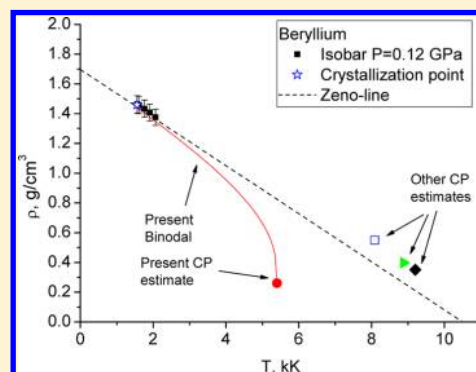


Estimate of Beryllium Critical Point on the Basis of Correspondence between the Critical and the Zeno-Line Parameters

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ABSTRACT: The critical-point coordinates of Beryllium have been calculated by means of recently found similarity relations between the Zeno-line and the critical-point parameters. We have used the NVT MC simulations and pseudopotential theory to calculate the Zeno-line parameters together with the data of isobaric measurements to construct the liquid branch of Beryllium binodal. The critical-point coordinates, determined this way, are lower than earlier estimates. We have shown that these previous estimates are in evident contradiction with available measurements data. Present investigation can resolve this contradiction if the measurements data are supposed to be reliable.



INTRODUCTION

The critical point (CP) of the liquid–vapor coexistence line plays an important role in the investigations of phase diagram of any substances or model systems. Its existence was established more than a century ago.^{1,2} By definition, it is the point where the first and the second derivative of the pressure over the density are zeros at constant temperature. (Below T denotes the temperature, P is the pressure, n is the particle density, $\rho = m_a n$ is the mass density, and m_a is the atomic or molecular mass. The subscript “c” denotes the values at the critical point.) The temperature T_c divides the phase diagram of a liquid into two parts: at the lower temperatures the transition vapor–liquid is observed, but at higher temperatures, there is only one-phase fluid. So CP coordinates are crucial for the determination of the phase equilibrium. Besides, CP is appeared to be very useful for construction of the equations of states (EoS). Initially, in classical van der Waals theory the critical point coordinates were used to establish the correspondence states law (CSL). Namely, van der Waals EoS becomes the same for all substances if it is written in reduced units, i.e., the dependence $P = f(n, T)$ is free of all material constants when it is written in the form: $P/P_c = f(n/n_c, T/T_c)$. Later the validity of CSL and its connection with the statistical physics for arbitrary substance (or model system) have been considered.^{3,4} It was shown that, if a system can be described by the potential (as a rule of pairwise type) with appropriate scaling properties, then CSL is valid. However, not just any substance can be described by such a potential. Consequently, CSL is also not valid for any kind of materials. For instance, the measurements have shown that it holds for noble gases, but it is not valid for arbitrary liquid consisting of diatomic molecules. Nevertheless, CSL had stimulated the search of other general volumetric regularities, known as the similarity laws, which would be valid for a wide class of

substances and could be used in EoS construction. The similarity laws are also very often related to the critical point coordinates and coexistence curve, like, for instance, the law of rectilinear diameter of binodal.^{5–10} Besides, according to the modern theory of the critical phenomena and the measurements,¹¹ the substances in the nearest CP vicinity demonstrate the universal behavior, which is independent of their interaction potentials. Namely, any substance has the infinite susceptibility with respect to an external perturbation in CP, which gives rise to the scaling laws with universal exponents for various physical values in the vicinity of CP. These universal exponents are the same for all materials.

Thus, the CP and its coordinates are indispensable objects for investigation of liquid phase diagrams and EoS construction. To apply the rigorous techniques of statistical physics for the phase equilibrium calculations one needs to know the interaction potential between the particles for a given system (or several potentials, if the system contains more than one component). In the case of many nonmetallic substances the chemical composition of the substance does not change in the region, where the vapor–liquid transition is observed. For instance, the noble gases (He, Ne, Ar, Xe, and Kr) consist of corresponding neutral atoms in gaseous, liquid, and two-phase regions. Therefore it is enough to get only one atom–atom potential for calculation of any interesting properties in the considered area. However, the situation is drastically changed for metals. In the gaseous phase, at relatively low temperatures, a metal consists of neutral atoms too. The corresponding potential for atomic dimers in metals in this case can be constructed on the basis of spectroscopic data.^{12,13} However, in

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the liquid phase, the same metal consists of two-components: ions and electrons. Various modern theories, like pseudopotential method¹⁴ or embedded atom method,¹⁵ allow one to reduce this two-component system to the one-component model with some effective potential (pairwise or many-particle). However, the effective potential in the liquid phase has an absolutely different nature than the dimer potential in the gaseous phase.¹⁶ Besides, we should remark that each of these potentials is valid in its own regions, which do not overlap. Moreover, in the course of liquid–vapor transition a metal get into intermediate area between the dense liquid and rarefied gas, where the two-phase region and the critical point are located. The question concerning the metal composition in this area is still opened. A metal can consist of the neutral atoms, molecules, clusters, various sorts of charged particles etc.¹⁷ So the choice of potentials in this region is, at least, ambiguous. Thus, there is no rigorous and unambiguous interaction potential (or group of potentials), which could describe all phases, which are necessary to calculate the liquid–vapor equilibrium in metals. That is the main obstacle for direct application of conventional methods of statistical physics. Presently only the use of ab initio techniques could overcome this drawback.¹⁸ However, other disadvantages usually appear within ab initio approaches, which have not allowed one to calculate the coexistence properties up to present time.^{18,19}

We should note that up to now CPs and the liquid–vapor coexistence curves have been measured for many substances and have been collected into the databases.²⁰ But the metals, which occupy the dominant part of the periodical table, are not amiable for these measurements. The main reason is that their critical temperatures are located in the high-temperature region, where the static measurements are difficult or even impossible to carry out. Presently, the critical points are measured only for two metals, Cs and Hg, which have relatively low critical temperatures^{21–23} (correspondingly 1924 or 1938 K for Cs and 1751 K for Hg). The estimates²⁴ of T_c for the other metals are located in the region of $T > 2000$ K, which is still inaccessible for appropriate measurements.

Consequently, up to now various approximated methods have been used to estimate the position of the coexistence curve and CP for metals. These approaches include the extrapolations of low-temperature thermophysical data to high temperatures, the above-mentioned similarity laws, the scaling relation etc.^{24–28} Recently, in our studies^{6–10} a new similarity relation has been considered. This similarity connects the critical point and the Zeno-line parameters (see below). Using this relation and the data of isobaric expansion measurements for several metals we have estimated the position of critical points for Al, Cu, W, U, and Zr (see ref 10). In present study we apply our technique to estimate the position of CP and liquid binodal branch for beryllium (Be).

We should note that, although Be is a simple alkaline-earth metal, the investigation of its properties (in particular, the estimates of binodal and CP positions) appears to be more difficult than those for the other metals of its group, like Mg, Ba, Sr, and Ca. There are two possible reasons causing the troubles. The first one is that in the liquid phase the number of thermophysical data for beryllium is less than for other alkaline-earth metals. For instance, the saturation pressures at low temperatures are measured²⁷ for Mg, Ba, Sr, and Ca. However, for Be analogous data are absent. (The estimates of CP position are usually based on these measurements.) The second point is that the shortage of measurement data could be some how

compensated if the corresponding states law would be applicable to Be. Then it would be possible to rescale available data for other alkaline-earth metals. In gaseous phase the potentials for alkaline earth dimers are almost conformal; that is, they coincide with being written in reduced units just like in the case of corresponding states law.¹² However, the potential for the Be₂ dimer in the ground state are not conformal with the others. Possibly, it was the reason that the construction of the Be–Be potential has encountered many problems.¹³ It makes the law of corresponding states inapplicable to Be, at least in the gaseous phase. As a result of the above obstacles, up to now there have been obtained only few CP estimates^{24,26,28} for Be.

The article is organized as follows. In the next section, we briefly describe our similarity relations. Then we discuss the potentials in liquid Be. After that we apply NVT MC technique to obtain the Zeno-line parameters, which are necessary to estimate CP position. Finally, we present our estimate for Be CP coordinates and the comparison with available data of other researchers.

■ ZENO-LINE SIMILARITIES

The concept of Zeno-line originates from the van der Waals EoS. In 1906 Batchinskii²⁹ considered the states (within van der Waals model), where the compressibility factor coincides with that one of an ideal gas, i.e., $Z \equiv P/(nT) = 1$. He found that corresponding points are located on the straight line in the density–temperature plane. During the next 50 years, this fact was considered as some curiosity only. Later the straight line for the unit compressibility factor had been observed in measurements for noble gases, hydrocarbons, water, and many other nonmetallic materials.^{5–10} In fact, this regularity appeared to be valid for a wider class of substances than the corresponding states law or the law of rectilinear diameter.⁵ In particular, we have analyzed the experimental data for mercury and cesium and showed that Zeno-line is a straight line for these metals as well.⁶ The investigation for some systems with model potentials⁹ (Square-Well, Sutherland et al.) have shown that there are at least two cases when Zeno-line is not a straight line. The first one is when a potential is too short-ranged. In this case the liquid–vapor transition becomes metastable with respect to the crystallization. In the second case the situation is the opposite; that is, the potential is too long-ranged. In this case, the triple point approaches too near to the critical one, which gives rise to a sharp bend of Zeno-line. Nevertheless, for many real substances, the curve of the unit compressibility factor is still the straight line. In this case its equation is

$$T/T_B + n/n_B = 1 \quad (1)$$

In eq 1 T_B is the Boyle temperature, which is defined as the temperature where the second virial coefficient is zero: $B_2(T_B) = 0$. The second parameter n_B (known as Boyle density) is the limiting density along the Zeno-line at $T \rightarrow 0$. This value can be also expressed by means of virial coefficients.⁷

One more regularity about Zeno-line has been established previously.^{6,30} Namely, at $T \rightarrow 0$ the extension of liquid binodal branch beyond the triple point tends to the Zeno-line asymptotically. Moreover, this asymptotic behavior of binodal is independent of the fact whether the Zeno-line is the straight line or not. So this property can be used for the description of the liquid binodal branch.^{6–10} To do it we have addressed to

the three-term Guggenheim equation. For the liquid binodal branch it has a form

$$n(T) = n_c + A\tau + B\tau^\beta, \quad \tau = 1 - T/T_B \quad (2)$$

In eq 2 β is the binodal critical index. (For the most of real materials¹¹ $\beta = 0.326$). Equation 2 has been successfully applied to many substances.³¹ The coefficients A and B are usually defined by some fitting to the measurements data. In our previous works^{8–10} we have offered to use the binodal asymptotical properties, mentioned above, to find A and B . Equation 2 should be transformed into eq 1 at $T \rightarrow 0$. Then, it is possible to find

$$A = \frac{\frac{T_c}{T_B}n_B - \beta n_B + \beta n_c}{1 - \beta}, \quad B = \frac{\left(1 - \frac{T_c}{T_B}\right)n_B - n_c}{1 - \beta} \quad (3)$$

Thus, the coefficients and the binodals (liquid branch) at T - n plane are defined by means of 4 parameters: T_B and n_B (the Boyle parameters) and T_c and n_c (the critical parameters). To check the validity of relations 2 and 3, we have calculated^{6–10} the binodals for some gases, liquids, and metals (Cs and Hg), where corresponding data are known from the measurements. We have obtained the agreement between the calculated and the measured binodals within few percents, excluding only for Hg. Besides, we have analyzed some models and supposed that between the Boyle and the critical parameters there are another simple relations

$$\frac{T_c}{T_B} + \frac{n_c}{n_B} = S_1(\beta) \quad (4)$$

$$\frac{n_c T_c - P_c}{n_B T_B} = S_2(\beta) \quad (5)$$

In eq 5 the Boltzmann constant is omitted. The parameters $S_1(\beta)$ and $S_2(\beta)$ are supposed to be weakly dependent on the interaction potential, but they are dependent on the critical index of a particular system. For real substances, which belong to the “Ising”-type systems, we have set $S_1(\beta = 0.326) \approx 0.67$ and $S_2(\beta = 0.326) \approx 0.076$. These values correspond exactly to the Lennard-Jones (LJ) system (which, of course, belongs to the “Ising” class). We will also refer to these values below as S_1^{LJ} and S_2^{LJ} . Many other models and real substances have the values of S_1 and S_2 close to 0.67 and 0.076 correspondingly.¹⁰ Further, we have supposed that the eq 1–4 are also valid for the metals, where the critical points measurements are still absent (like Al, Cu, and others). But if the measurements for low temperature part of binodals are presented, then these relations can be used to estimate the critical points positions. Namely, one can construct the tangent to this low-temperature part of binodal. It gives the Zeno-line and the Boyle-parameters. Here we have calculated the Zeno-line position and found T_B and n_B using MC NVT simulation and pseudopotential technique (see next section). Then for known Boyle parameters eqs 2, 3, 4 allow one to calculate the liquid binodal branch, which would depend only on the single parameter. In the present study, it was n_c ; that is, we can rewrite eq 2 as $n^{\text{binodal}} = n(T, n_c)$. The parameter n_c can be found by fitting the calculated binodal to the measurements data (in low-temperature part), using the corresponding minimization procedure similar to the well-known least-squares technique. The full description of this minimization technique is presented in refs 7 and 10. Below, in

the third section, we will give necessary detail in context of present study.

We should also note that the available measurements in liquid phase for many metals (including Be) do not belong to the binodals. They are measured at the isobar curves. But the isobars in liquid state are located very close to the binodals and practically coincide with it, because of the low compressibility of the liquids (see the considerations in ref 32). Therefore, we can use these data to estimate the critical points coordinates on the basis of our approach. Here we will apply it for Be. Besides, we have used the pseudopotential theory to calculate the Zeno-line position in the low temperature liquid region. In the next section, we will describe this calculation in more details. We will show that the available isobar and the Zeno-line are really located close to each other as we have just mentioned.

■ ZENO-LINE AND THE BOYLE PARAMETERS FOR BE

To describe the properties of liquid metals one can use various approaches as we have mentioned in the Introduction. Here we used the pseudopotential technique, which had been created and theoretically grounded approximately half a century ago (see the book by Harrison, ref 14). Initially this technique was developed for the crystalline phase of simple metals. However, nothing prevents us from applying this approach to the liquid state of the same metals.¹⁴ So during the following decades the transferability of some pseudopotentials to the liquid state was demonstrated.^{33–35} The description of the considered approach is presented everywhere.^{14,36} Here we give only necessary details. Initially a metal is considered as a two-component media. The positive ions (subscript “i”) with fixed charge Z_i ($Z_i = 2$ for all alkaline-earth metals, including Be) are immersed into the bath of nearly-free conduction electrons (subscript “e”). Thus, the system is electrically neutral. In addition, the corresponding Schrödinger equation is considered. To solve it, the exact potential for the electron–ion interaction is changed by a weak pseudopotential, so that one can apply the perturbation theory.^{14,33,34,36} As a result, one can construct the effective ion–ion pair potential within the second order of the perturbation theory. Then it is possible to calculate various thermodynamic properties of a metal using this effective pair potential. The latter object is composed of direct Coulomb repulsion and of the term arising due to the response to the e–i interaction, described by the pseudopotential $w_{ei}(r)$. In the Fourier-space the effective ion–ion pair potential is expressed as (in atomic units $\hbar = m_e = e = 1$)

$$\tilde{U}_{ii}(q) = \frac{4\pi Z_i^2}{q^2} + \chi(q) |\tilde{w}_{ei}(q)|^2 \quad (6)$$

Here the first term is the Fourier transform of Z_i^2/r , $\tilde{w}_{ei}(q)$ is the Fourier transform of $w_{ei}(r)$, and $\chi(q)$ is the dielectric response function.^{14,36} The inverse Fourier-transform of eq 6 gives the effective pair potential $U_{ii}(r)$ in real space. The function $\chi(q)$ can be obtained within the linear response theory³⁶

$$\chi(q) = \frac{\chi_0(q)}{1 - \nu(q)(1 - G(q))\chi_0(q)}, \quad \nu(q) = 4\pi/q^2 \quad (7)$$

In eq 7 $\chi_0(q)$ is the well-known Lindhard dielectric response function,^{14,36} which describes the response of noninteracting degenerated electron gas. $G(q)$ is the local field correction, which takes into account e–e electrostatic interaction and

exchange–correlation effects. For the present calculations, we have used $G(q)$ obtained by Ichimaru and Utsumi,³⁷ which is considered now as one of the most reliable. Besides, we have used the local pseudopotential $w_{ei}(r)$ proposed by Fiolhais et al. (ref 38). Previously this pseudopotential has been used for calculations of thermodynamic, structural, and transport properties in liquid alkali^{33,35} and alkaline-earth metals.³⁴ It has the form (in a.u.)

$$w_{ei}(r) = -\frac{Z_i}{r_0} \left(\frac{1}{x} [1 - (1 + \beta x)e^{-\alpha x}] - Ae^{-x} \right), \quad x = \frac{r}{r_0}$$

$$\beta = \frac{\alpha^3 - 2\alpha}{4(\alpha^2 - 1)}, \quad A = \alpha^2/2 - \alpha\beta \quad (8)$$

The potential in eq 8 depends on two parameters: r_0 and α . In ref 38 there were offered two routes to define these values, “universal” and “individual”. Here we have used for Beryllium the “universal” version; that is, $r_0 = 0.197a_B$ and $\alpha = 4.547$ (a_B is the Bohr radius).

Thus, applying eqs 6–8, one can construct the effective potential. The internal energy per particle within the second order of the perturbation theory is expressed as^{14,33,34,36}

$$\frac{E}{N_i} = \frac{3}{2}k_B T + 2\pi n_i \int_0^\infty U_{ii}(r) g_{ii}(r) r^2 dr + V(n_i) \quad (9)$$

In eq 9, $g_{ii}(r)$ is the pair correlation function ion–ion. If the potential $U_{ii}(r)$ would be the true potential, then the first two terms in the right side of 9 would express^{1,2} the exact internal energy of a statistical system for given T and n_i . However, it is only effective potential, so there appears the structure-independent term $V(n_i)$, which is peculiar in metals.³⁶ Besides, the response function $\chi(q)$ in 7 depends on the free electron concentration n_e . Due to the electroneutrality condition $n_e = Z_i n_i$. So the effective ion potential depends on the density as well; that is, $U_{ii}(r) = U_{ii}(r, n_i)$. Consequently, the expression for pressure should contain additional density dependent terms^{33,34}

$$P = \frac{3}{2}n_i k_B T - \frac{2}{3}\pi n_i^2 \int_0^\infty g_{ii}(r) \frac{dU_{ii}(r, n_i)}{dr} r^3 dr$$

$$+ n_i^2 \frac{dV(n_i)}{dn_i} + 2\pi n_i^2 \int_0^\infty g_{ii}(r) \frac{dU_{ii}(r, n_i)}{dn_i} r^3 dr \quad (10)$$

Equation 10, being the consequence of the pseudopotential theory, is valid only for the liquid state at relatively high densities. The same is also true for the density dependent potential U_{ii} . The sum of the first and the second terms, just like in case of eq 9, gives the expression for the pressure of a one-component system, if the potential is density-independent. If eq 10 would be correct at low densities, then one can expand eq 10 into density series to find the Boyle parameters. However, as far as eq 10 is not correct at low densities, we have used another way to find them (see below). The term $V(n_i)$ is given in accordance with results of Hasegawa and Watabe³⁹ (in atomic units)

$$V(n_i) = V_0 - \lim_{q \rightarrow 0} \left[2\pi Z_i^2 n_i \left(\frac{\pi}{4k_F} - \frac{G(q)}{q^2} \right) \right]$$

$$- \frac{Z_i^2}{\pi} \int_0^\infty \chi(q) |\tilde{w}_{ei}(q)|^2 dq$$

$$k_F = (3\pi^2 n_e)^{1/3} = (3\pi^2 Z_i n_i)^{1/3} \quad (11)$$

In this equation V_0 is the ground state energy of electron gas, k_F is Fermi wave-vector.³⁶ The expression for V_0 is presented in ref 40 (in atomic units)

$$V_0 = \frac{Z_i}{2} \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.031 \ln(r_s) - 0.115 \right) \quad (12)$$

Here r_s is the dimensionless Bruckner parameter, which is used to characterize the density dependence in the degenerated system.^{14,36} In particular, the density dependence of ion–ion effective potential 6 is usually expressed as $U_{ii}(r, r_s)$. By definition, r_s is the ratio of average distance between the electrons to the Bohr radius; that is, $a_B^3 r_s^3 = 3/(4\pi n_e)$.

Thus, one can calculate the pressure in liquid metals using eqs 6–12. We should note, that the ion charge within the present approach is supposed to be constant ($Z_i = 2$). It is also independent of the temperature and the density. As we have mentioned in the Introduction, when the temperature is increased (or density decreased) the composition of a metal should change. In present form the pseudopotential approach does not take into account this effect. So, we have limited our calculation by $T = 2300$ K, when the ion charge is still constant.

In Figure 1 we have presented the effective ion–ion potential 6 for several values of r_s , corresponding to the liquid metal

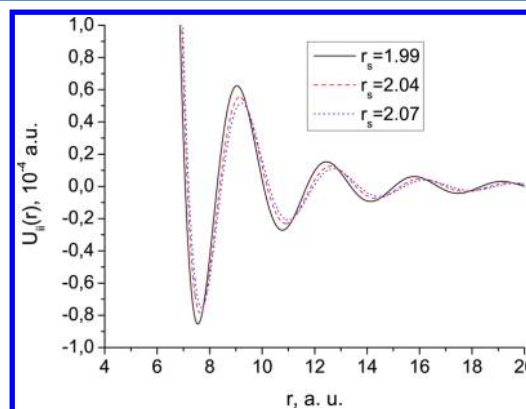


Figure 1. Effective ion–ion potential (6) for different r_s values.

densities. Although the values of Bruckner parameters are close to each other, the density dependence of the potential is evident. The oscillations in the tail of the potential (so-called Friedel oscillation) are due to the electron screening. This wave-like behavior is many-particle effect, which is characteristic for simple metals in liquid and solid phases. In gaseous state the interaction has quite different nature, which gives rise to Morse-like form of potential for beryllium dimer (without tail oscillations).^{13,16}

The Zeno-line has been determined according to eq 10. Namely, we have fixed the temperatures in the range between 1560 and 2300 K ($T = 1560$ K is the melting or crystallization temperature of Be at normal conditions²⁰). Then the density has been varied to obtain the compressibility factor $Z \equiv P/(nT)$

= 1. As we have said above, the first two terms in eq 10 correspond to usual statistical system. Therefore, to calculate them, we have used the conventional Metropolis Monte Carlo technique within the canonical ensemble² (NVT MC). Earlier this technique was used for the calculations of Zeno-lines points and the structure factors in some systems with model potentials.^{9,41} The pair correlation functions $g_{ii}(r)$, necessary to obtain two other terms in (10), have been also calculated by means of NVT MC. We have used the same parameters for present simulations as in our previous work.⁹ We have placed $N = 2000$ particles in the simulation cell with periodic boundary conditions. The cutoff radius r_{cut} was equal to the half-length of the simulation cell. For the distances greater than r_{cut} we have used conventional long-ranged correction^{2,9} by set $g_{ii}(r) = 1$, $r > r_{\text{cut}}$. To reach the equilibrium state we have used 500 configuration. Each configuration consists of random moves of all 2000 particles. Next 1000 configurations have been used for calculations of average values. The maximum statistical error in resulting pressure was less 2% as in our previous calculations.⁹ NVT MC calculations give us the first two term of eq 10. The third term and the potential derivative over density in the fourth term were obtained by numerical differentiation. Then to complete the pressure calculations we have numerically calculated the integral with potential derivative in eq 10.

In Figure 2 the continuous line is the Zeno-line, calculated within the pseudopotential approach. There are very few

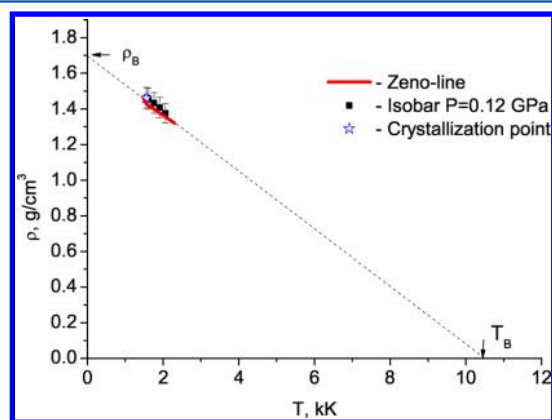


Figure 2. Zeno-line of Be calculated according to eqs 6–12 (continuous line) and the experimental isobar⁴² (filled squares with error bars). The asterisk marks the crystallization point. The dashed line is the extension of Zeno-line up to the crossing with axes.

experimental results published for liquid Be. In particular there are measurement data for isobar $P = 0.12$ GPa (ref 42) in crystalline and liquid phases. We should also mentioned that the measurement data concerning the liquid Be expansion, i.e., the dependence $\rho(T)$, are presented in ref 43. However, the pressure values are not shown in this work. So the isobaric data of ref 42 seemed to be more reliable. These data in liquid phase are presented as filled squares with error bars in Figure 2. The error of volume measurement was estimated in ref 42 as 4%, which is greater than the accuracy of present MC simulations. Thus, one can see that the experimental isobaric curve and the Zeno-line practically coincide (as we have mentioned in the previous section). We have also marked by asterisk the crystallization point. According to measurements data⁴² it is located at $T = 1564$ K and $\rho = 1.463$ g/cm³. Besides, one can see that the Zeno-line is a really straight line (at least in the area

where the pseudopotential technique is applicable). Now we can extend the Zeno-line up to the crossing with axes and find the Boyle parameters. To do it we have used the least-squares technique for the points obtained by the MC NVT simulations. The result is presented in Figure 2 by dashed line. The maximum relative deviation between this dashed line and the continuous line is 0.3%, which is much smaller than the error of MC simulations (2%, see above). Finally, the values of Boyle parameters are $T_B = 10.5$ kK and $\rho_B = 1.697$ g/cm³. Now we can go to the critical point coordinates.

■ CRITICAL-POINT COORDINATES

Using the Boyle parameters we can calculate the critical-point coordinates. Let us denote the experimental points for the low-temperature part of binodal as $n_{\text{exp}}(T_i)$, where the subscript “i” numerates these points. The calculated binodal is denoted as $n^{\text{binodal}} = n(T, n_c)$ (see above). Then one should find the minimum value of parameter $\delta = \sum_i |1 - n(T_i, n_c)/n_{\text{exp}}(T_i)|$ varying n_c . The available experimental data contains only 5 points. Nevertheless, the parameter δ in the present case has an evident minimum ($\delta = 0.01$) at the density $\rho = 0.26$ g/cm³. For instance, at $\rho = 0.27$ g/cm³ the parameter value is several times higher ($\delta = 0.05$). As a result, this minimization procedure together with $S_1 = S_1^{\text{LJ}} = 0.67$ gives the critical temperature and density: $T_c = 5400$ K and $\rho_c = 0.26$ g/cm³. The critical pressure according to eq 5 with $S_2 = S_2^{\text{LJ}} = 0.076$ is $P_c = 4.6 \times 10^7$ Pa = 460 bar.

At first, let us compare our CP with the estimates of other researchers (see Table 1). It is easy to see that our critical point

Table 1. Critical-Point Coordinates According to Different Estimates

T_c , K	ρ_c , g/cm ³	P_c , bar	ref
8080	0.55	11 700	24
9200	0.35	12 200	26
8877	0.398	2870	28
5400	0.26	460	present work, $S_2^{\text{LJ}} = 0.076$

has lower coordinates than other data. Especially it is evident for the critical pressure, obtained at $S_2^{\text{LJ}} = 0.076$. Possible reason of so low P_c is that the value S_2^{LJ} is not always correct. Recently, we have analyzed eqs 4 and 5 for various substances and model systems.⁴⁴ We have found that the critical temperatures and the critical densities satisfy well eq 4 with $S_1 = S_1^{\text{LJ}} = 0.67$. But the agreement with eq 5 for the critical pressure was not so good (at $S_2 = S_2^{\text{LJ}} = 0.076$). So we have supposed that the value of S_2 in eq 5 should be corrected.⁴⁴ Thus, eq 5 is, possibly, not as universal as eq 4. Namely, we have mentioned above, that the parameters S_1 and S_2 are dependent on the critical index β (see also our analysis in ref 9). The index β is the same⁹ for “Ising” group of criticality for 3D systems ($\beta = 0.326$), which contains usual substances and some model systems. So within this group S_1 and S_2 should be also the same. It is true for S_1 . We have checked it^{9,10,44} for various gases, metals and model systems. But the parameter S_2 is seemed to be dependent not only on the index β . In particular, for noble gases, some molecular and organic liquids^{10,44} $S_2 \approx 0.076 = S_2^{\text{LJ}}$ like it was initially supposed on the basis of data for the Lennard-Jones system. However, for water and for mercury and rubidium¹⁰ $S_2^{\text{Water}} = 0.11$, $S_2^{\text{Hg}} = 0.065$, and $S_2^{\text{Rb}} = 0.069$ correspondingly. It means that S_2 can be different for the groups of substance, with the same β , but which are different in other properties. So we can admit that S_2

$= S_2(\beta, a)$, where a denotes such a group. Evidently, the noble gases belong to some group; organic liquids, to another (although with the same value for S_2); metals, to the third. The latter can have $S_2 \neq S_2^{\text{IJ}}$. This can be true for Be. For instance, if we suppose that for Be $S_2^{\text{Be}} \approx S_2^{\text{Hg}} = 0.065$ like for mercury, then it is easy to obtain from eq 5 a new value $P_c = 2.24 \times 10^8 \text{ Pa} = 2240 \text{ bar}$. Analogous estimate with $S_2^{\text{Be}} \approx S_2^{\text{Rb}} = 0.069$ gives $P_c = 1616 \text{ bar}$. Both new estimates are much closer to the results of other researchers than the value with $S_2^{\text{IJ}} = 0.076$ (see Table 1). We should note that the values S_2^{Hg} and S_2^{Rb} used here only as examples and that real value of S_2 for Be can be different from all previous data. However, we should emphasize that the inaccuracy of eq 5, as well as indefiniteness of parameter S_2 for Be, does not change the fact, that available P_c estimates for Be, even without our P_c , are still 4–5 times different in magnitude. So this question still needs in further investigation.

Now let us consider the estimates of two other coordinates of CP. The dispersion in the estimates of the critical densities and temperatures in Table 1 is smaller than for the pressures. Moreover, the maximum variation in T_c given by refs 24, 26, and 28, is only 13%. Our T_c is 33% lower than the smallest of them. But now this difference can not be explained by inexactness of eq 4 only. In Figure 3 we have presented the

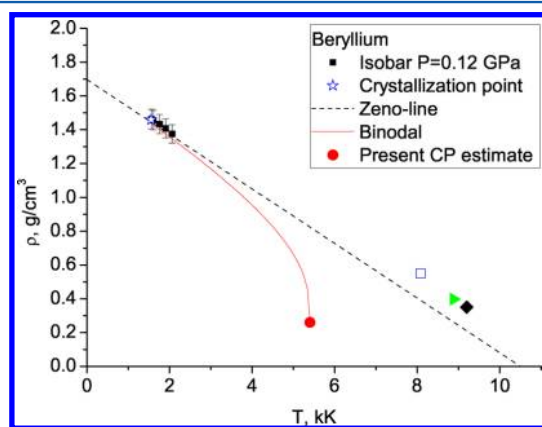


Figure 3. Be binodal (liquid branch) calculated according to eq 2 (continuous line). The asterisk marks the crystallization point; the dashed line is the Zeno-line; the filled squares with error bars are the experimental isobar⁴² (like in Figure 2). The separate symbols present various estimates of the critical point positions: our estimate, filled circle; ref 24, empty square; ref 26, filled diamond; ref 28, filled triangle.

liquid branch of binodal on T – ρ plane, calculated here by means of eqs 2, 3 with our T_c and ρ_c . The other estimates are presented too by separate symbols. The experimental points⁴² of isobar $P = 0.12 \text{ GPa} = 1200 \text{ bar}$ are also shown in Figure 3. The dashed line in Figure 3 is the Zeno-line, obtained above. The isobaric points at $P = 0.12 \text{ GPa}$ would belong to the subcritical region if the critical temperatures correspond to any of them above T_c , excluding ours. We know that at low temperatures the liquid branch of binodal should go along the subcritical isobars because of the low compressibility of liquids, as we mentioned above (see also corresponding data in refs 21–23 and the discussion in ref 32). However, as one can see from Figure 3, to reconcile this low-temperature behavior of binodal and the value $T_c > 8000 \text{ K}$, one needs to suppose the liquid binodal branch is nonconvex. It is hardly possible. The estimates^{24,26,28} of CP position are based on other data than the measurements of ref 42. (For instance, the heat of evaporation

data were used in ref 24, the van der Waals-type EoS together with the percolation theory was applied in ref 26, and the wide-ranged semiempirical EoS was constructed in ref 28) So, there is evident contradiction between various CP estimates, obtained on the basis of different approaches or measurements. We should also note that this situation is not unique. In particular, in analogous contradiction was found⁴⁵ for T_c estimates of uranium oxide and the possibility of nonconvex binodal was considered. However, Be is a simple metal, and its coexistence curve should be similar to other simple metals, like Cs, i.e., convex. Consequently, either the high T_c values are incorrect or the measurements of ref 42 are inaccurate. In the present investigation we have used the pseudopotential technique to construct the Zeno-line in the region where this technique is applicable. The coincidence of Zeno-line with the isobaric data of ref 42 indirectly witnesses about the correctness of the measurements. Now there are more exact techniques for the pressure calculations (see the Introduction). However, these techniques could hardly change the Zeno-line position, obtained here. The notable change could happen if the Fiolhais potential³⁸ is not accurate enough in considered region. Only the comparison with another measurements data could give the final answer to the question about accuracy of the potential. The same relates to the accuracy of data of ref 42. Unfortunately, for Be we have not found another coexistence curve or isobar measurement data that can confirm or disprove the results of ref 42. Thus, additional experiments and, possibly, calculations with another potential are still needed. However, it does not change the fact that the previous estimates of the CP temperature and density should be shifted down, closer to present results, if the isobaric curve obtained in ref 42 is supposed to be reliable.

CONCLUSION

The critical point parameters for Be were estimated on the basis of recently found similarity relations between the Zeno-line and critical parameters. To find the Zeno-line (Boyle) parameters we have used NVT MC simulations and the pseudopotential technique for simple metals. The Boyle parameters together with the low-temperature isobaric data allow us to construct the liquid binodal branch. Thus obtained values for T_c , ρ_c and P_c are evidently less than other available estimates. Although for the critical pressure this difference can be explained by possible inexactness of our similarity relations, it is not the case for the critical temperature and density. Moreover, there is clear contradiction between presently available experimental isobaric data and the CP position estimates obtained until recently. Present results eliminate this contradiction if the measurements data are reliable. However, to confirm the latter fact, additional experiments are necessary.

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Notes

The authors declare no competing financial interest.

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