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Note: The universal relations for the critical point parameters

ARTICLE *in* THE JOURNAL OF CHEMICAL PHYSICS · JULY 2013

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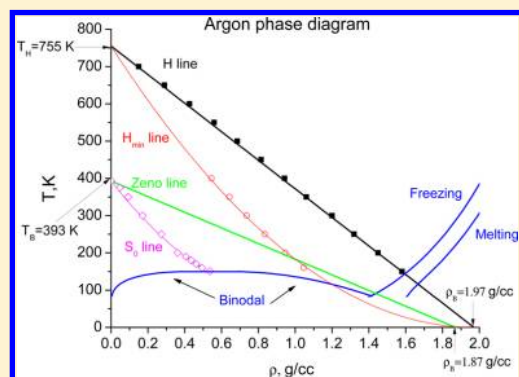
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Regarding the Universality of Some Consequences of the van der Waals Equation in the Supercritical Domain

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ABSTRACT: We show that some of the thermodynamic regularities, following from the van der Waals (VDW) equation, are valid for the real substances and models described by completely different equations of state. These regularities relate to lines of ideal enthalpy, enthalpy minima, and isothermal compressibility maxima. The first one appears to be the straight line on the density–temperature plane, while for the two others there are universal relations, which are the same for various substances and models (argon and Lennard-Jones system as examples). The model systems were studied by Monte Carlo simulations (NVT MC), while experimental data were analyzed for the real substances. Our numerical calculations and the analysis of experimental data have shown that for the considered systems these curves are similar to the VDW ones.



INTRODUCTION

The famous van der Waals (VDW) equation has amazing features associated with the fact that some of its consequences are valid for a great number of various model and real systems described by completely different equations of state. The corresponding states principle and the rectilinear diameter law are the well-known examples of these features.^{1,2} An important consequence of the VDW equation is the existence of a line where the compressibility factor Z is unity (i.e., $Z = P/\rho T = 1$, where P is the pressure, ρ is the particle density, and T is the temperature). The contour $Z = 1$ is referred to as the Zeno line (ZL) or Z line. It is easy to show that ZL is a straight line on the density–temperature plane for the van der Waals system^{3–7} for many real substances^{4–7} and model systems.⁸ Moreover, this phenomenon (ZL straightness) has a wider applicability than other similarity laws. For example, ZL is the straight line for organic materials,^{4,5} noble gases,^{6,10,11} and even some metals,^{8–12} for example, Cs and Hg.

Another less known consequence of the VDW equation is that the curve of ideal enthalpy is also a straight line on the density–temperature plane¹³ (like it is for ZL). The enthalpy H coincides with an ideal gas enthalpy along this line. By analogy with the line for a unit compressibility factor (Z line), we can call this line the H line. Despite the fact that this line can contain important information about the behavior of matter in the supercritical region, to date there are not any checks of the straightness of the H line for any other models or real systems.

Besides the H line, there are more contours which can be easily constructed^{14–16} within the VDW system on the density–temperature plane. One of them is the curve of maxima for the isothermal compressibility where $(\partial^2 P / \partial \rho^2)_T = 0$. This is one of two necessary conditions for the existence of the critical point (CP). Therefore, this line should start (or end) at the CP in the one-phase region. Besides, the isothermal

compressibility is equal^{1,2} to the value of the structure factor at zero wave vector, $S(0)$. Therefore, we will refer to this line as the S_0 line. Here we will also consider another curve. This is the curve of minima for the enthalpy (H_{\min} line). Analogous curves on the density–temperature plane exist for the systems other than VDW. Here, for the first time, we will show that the equations of these curves, written in the reduced variables, are valid not only for the VDW equation, but also for other systems too. We will consider the Lennard-Jones (LJ) model system and a group of real substances, satisfying the corresponding states principle, taking argon as an example. All these lines are located mainly in the supercritical region where there is a noticeable gap in our knowledge of the thermophysical properties of matter.^{15,16} This work partly attempts to bridge this gap.

At first we consider the van der Waals equation, where the straightness of the H line has already been established in ref 13. Then we present explicitly derived equations for the S_0 and H_{\min} curves for the VDW system (see also refs 14–16). The density–temperature phase diagram with the binodal position and all above-mentioned lines, including the Z line, is the result of this consideration. After that we study the behavior of the binodal and the same curves both for the LJ system (numerically, applying the Monte Carlo simulation technique) and for a real substance—argon (using the information from the NIST database¹⁷). The latter belongs to a group of substances satisfying the corresponding states principle. Consequently, the regularities established for argon should be valid for other substances of this group. Our investigation has discovered that there is a full similarity between the behavior of

Received: April 26, 2013

Revised: May 24, 2013

Published: May 31, 2013

the above-mentioned lines (Z , H , S_0 , and H_{\min} lines) on the density–temperature plane for these systems and VDW. To confirm this, we constructed a combined plot of phase diagrams for all of the cases, using the values of density and temperature reduced to the Boyle values (defined below). A similar plot for the binodals and the Z lines has been discussed previously in ref 11.

VAN DER WAALS EQUATION

The van der Waals equation is probably the most convenient object to study various thermodynamic phenomena. Thus, there are many investigations of it in application of various tasks, including the special lines. In particular, the behavior of the S_0 line for the VDW system was studied in refs 14–16. This line also appeared to be the line of density fluctuation maxima, which describes the ridges in the supercritical region.^{14–16} Therefore, it is directly connected with possible separation of the supercritical region into gaslike and liquidlike phases.¹⁶ Besides the S_0 line, the VDW equation allows one to easily obtain other special lines: the line of maxima of the thermal expansion coefficient, the line of the maxima of the heat capacity, and many others.^{15,16} Here we will use the VDW equation to consider the H and H_{\min} lines and how they are located with respect to other special lines.

The van der Waals equations for the pressure, factor of compressibility, and enthalpy are

$$P = \frac{\rho T}{1 - b\rho} - a\rho^2 \quad Z = P/\rho T = \frac{1}{1 - b\rho} - \frac{a\rho}{T}$$

$$H = \frac{3T}{2} - 2a\rho + \frac{T}{1 - b\rho} \quad (1)$$

where a and b are the material constants of the VDW equation. Let us introduce the Boyle units: $\rho_B = 1/b$, $T_B = a/b$, and $P_B = a/b^2$. Then one can introduce reduced pressure, density, temperature, and enthalpy: $P' = P/P_B$, $\rho' = \rho/\rho_B$, $T' = T/T_B$, and $H' = H/T_B$. In these reduced units the critical parameters are $P'_c = 1/27$, $\rho'_c = 1/3$, and $T'_c = 8/27$. Then the expressions in eq 1 can be represented in the form containing no constants:

$$P' = \frac{\rho' T'}{1 - \rho'} - (\rho')^2 \quad Z = \frac{1}{1 - \rho'} - \frac{\rho'}{T'}$$

$$H' = \frac{3T'}{2} + \frac{T'}{1 - \rho'} - 2\rho' \quad (2)$$

The equation of the line where $Z = 1$ (Z line) can be written as

$$\rho' + T' = 1 \quad (3)$$

The equation of the line where the values of the enthalpy are equal to an ideal gas enthalpy can be written as

$$H' - H'_{\text{id}} = \frac{3T'}{2} + \frac{T'}{1 - \rho'} - 2\rho' - \frac{5T'}{2}$$

$$= \frac{T'\rho'}{1 - \rho'} - 2\rho' = 0 \quad (4)$$

From eq 4 it follows that

$$\rho' + T'/2 = 1 \quad (5)$$

Let us rewrite eq 3 for the values of the unit compressibility factor (Zeno line) and eq 5 for the ideal gas enthalpy line (H line) in the units reduced to the critical values ($\rho_c = 1$, $T_c = 1$,

$P_c = 1$). We will use these units here and below for the VDW equation. Then we obtain

$$\frac{\rho}{\rho_B} + \frac{T}{T_B} = 1 \quad \frac{\rho}{\rho_B} + \frac{T}{2T_B} = 1 \quad (6)$$

where for the VDW equation $\rho_B = 3$ and $T_B = 27/8$. Note that most of these lines are located in the supercritical region.

In addition to the above straight lines, there are loci of extrema for some other thermodynamic quantities, easily obtained for the VDW system. We consider them, partly following refs 14–16. At first we will consider the line of minima for the enthalpy isotherms (H_{\min} line). We can find the equation for this line from eq 4:

$$T_{H_{\min}}(\rho) = T_H(1 - \rho/\rho_H)^2 \quad (7)$$

where $T_H = 2T_B$. The value of $T_{H_{\min}}$ tends to T_H when $\rho \rightarrow 0$. Also of interest is the line along which

$$(\partial^2 P / \partial \rho^2)_T = 0 \quad (8)$$

The latter condition is one of the necessary conditions for the existence of the critical point. At the same time, this condition is equivalent to the presence of maxima along the line of isothermal compressibility: $\zeta_T = T(\partial \rho / \partial P)_T = S(0)$. The position of the maxima of the S_0 line for the VDW system satisfies the equation (see also eq 3 in ref 15)

$$T_{S_0}(\rho) = T_B(1 - \rho/\rho_B)^3 \quad (9)$$

The value of T_{S_0} tends to T_B when $\rho \rightarrow 0$. At the critical point, where $\rho = \rho_c = \rho_B/3$, the temperature $T_{S_0} = T_c = 8T_B/27$.

As we mentioned above, the VDW system contains many other special lines. Some of them have been described in refs 14–16. One of them is, for instance, the line of the maxima of the heat capacity c_p , which does not depend on the temperature and is determined by a simple condition, $\rho = \rho_c$. Another one pertains to the thermal expansion coefficient,^{15,16,18} which is

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = \frac{4(3 - \rho)}{12T - 3\rho(3 - \rho)^2} \quad (10)$$

The line of the maxima of the thermal expansion coefficient is given by the equation^{15,16}

$$T_\alpha = T_H(1 - 2\rho/\rho_B)(1 - \rho/\rho_B)^2 \quad (11)$$

The value of the temperature T_α tends to T_H at $\rho \rightarrow 0$.

The phase diagram of the VDW system, including all the lines, is presented in Figure 1 at the density–temperature plane. Most of the lines in Figure 1 are located in the supercritical domain. Now let us consider whether these regularities valid for the VDW system can be deduced from the virial expansions and whether they are valid for other systems.

DENSITY POWER EXPANSION FOR H LINES. CONDITIONS OF IDEALITY

The simplest and the most direct way to analyze the behavior of the straight lines in the density–temperature plane is the expansion into a series on density power. Earlier^{8–10} such analysis was performed for the Z line on the basis of virial expansion. Here we construct a similar expansion for the H line. The expansion of the enthalpy per particle h into a series on density powers up to the second order gives us the following expression:

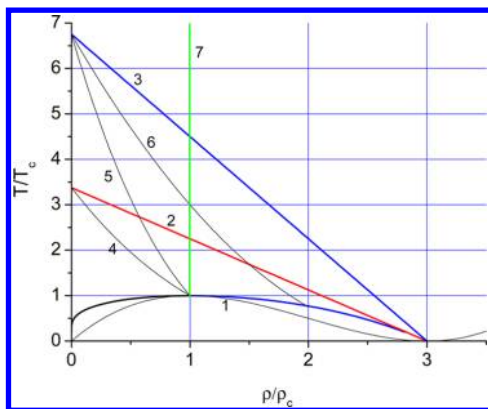


Figure 1. Phase diagram for the VDW system. Lines: 1, binodal; 2, Z line; 3, H line; 4, S_0 line; 5, line of the maxima of the thermal expansion coefficient; 6, H_{\min} line; 7, heat capacity maxima line.

$$h \equiv \frac{H}{N} = \frac{5T}{2} + \rho \left[B(T) - T \frac{dB(T)}{dT} \right] + \rho^2 \left[C(T) - \frac{T}{2} \frac{dC(T)}{dT} \right] + \dots \quad (12)$$

where $B(T)$ and $C(T)$ are the second and the third virial coefficients correspondingly and N is the particle number. The enthalpy (per particle) of an ideal gas is $h = 2.5T$. Consequently, eq 12 for the H line takes the form

$$\left[B(T) - T \frac{dB(T)}{dT} \right] + \rho \left[C(T) - \frac{T}{2} \frac{dC(T)}{dT} \right] = 0 \quad (13)$$

If the ideal enthalpy curve is a straight line, then it can be presented in a form analogous to that of eqs 3 and 6 for the Z line, i.e.

$$\frac{T}{T_H} + \frac{\rho}{\rho_H} = 1 \quad (14)$$

In the particular case of the VDW system eq 13 is transformed into eq 5 (see above). Here T_H and ρ_H are the segments which the H line cuts on the temperature and density axes correspondingly. These parameters are similar to the meaning of the Boyle parameters T_B and ρ_B for the Z line considered in previous studies (see refs 4 and 8–10). (The Boyle temperature T_B is defined by the condition $B(T_B) = 0$, while the Boyle density $\rho_B = T_B B_T'(T_B/C(T_B))$). One can obtain the following expressions defining T_H and ρ_H from eq 12:

$$\left[B(T) - T \frac{dB(T)}{dT} \right]_{T=T_H} = 0$$

$$\rho_H = \left[\frac{-T^2 \frac{d^2B(T)}{dT^2}}{C(T) - \frac{T}{2} \frac{dC(T)}{dT}} \right]_{T=T_H} \quad (15)$$

For example, for the VDW equation, in Boyle units, the second and the third virial coefficients are $B(T) = 8/9 - 3/T$ and $C = 8/27$. In this case expressions in eq 15 give $T_B = 27/8$, $\rho_B = \rho_H = 3$, and $T_H = 2T_B = 27/4$, in accordance with the results of the

previous section. The virial expansion for the pressure derivatives gives

$$\frac{1}{T} \left(\frac{\partial P}{\partial \rho} \right)_T = 1 + 2B(T)\rho + 3C(T)\rho^2 + \dots \Rightarrow \zeta_T$$

$$\equiv T \left(\frac{\partial \rho}{\partial P} \right)_T = \frac{1}{1 + 2B(T)\rho + 3C(T)\rho^2 + \dots} \quad (16)$$

Thus

$$\left. \frac{\partial \zeta_T}{\partial \rho} \right|_{\rho=0} = -2B(T) \quad (17)$$

If $B(T)$ is a monotonic function of the temperature, such as $B(T < T_B) < 0$ and $B(T > T_B) > 0$, then the line of the maxima of ζ_T in the density–temperature plane should start from the point $\rho = 0$, $T = T_B$.

The condition of thermodynamic stability requires that $(\partial P / \partial \rho)_T \geq 0$. For the supercritical region the exact equality is reached only at the critical point, where $\zeta_T = +\infty$. This means that the line of the maxima of ζ_T should end at the critical point.

The density power expansion for the H line shows that the ideal lines are straight in the low-density limit. In our previous research^{8–11} we have shown that in some cases the Z line can keep this property up to the highest densities, where the virial expansion is no longer applicable. More exactly, the studies of various model systems with pairwise potential⁸ have shown that the Zeno line is not straight in the case where the potential is too short-ranged or too long-ranged. However, in other cases the Zeno line is still straight, and moreover, it coincides with the straight line given by the virial expansion. However, for the H line corresponding studies are absent. One of the goals of this study is to find out whether the H line keeps its straightness at high densities. To do this, we consider a model system with a given interaction potential.

■ LENNARD-JONES SYSTEM

Let us now consider the same ideal lines and lines of extrema of different physical quantities for the Lennard-Jones (LJ) system. The density power expansions (eqs 12–17) for this system give rise to the following values of the ideal curve parameters:

$$T_B = 3.418 \quad \rho_B = 1.14 \quad T_H = 6.431$$

$$\rho_H = 1.24 \quad (18)$$

The temperature T_H is slightly less than $2T_B$, but the density ρ_H is a little more than the value of ρ_B . These values are equal in the case of the VDW equation.

The Z and H lines can be calculated by various approaches developed in statistical physics. In particular, previously^{8,19} we have calculated the Z line for the LJ system by means of the integral equation approach and by means of conventional NVT Monte Carlo simulations. Both techniques have given rise to the same results within numerical errors. The Z line for the LJ system, calculated in this way, also coincides with the straight line given by the virial expansion. One can see this in Figure 2, where the Z line, calculated in MC simulations¹⁹ is presented by triangles (symbols 10), while the Z line following from the virial expansion is presented by line 3.

In this study, to calculate the H line, we have also used MC NVT simulations. The detailed descriptions of this technique

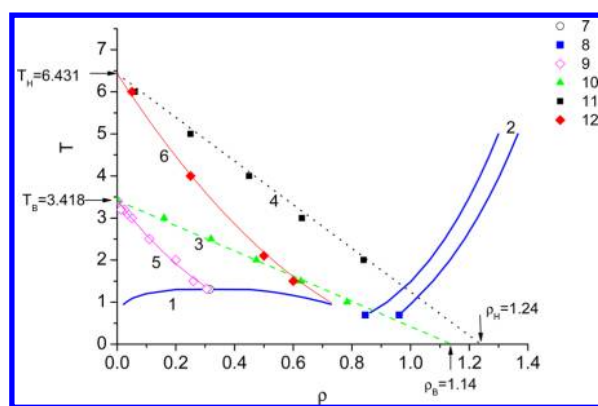


Figure 2. Phase diagram for the LJ system. Lines: 1, binodal;²³ 2, melting lines;²⁴ 3, Z line (virial expansion); 4, H line (virial expansion); 5, S_0 line according to eq 9; 6, H_{\min} line according to eq 7. Symbols: 7, critical point;²³ 8, triple points.²⁴ Symbols for calculations of this work: 9, S_0 line values; 10, Z line (MC calculation); 11, H line (MC calculation); 12, H_{\min} line.

are described in many sources (see, for instance, ref 18). $N = 2000$ particles in a cubic cell with periodic boundary conditions is used. This number of particles is enough to avoid the scaling effects. The cutoff radius was chosen to be equal to the half-length of the simulation cell. For a distance greater than the cutoff radius r_{cut} we use conventional long-range correction,²⁰ i.e., the pair correlation function $g(r > r_{\text{cut}}) = 1$. The equilibration took 500 configurations. Each configuration consisted of random moves (or their absence) of all 2000 particles. The averaging took 1000 configurations. The maximum statistical error in the resulting pressure P and internal energy U was $\sim 2\%$.

To find the H line, we fixed the temperature T and looked for the density where $H = H_{\text{ideal}}$. The results of the calculations are presented in Figure 2 by symbols 11. The H line obtained from the virial expansion is denoted by the number 4. Within numerical error both symbols 11 and straight line 4 coincide. Thus, our calculations show that the H line for the LJ system is also straight just as in the case of the Z line.

The isothermal compressibility ζ_T can be calculated by direct numerical differentiation of the pressure along the isotherm. The equation of state and other properties for the LJ system were calculated in many studies. See, for instance, ref 21 and references therein. Therefore, we have used the data of ref 21, obtained via molecular dynamics simulations, to calculate ζ_T . However, this approach can result in excessive numerical error if the step in density sampling is not small enough. Therefore, it may be better to use the well-known relation^{1,2} $\zeta_T = S(0)$, mentioned above. The structure factor $S(k)$ can be easily calculated within the integral equation (IE) technique.^{1,19,22} Here this approach was applied to control the accuracy of the results obtained by numerical differentiation of MD simulation data from ref 21. The IE algorithm we use is described in ref 22. The results of the calculations of $S(0)$ by means of the IE technique and ζ_T by means of numerical differentiation are in agreement within the numerical errors, just like in the case of the Z line.¹⁹ The S_0 line is presented in Figure 2 by symbols 9. It is started from the Boyle temperature at zero density and goes to the critical point in accordance with the analysis made in the previous section (eqs 16–17). Line 5 in this figure represents the calculations according to eq 5 with the parameters T_B and ρ_B determined by eq 18 for the LJ system.

The latter line is in good agreement with the numerical data (symbols 9).

The H_{\min} line can also be extracted from the data of the MD simulation of ref 21. Corresponding data are presented by symbols 12 in Figure 2. The corresponding dependence following from the VDW equation is given by eq 7. This dependence also is in excellent agreement with the numerical data (symbols 12). Hence, eqs 7 and 9 for the H_{\min} and S_0 lines, found from the VDW equation, are applied for the LJ system too.

■ ARGON

It is a challenge to make a similar analysis for a real substance, for example, argon, thermodynamical functions of which are known. There is a wealth of experimental information on the thermodynamic properties of this substance, which can serve as a test for our theoretical consideration. The thermodynamic functions for this substance are collected in various databases.^{6,17} Using these data, we can reproduce all the constructions of the previous sections and check whether the above-mentioned universality of the VDW lines is valid for argon. The relevant phase diagram of argon is presented in Figure 3, where the units for density are grams per cubic

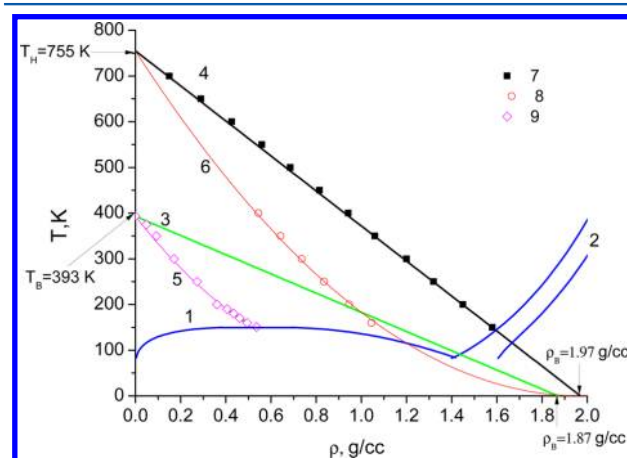


Figure 3. Phase diagram for argon. Lines: 1, binodal;¹⁴ 2, melting line;⁶ 3, Zeno line;^{9,10} 4, H line obtained by fitting our calculated data; 5, S_0 line according to eq 9; 6, H_{\min} line according to eq 7. Symbols represent the values obtained in this work: 7, H line; 8, H_{\min} line; 9, S_0 line.

centimeter and those for temperature are kelvin. The straightness of the Z line for argon has been shown previously^{6,10} with the values of the Boyle parameters $T_B = 393$ K and $\rho_B = 1.87$ g/cm³. The Z line is denoted by the number 3 in Figure 3. The symbols 7, obtained from refs 6 and 17, show that the H line is straight too. The linear fit of this line (line 4) gives the values of $T_H \approx 755$ K and $\rho_H \approx 1.97$ g/cm³. Symbols 8 and 9 correspond to values belonging to the H_{\min} and S_0 lines, respectively. Lines 5 and 6 are the calculations according to eqs 9 and 7, respectively, with the corresponding values of the parameters for the Z and H lines. The points obtained from the databases are in good agreement with the predictions of eqs 7 and 9. Consequently, the regularities under study are valid for argon (i.e., the straightness of the H line and the universality of eqs 7 and 9). As far as other noble gases satisfy the principle of corresponding states, we can state that these regularities are valid for other noble gases too.

■ EXTENDED TRIANGLE OF STATE

The notion of a triangle of state have been proposed previously in our work.^{11,25} According to this conception, it is convenient to combine the Z lines for different substances on the density–temperature plane, introducing the coordinates reduced to the Boyle parameters (as was done above). Then the Z line appears as the universal straight line for all substances, which cuts off the unit segments at the axes. An analogous combined phase diagram is presented in Figure 4 for the VDW and LJ models

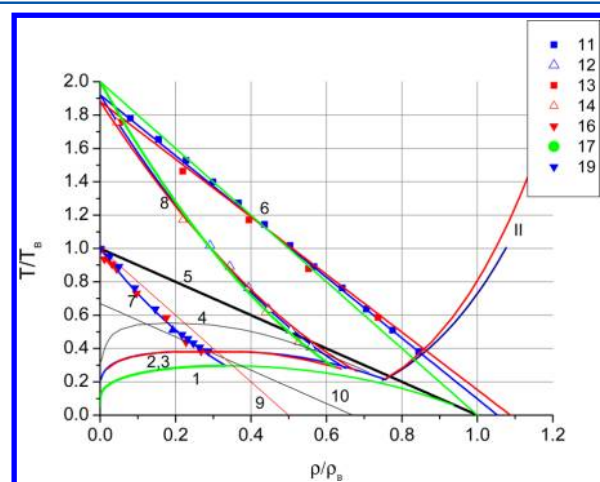


Figure 4. Extended triangle of states. Green, blue, and red colored lines correspond to the VDW and LJ models and argon, respectively. Lines 1, 2, and 3 are the corresponding binodals. Line 4 is the cesium binodal according to the experimental data (see refs 9, 10, and 23). Remaining lines: 5, Z lines; 6, H lines; 7, S_0 lines; 8, H_{\min} lines. The symbols represent our calculated values: 11 and 13 are for the H lines for the LJ system and argon, respectively, 12 and 14 are for the H_{\min} lines, 16 and 19 are for the S_0 lines, and 19 is the critical point for the VDW equation.

and argon. We have also added the metal parameters to this figure, namely, the cesium binodal and CP, as we have done previously¹¹ to complete the picture. All considered binodals are inscribed in the triangle formed by the Z line and the axis. All critical points lie at the S_0 line, including the cesium critical point. In these reduced units the lowest critical temperature and highest density correspond to the VDW equation. Cesium, conversely, has the highest critical temperature and lowest density.²⁶ The LJ model and argon, which have close binodals, are located at the intermediate values. Lines 9 and 10 correspond to the position of the CP line, which has been suggested in our previous studies^{11,25} on the basis of empirical considerations. Lines 9 and 10 are close to each other and to the S_0 line. One can see from Figure 4 that the positions of the H and H_{\min} lines only weakly depend on the type of model or sort of substance, at least those considered in this study.

■ CONCLUSIONS

In this study, we have demonstrated that, in addition to the well-known laws of corresponding states, rectilinear diameter, and Z line regularity, perhaps there are other universal consequences of the VDW equation. Investigations of the LJ system and argon have shown that the ideal enthalpy contour (H line) is straight for these systems too. Besides, for the first time we have applied to the above systems two other VDW relations, i.e., the relations for the isothermal compressibility

maxima (S_0 line) and for the enthalpy minima (H_{\min} line). We have shown that these relations are the same for the considered systems. These findings are preliminary, since the amount of evidence is not great. However, we can already claim that, due to the law of corresponding states, the similarity relations obtained in this work will be valid at least for all substances that satisfy this law.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by RFBR (Russian Foundation for Basic Research) Grants 12-02-90433-Ukr-a and 13-08-12248.

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