with aid of the data of ref 18, (6)  $Z$ -median corresponding to line 5.



**Figure 5.** Same plot as in Figure 4 for mercury: (1) binodal, (2) average diameter (these lines are constructed according to the experiments of refs 19 and 20), (3)  $Z = 1$  line calculated in ref 9, (4)  $Z$ -median calculated in ref 9.

through the investigation of the van der Waals equation. The average diameter for mercury deviates from rectilinear behavior as the critical point approaches. The reason for this diameter anomaly is widely discussed.<sup>21</sup>

**Cesium.** The binodal (curve 1) and average diameter (curve 2) for cesium are drawn in Figure 6 on the basis of experimental data.<sup>22</sup> We have used the equation of state data from this work



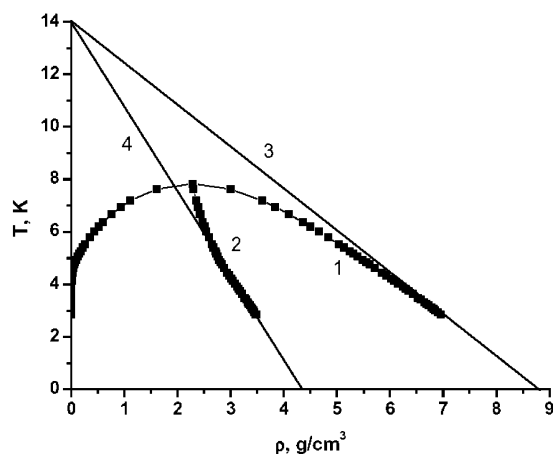
**Figure 6.** Same plot as in Figure 4 for cesium: (1 and 2) binodal and average diameter according to the experimental data of ref 22, (3)  $Z = 1$  line calculated on the assumption that cesium vapor consists of a monatomic gas, (4)  $Z = 1$  line calculated on the assumption that the cesium vapor consists of polyatomic clusters in refs 24 and 25, (5)  $Z$ -median corresponding to line 4.

to calculate the  $Z = 1$  line. Line 3 in Figure 6 is constructed assuming that the cesium vapor is an ideal monatomic gas, which has a pressure  $p = \rho T/m$ . The density along this (practically straight) line is noticeably greater than the density of the liquid branch of the binodal. There is no tendency of this line to become a binodal with a decrease of temperature. The reason for the deviation is the complex composition of cesium vapor. Attention was drawn in a number of works to the fact that the dense cesium vapor consists of polyatomic clusters.<sup>23–25</sup> We have used the equation of state<sup>24,25</sup> for calculation of the vapor pressure which allows formation of polyatomic clusters

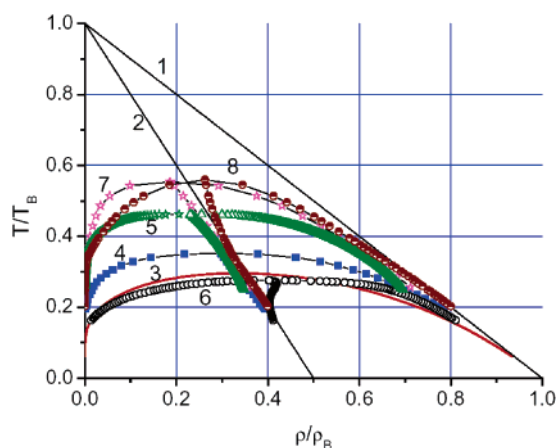
$$p(\rho, T) = \frac{p_g}{2} \left( 1 + \sqrt{1 + \frac{4p_i}{p_g}} \right) \quad (27)$$

where  $p_i = kT\rho/m$  is the ideal gas pressure and  $p_g = 2 \times 10^{21} kT(T/11600)^{-1/2} [\exp(0.44(T/11600)) - 1]^{-1}$  is the typical cluster pressure. In the next step, we found the coordinated  $(\rho, T)$  of the intersection points of the isotherms, calculated according to data,<sup>22</sup> with the isotherms, defined by eq 27. The  $Z = 1$  line obtained in this way is shown in Figure 6 as line 3. The corresponding  $Z$ -median is shown as line 4. As one can see, the calculation, which takes into account the cluster structure of the dense cesium vapor, leads to a significant convergence of the experimental density along the average diameter and  $Z$ -median.

**Copper.** Metals, which have critical parameters inaccessible for direct measurements because of high temperatures and pressures, are of particular interest to our consideration. This is the case for copper. The semiempirical binodal for copper has been constructed on the basis of shock wave experiments and low-temperature data.<sup>26</sup> The binodal and average diameter for copper are given in Figure 7. As one can see, the dependence of the liquid phase density and the average diameter on the temperature have almost a linear form for low temperatures. Taking into consideration that the presented data are approximate, we worked in reverse order. We reconstructed the  $Z$ -median using the rectilinear part of the middle diameter. To do this, we drew straight line 4 over the rectilinear part of the average diameter. Then, we supposed that the straight line with double density corresponds to the  $Z = 1$  line. Thus, we found that for copper  $T_B = 14\,000$  K and  $\rho_B = 8.8$  g/cm<sup>3</sup>. We note



**Figure 7.** Same plot as in Figure 4 for copper: (1 and 2) binodal and average diameter built according the data of ref 26, (3 and 4)  $Z = 1$  line and  $Z$ -median constructed over the average diameter.



**Figure 8.** Dependence of temperature on the density along the phase coexistence line in parameters reduced to the Boyle point for different substances: (1)  $Z = 1$  line, (2)  $Z$ -median for all substances. The binodals and average diameters were calculated for the following substances from the following sources: (3) according to the van der Waals equation, (4) argon ref 7, (5) water refs 17 and 18, (6) mercury refs 19 and 20, (7) cesium ref 22, (8) copper ref 26.

that the liquid branch of the binodal and the  $Z = 1$  line coincide practically up to  $T \sim 5000$  K with correspondence to the discussion in section 3.

## 6. Triangle of States

The preceding analysis shows that the mutual positions of the binodal and average diameter on one hand and the lines  $Z = 1$  and  $Z$ -median on the other hand for different substances are similar. It is convenient to combine the  $Z = 1$  lines for different substances, introducing parameter coordinates reduced to the Boyle point,  $\tilde{\rho} = \rho/\rho_B$  and  $\tilde{T} = T/T_B$ , where  $\rho_B$  and  $T_B$  are the segments of the density and temperature, correspondingly, which the  $Z = 1$  line cuts off on the axes (see Figure 8). In these coordinates, the  $Z = 1$  line is the straight line, universal for all substances, and this line cut off unit segments on the axes. The binodals of all substances inscribe into a triangle, formed by the  $Z = 1$  line and the axes. The critical parameters lie close to the median of this triangle. It is significant that the critical temperature and density reduced to the Boyle point parameters lay in the sufficiently restricted area and differ less than twice in value. This range is determined by the extreme points located near the  $Z$ -median. One extreme point has the

maximum value  $\rho_c/\rho_B \approx 0.4$  and the simultaneously minimal  $T_c/T_B \approx 0.278$  and corresponds to the mercury critical parameters. The other extreme point has the minimal  $\rho_c/\rho_B \approx 0.2$  and maximal  $T_c/T_B \approx 0.55$  and corresponds to the metals cesium and copper. The critical parameters for other substances, considered in this paper, lie between these extreme values.

## 7. Conclusions

We have shown that for a wide group of substances it is possible to construct a triangle with the top at the Boyle point. The binodals all of these substances inscribe into this triangle, and the critical parameters lie near its median. This triangle has a feature of universality, which cannot be explained on the basis of the laws of similarity that are a foundation of the scaling theory. The straight line, presenting the hypotenuse of the triangle, is located far from the critical point (the Boyle temperature exceeds the critical temperature by a factor of 3). We also have shown that the law of rectilinear diameter can be considered as the consequence of the linear dependence of the Zeno line at low temperatures. The open question is why the  $Z = 1$  is a straight line for many very different substances independent of their interaction potential. The other question is why the reduced temperature for the critical points  $\tilde{T} = T/T_B$  changes between 0.26 and 0.57 and what parameter determines these variations. We hope that further theoretical and experimental investigations can shed light on these issues.

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