Is the thermodynamic behavior of the noble fluids consistent with the Principle of Corresponding States?

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Abstract

The applicability of the Principle of Corresponding States (PCS) for the noble fluids is discussed. We give the thermodynamic evidences for the dimerization of the liquid phase in heavy noble gases like argon, krypton etc. which manifest itself in deviation from the PCS. The behavior of the rectilinear diameter of the entropy and the density is analyzed. It is shown that these characteristics are very sensitive to the dimerization process which takes place in the liquid phase of heavy noble gases.

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I. INTRODUCTION

The principle of thermodynamic similarity is one of the fundamental guiding principle in investigation the thermodynamic properties of matter. It allows to determine the classes of the substances with similar thermodynamic behavior based on the similarity of the inter-particle interactions, which in its turn is based on the similarity of the particles (electronic shells, molecular excitation spectra etc.) and as a sequence the similarity of the interparticle interactions. The existence of the universality classes of critical behavior can be considered as the extension of the thermodynamic similarity principle to the long range fluctuations since the short range effects does not change the asymptotic behavior of the thermodynamic quantities. In particular, for the systems obeying the the thermodynamic similarity principle the dimensionless critical amplitudes should coincide. The demand of the thermodynamic similarity and as the consequence the principle of corresponding states (PCS) is very strong condition which in fact assumes the similarity of the energy spectrum of the systems since the thermodynamics depends on both the external and the internal molecular degrees of freedom.

It is well known that the thermodynamics is determined by the integral characteristics of the interaction potential. The classical PCS states the trivial fact that the systems with if the interaction potential is of two-particle character and has the form:

$$U = U_0 f(r/r_0),$$

where $U_0$ is the depth of the potential well and $r_0$ is the characteristic molecular size correspondingly. Then the corresponding equation of state (EOS) has the universal dimensionless form

$$p^* = p(v^*, T^*),$$

where $p^* = P r_0^3/U_0$ is the dimensionless pressure $P$, $T^* = T/U_0$ and $v^* = v/r_0^3$ are the dimensionless temperature $T$ and the specific volume $v$ correspondingly. The famous van der Waals (vdW) equation of state is the illustration of the PCS. Throughout the paper we use the units where $k_B = 1$. In particular the locus of the critical point (CP) depends on the potential depth $U_0$ and the molecular radius (hard core radius) and it is expected that the locus of the triple points are the same too.

Sure that such a simple form of the interparticle interaction is nothing than oversim-
TABLE I: Basic geometric and energetic parameters of the dimers and the molecules. Notations: $r^{vdW}$ is the van der Waals radius of the molecule, $l_{bond}$ bond length of the dimer, $\varepsilon_{diss}/T_c$ is the dissociation energy of the dimer in units of $T_c$, $Z_c$ is the compressibility factor.

|        | $He$ | $H_2$ | $Ne$ | $Ar$ | $Kr$ | $Xe$ |
|--------|------|-------|------|------|------|------|
| $r^{vdW}$, Å | 1.40 | 1.54  | 1.54 | 1.88 | 2.02 | 2.16 |
| $l_{bond}$, Å  | -    | 4.2   | 3.10 | 3.76 | 4.01 | 4.36 |
| $\varepsilon_{diss}/T_c$, [5, 11] | 0.0  | 0.11  | 0.95 | 0.96 | 0.96 | 0.97 |
| $Z_c = \frac{P_{sic}}{T_c}$ | 0.30 | 0.30  | 0.30 | 0.29 | 0.29 | 0.29 |
| $N_{vib}$, [3] | -    | 2     | 3    | 8    | 13   | 21   |

plification since the classical potential $U(r)$ is the effective interaction. It is obtained via integrating out the electronic degrees of freedom and in fact becomes dependent on the atomic number $A$ and the de Boer parameter $\Lambda = \frac{h}{r_0\sqrt{mU_0}}$ (note that $m = Am_p$, where $m_p$ is the proton mass). For the noble fluids the latter varies in wide range from $\Lambda_{He} = 2.7$ to $\Lambda_{Xe} = 0.06$ [1, 2, 3].

Nevertheless the quantum effects manifest themselves in dual way: a) the corrections to the asymptotic of classical interaction [4]; b) the formation of bound states (e.g. dimers, trimers etc.). In the first case the potential conserves its structure in essential. The bound states lead to the additional contributions to the basic thermodynamic quantities (the specific volume, heat capacity etc.). The system becomes the mixture of monomers, dimers etc. The formation of dimers in noble gases is known [3]. They manifest itself in various effects based on the anisotropy structure of the dimers, e.g. in Raman spectra [6, 7, 8], depolarization of the light scattering [9, 10] etc. But their existence in liquid phase near the CP has not been discussed. Note that the dimers have finite lifetimes but in equilibrium there is certain amount of them.

As it follows from the Table the number of the vibrational levels $N_{vib}(U_0)$ is different for heavy noble gases. The dimerization breaks the PCS. The manifestation of this effect is expected in gaseous phase of low density (see below). But the degree of dimerization is low for dense liquid states. Only in the vicinity of the critical point the contribution from the dimers could be great enough to break the applicability of the PCS.
Therefore the equation of state (EOS) takes the form:

\[ p^* = p(T^*, v_1^*, v_2^*, \ldots) + p_q(T^*, \Lambda, v_1^*, v_2^*, \ldots), \]  

(2)

where subscript “q” stands for quantum correction and \( v_i^* \) are the dimensionless specific volumes of monomers, dimers, etc.

Because of the complete electronic shells and as a sequence the spherical symmetry of the ground state the noble fluids are ideal substances for the test of the PCS.

The aim of this paper is the analysis of the applicability of the PCS for the noble fluids and the interpretation of the data from the point view of dimerization processes in these substances. More exactly we analyze 1) the applicability of the PCS for the description of the noble gases on their coexistence curves; 2) the manifestation of the dimerization effects on the temperature behavior of their the rectilinear diameters; 3) the influence of the dimerization on the peculiarities of the critical fluctuations.

In accordance with this Section II is devoted to the careful analysis of the experimental data (all the data are from NIST open database). In Section III the purposeful choice of the reference system is discussed. In Section V we consider simple model to account the dimerization process for noble fluids. The mean field behavior of the rectilinear diameters are considered in Section IV and the critical anomaly is discussed in Section VI.

II. EXPERIMENTAL FACTS

In this Section we discuss: 1) the comparable behavior of the coexistence curves (CC) for noble fluids; 2) the behavior of the number density along the CC. Further we will use the variables reduced to the CP values:

\[ \tilde{p} = P/P_c, \quad \tilde{T} = T/T_c, \quad \tilde{n} = n/n_c. \]

First we consider the role of the quantum effects in the EOS. On Fig. 1 we give the CC in “\( \tilde{p} - \tilde{T}^* \)” coordinates for classical the noble fluids (Ne, Ar, Kr, Xe) and the quantum ones (He and H_2). We see that in “\( \tilde{p} - \tilde{T}^* \)” coordinates the classical noble fluids obey the PCS. The deviation from the classical behavior is connected with the quantum effects in accordance with Eq. (2). They are greater for He than for molecular hydrogen. Note that “\( \tilde{p} - \tilde{T}^* \)” diagram is the robust thermodynamic characteristics which does not allow to distinguish
FIG. 1: The CC in $\tilde{p} - \tilde{T}$ coordinates.

fine details of the thermodynamic behavior. The variables $\tilde{n}, \tilde{T}$ are more suitable in this sense.

Let us consider the dimensionless ratio $R(2, 1) = \tilde{n}_2/\tilde{n}_1$ of the dimensionless densities of noble fluid "2" to the density of noble fluid "1", which in some reason is chosen as the reference fluid. The results of comparison for the liquid and gaseous branches of Kr and Xe with respect to Ar are presented in Fig. 2. As is seen from it the deviation from unity for liquid branch within the range of the experimental errors (<1%). For the gaseous phase the difference between the $\text{Kr}$ and $\text{Xe}$ curves reaches 3%.

The deviation from unity can be considered as the measure of the violation of the PCS. In accordance with said above the deviation is noticeable in the gaseous phase where the dimerization is more explicit. The physical ground for the existence of the dimers in near critical region is the almost free rotation of the dimers allowed at low enough density. As is known this leads to the existence of the metastable states for the dimers with a wide range of life time because of the centrifugal barrier [3, 12]. In liquid phase the deviation becomes essential in the near critical region. In order to clarify the physical nature of such deviation we take into account that along the CC the density is the sum of classical and quantum contributions. According to Eq. (2) for the density we have:

$$\tilde{n} = \tilde{n}_{cl}(\tilde{T}) + \tilde{n}_q(\tilde{T}; \Lambda) \quad (3)$$

Note that the quantum correction $n_q(\tilde{T}; \Lambda)$ is monotonous decreasing function on $T$. As is follows from the results presented in Fig. 3 for classical noble fluids the quantum corrections are negligibly small. Therefore the deviation $R$ from 1 in liquid and gaseous phase is naturally to connect with the dimerization. In order to estimate the dimerization degree it is useful
to search for the reference fluid in which the dimerization is depressed.

In the following section we show that molecular hydrogen or Ne can be chosen that such fluid.

III. REFERENCE SYSTEM

Let us give the arguments that 1) the molecular hydrogen \( H_2 \) is the simplest semiquantum fluid and 2) Ne is the simplest classical fluid. This means that in liquid and gaseous phases of these fluids in near critical region the amount of the dimers is very small and does not affect the thermodynamic behavior. It becomes clear from the value of the dissociation energy \( \varepsilon_{\text{diss}} \) reduced to the critical temperature \( T_c \). In molecular hydrogen the dissociation energy for its dimer is an order of magnitude smaller than the critical temperature \( \varepsilon_{\text{diss}}/T_c \approx 0.11 \). In He no dimers exists except for the giant states [13] which is out of the scope of the paper. For Ne the dimerization is weak in comparison to other classical noble fluids. Ne is the closest to \( H_2 \) among the classical noble fluids. The comparison assumes that the classical constituent of the density for Ne and \( H_2 \) is different from that of heavy noble gases. Note that their critical temperatures is pretty close \( T_c \approx 44.5 \) K and \( T_c \approx 33. K \) correspondingly and high enough so that the difference of these light noble gases from the heavy ones can not be attributed to quantum corrections which negligible in near critical region.

In accordance to Table [14] the formation of the dimers takes place mainly in classical noble fluids. Though the formation of dimers for Ne is possible the number of vibrational levels is not big and the dimerization can be neglected in comparison with other classical noble gases.
FIG. 3: Residual specific heat (in units of $k_B$, $C_{V}^{id} = 3/2$ is the specific heat of the monoatomic ideal gas) of the noble gases along liquid (black) and vapor (gray) branches of the binodal. The inset shows the increment of the specific heat caused by the dimerization in near critical liquid phase (bold segment of the curve).

In order to estimate the fraction of dimers in liquid phase we use the specific (per atom) heat data (see Fig. 3). Here we see the monotonic change of the residual (after subtraction of the specific heat of the monoatomic ideal gas contribution) specific heat in gaseous phase due to increase of interparticle interaction with the density up to the temperature $T/T_c \approx 0.95$, which has the meaning of the Ginzburg temperature [14]. Note that in this phase for $T/T_c \lesssim 0.95$ the specific heat of Ar is noticeably less than that for Kr and Xe due to more strong interparticle interaction. The opposite behavior of the specific heat takes place in liquid phase. Since the density of the liquid phase decreases along the binodal the corresponding decrease of the residual specific heat is observed in the temperature region $T/T_c \lesssim 0.95$. For $T/T_c > 0.95$ the specific heat of both phases diverges due to critical fluctuations.

From the physical point the decrease of the specific heat of the liquid phase outside of the fluctuational region is connected with the decrease of the average interparticle interaction as the density decreases. The existence of the minimum at $T_{min} \approx 0.87$ and the subsequent increase of $C_V$ until $T_{diss} \approx 0.95$ (see Fig. 3) can be attributed to the formation of the dimers. Representing the specific heat as

$$C_V = \frac{3}{2} N_1 + \frac{7}{2} N_2$$

where $N_1$ is the number of atoms and $N_2$ is the number of the dimers, we get the estimation for the degree of dimerization (the ratio of the number of dimers to the total number of
 atoms):
\[ \frac{N_2}{N_0} = \frac{2}{7} \frac{\Delta C_V}{N_0} \approx 0.05. \]
where \( N_0 = N_1 + 2N_2 \) is the total number of atoms, \( \Delta C_V = C_V(T_{\text{diss}}) - C_V(T_{\text{min}}) \) is the increment of the specific heat due to the formation of the dimers. Here it is assumed that the dimer has 6 degrees of freedom (3 translational, 2 rotational and one vibrational).

Of course the dimerization in liquid phase should manifest itself in the behavior of the entropy too (see Fig. 4). Here we see that up to the temperature \( T \approx 0.87 \) the monotonous behavior of \( S_{Ne} - S_{Xe} \) takes place. It signifies about the absence of the clusterization ordering in \( Xe \). Noticeable diminishing the monotonic decrease in the temperature interval \( 0.87 < T/T_c \leq 0.95 \) is naturally explained by the dimerization of \( Xe \) leading to decrease of its entropy in comparison with that of \( Ne \).

This energetic condition should complemented with the geometric condition of free rotation of the dimers. Two molecules occupy in the average the volume \( 2/n \), therefore the radius of the effective cell for a dimer is \( r_{\text{eff}} \approx \left( \frac{3}{2\pi n} \right)^{1/3} \). The rotating dimer occupies the volume of the radius \( r_d = \frac{r_{\text{eff}}}{2} \). The ratio \( r_{\text{eff}}/r_d \) which is shown in Fig. 4 and becomes greater than unity in the vicinity of the CP.

Let us consider one of the light noble fluid as the reference system. One can conclude that the ratio of the densities for the heavy and light noble gases:
\[ R_i = \frac{\tilde{n}_{cl}^{(i)}(\tilde{T})}{\tilde{n}_{cl}^{(ref)}(\tilde{T}) + \tilde{n}_{q}^{(ref)}(\tilde{T}, \Lambda)} \]

is monotonous along the coexistence curve provided that the classical contributions are the same. In Fig. 5 we give the ratio \( R \) for heavy noble fluids (\( Ar, Kr, Xe \)) with respect to the
lighter ones ($H_2, Ne, He$). It shows that in the near critical region according to the molecular hydrogen is more like $Ne$ than $He$. The additional support in favor of the thermodynamic similarity $H_2$ and $Ne$ is the closeness of their CP locus. Note that in gaseous phase the significant deviation of $R$ from 1 with lowering the temperature (density of saturated vapor decreases too) is connected with the dimerization in accordance with what has been said in the Introduction. From Fig. [11] we can conclude that the dimerization degree in gaseous phase is more than 10%.

From what has been said above the nonmonotonic change of $R$ can be attributed to the temperature behavior of the classical part $\tilde{v}_{cl}$ of the specific volume only. The classical behavior for the noble fluids is not the same as for $H_2$ because of formation of the dimers. That mean that the classical part of the thermodynamic functions corresponds to the monoatomic vdw fluid.

![Graphs](image)

**FIG. 5:** The ratio $R_i$ along the binodal for $Ar$ (dotted), $Kr$ (dashed), $Xe$ (bold) and different reference fluids (see the captions).

The dissociation energy for dimers of heavy noble fluids is close to the dimer bound energy.
FIG. 6: The dimensionless distance $\tilde{r} = 2 \left( \frac{3n}{2\pi} \right)^{1/3} / (l_{\text{bond}} + \sigma)$

(the critical temperature slightly $(4\% - 6\%)$ higher than the dissociation energy of the dimer $\varepsilon_{\text{diss}}/T_c \approx 0.95$, see Table 1). From Fig 6 one can see that nonmonotonic change in the ratio $R$ occurs right at the temperature $kT \approx \varepsilon_{\text{diss}}$.

It can be seen that the geometric (see Fig. 6) and energetic conditions give the ground to expect the nonzeroth dimerization of heavy noble fluids in the vicinity of the CP. One can choose either Ne or molecular hydrogen as the reference fluid since they can be treated without taking into account of the dimers $Ne_2$ or $(H_2)_2$. In Ne although the energetic condition allows the formation of dimers the number of the bound states is low and its dimerization in near critical region is negligibly small in comparison with heavier noble fluids. The spectrum of dimers of heavy noble fluids have many vibrational states. Thus the dimers of heavy noble fluid are more stable. From this point of view the molecular hydrogen and Ne are indeed the “simplest“ molecular liquids. The quantum effect for $H_2$ should be taken into account via the representation Eq. (2).

From here we can conclude that the formation of dimers in liquid phase takes place in near critical region where the density is low enough so that both energetic and geometric conditions are valid. Therefore there is the difference in short range correlations in light and heavy noble fluids which is based on the formation of bound clusters.

In fact, the liquid phase of a noble gas is the mixture of monomers and small quantities of dimers. Since their concentration depends on the kind of matter, the critical amplitudes for different noble gases will take values deviating from those, which follow from the principle of corresponding states. In this sense one can say that the quantum properties, namely the stability properties of bound states, influence the critical parameters of the classical noble
fluids. This result was noticed in numerical simulations [15].

IV. THE BEHAVIOR OF THE RECTILINEAR DIAMETER

The rectilinear diameter for the density:

\[ n_d = \frac{n_l + n_g}{2n_c} - 1 \]  \hspace{1cm} (6)

is important characteristic of the phase coexistence. Such a quantity measures the asymmetry of the phases with respect to the order parameter chosen. This asymmetry is related to the particle-hole asymmetry [16] and is sensitive to the interparticle correlations which governs the expansion rate of the phases below the CP.

Let us make some general comments about the temperature behavior of the rectilinear diameter. Obviously one can distinguish between three characteristic regions: a) fluctuation region \( T_{Gi} < T < T_c \) where \( T_{Gi} \) is the Ginzburg temperature [17]; b) normal states near the triple point \( T \gtrsim T_{tr} \); c) the intermediate one \( T_{tr} < T < T_c \). The temperature dependence of the rectilinear diameter of the density is governed by the different physical mechanisms in these regions. Near the triple point the hard core interactions in liquid phase play the dominant role so one can expect that the behavior in this region should be determined by the hard core interactions only. The near critical behavior is governed by long range fluctuations. The specific temperature behavior in the intermediate region depends on the balance of the short range and long range correlations. Thus the rectilinear diameter characterizes quantitatively to what extent the rate of short range ordering in liquid phase overcomes the rate of disorder in coexisting vapor.

These general remarks are illustrated by the data for the rectilinear diameter of the density (see Fig. 7). The quantity \( \rho_d \) is sensitive to the order in the local configuration. In mono atomic liquids like noble ones the monotonic change of this quantity takes place. This is because of the stronger correlations in liquid phase. The role of the long range correlations in the formation of non monotonic behavior of \( n_d \) in the near critical region is discussed below in Section VII.

In the fluids with polyatomic molecules the volume available for the thermal motion of the molecule modifies the rotational motion in the effective “cavity”. It leads to the fact that the contribution of the inner degrees of freedom, in particular the rotational ones,
becomes dependent on the specific volume. As a consequence the critical amplitudes should be different and this is demonstrated by the behavior of the rectilinear diameter in near critical region (see Fig. 7). Note that the temperature behavior of the rectilinear diameter of the density is the fine criterion for the validity of the EOS.

The natural characteristic of the ordering process in the coexistent phases is the entropy. Therefore the qualitative difference in the ordering in coexisting phases can be also characterized by the rectilinear diameter for the specific (per particle) entropy:

$$S_d = \frac{S_l + S_g}{2} - S_c.$$  \hspace{1cm} (7)

The behavior of $S_d$, as well as $n_d$, for different substances which obey the PCS should be the same. For comparison on Figs. 8 we show the data $S_d$ for noble fluids. Except the critical region the behavior of $S_d$ within the mean field approximation differs from the experimental curve by the shift of order $\Delta S$. The appearance of this difference is naturally explained by the the fluctuation shift of the critical temperature:

$$\Delta S = S^{(mf)} - S_c \approx c_v^{(mf)} \ln \frac{T_c^{(mf)}}{T_c} \approx \frac{T^{(mf)} - T_c}{T_c},$$

where $c_v^{(mf)}$ is the dimensionless value of the mean field value of the specific heat, which for the heavy noble fluids takes the value $c_v^{(mf)} \approx 2)$. So that the entropy diameter value at the CP is less than that in the mean field approximation.

Let us state the relation between the behavior of diameters of the entropy $S_d$ and the density $n_d$. We start from the basic thermodynamical representation of the entropy in dimensionless units (in units of the Boltzmann constant $k_B$):

$$S = S_c + c_v \ln \frac{T}{T_c} + f(n) - f(n_c),$$  \hspace{1cm} (8)
where $S_c$ is the entropy at the CP, $c_v$ is the dimensionless specific heat, $f(n)$ is some function describing the density dependence of the entropy. From Eq. (8) one can conclude that:

$$S_d = \frac{c_v^{(l)}}{2} + \frac{c_v^{(g)}}{2} \ln \frac{T}{T_c} + \frac{f(n_l) + f(n_g)}{2} - f(n_c).$$  \tag{9}$$ 

In the mean filed region below the CP we have:

$$\frac{\delta n_{l,g}}{n_c} = \pm b \sqrt{\tau} + a |\tau| + \ldots, \quad \tau = \frac{T - T_c}{T_c} < 0$$  \tag{10}$$

where $\delta n = n - n_c$, and the indices $l, g$ stand for the coexisting liquid and gas phases correspondingly. The searched relation between $S_d$ and $n_d$ near the CP is obtained by the expansion of Eq.(9) with respect to the density:

$$S_d = n_c \frac{\partial S}{\partial n_c} |_{n_c} n_d + \frac{c_v^{(l)} + c_v^{(g)}}{2} \ln \frac{T}{T_c} + \frac{1}{4} \left( \frac{\partial^2 S}{\partial n^2} |_{l} \delta n_l^2 + \frac{\partial^2 S}{\partial n^2} |_{g} \delta n_g^2 \right) + \ldots. \tag{11}$$

Further we use the thermodynamic relations [17]:

$$\frac{\partial S}{\partial n_c} |_{c} = -\frac{1}{n_c^2} \frac{\partial p}{\partial T_c} |_{c} < 0,$$

$$\frac{\partial^2 S}{\partial n^2} |_{c} = \frac{2}{n_c^3} \frac{\partial p}{\partial T_c} |_{c} - \frac{1}{n_c^2} \frac{\partial^2 p}{\partial T_c \partial n_c}.$$  \tag{12, 13}$$

Omitting the irrelevant terms near the critical point we get:

$$S_d = - \left[ \frac{1}{n_c} \frac{\partial p}{\partial T_c} |_{c} \left( a - b^2 \right) + b^2 \frac{\partial^2 p}{\partial n \partial T} + \frac{c_v^{(l)} + c_v^{(g)}}{2} \right] |\tau| + o(|\tau|).$$  \tag{14}$$

The coefficient $b$ depends on the parameters of the EOS. In particular for the vdW EOS $a = \frac{2}{5}, b = 2$ and $\frac{ds}{dT} = 0.6$, for the Bertlo EOS $a = \frac{2}{5}, b = 2\sqrt{2}$ with $\frac{ds}{dT} = 1.35$ in near
The behavior of the residual entropy $S^{(\text{int})}$ of the noble gases. 

The behavior of the diameters for the total and residual entropy.

FIG. 9: The rectilinear diameter $S_d$ of the total entropy and the residual one $S_d^{(\text{int})}$ of the noble gases Ne (doted) and Ar, Kr, Xe (bold).

critical mean-field region. The slope of $S_d$ increases with the density asymmetry which is described by the coefficient $a$. For lighter noble fluids the slope of the entropy diameter is opposite to that for the heavy noble fluids. This is because of the fact that for light noble fluids the density asymmetry is weak (see Fig. 7) and the specific heat for the liquid phase is smaller in comparison with that for the heavy noble ones (see Fig. 7).

The difference between the behaviors of $S_d$ for light and heavy noble gases is explained by the dimerization effects (see Fig. 8). The calculation of the diameter for the total entropy $S_d$ as well as for its the residual part:

$$S_d^{(\text{int})} = \frac{S_l^{(\text{int})} + S_g^{(\text{int})}}{2} - S_c^{(\text{int})},$$

where

$$S^{(\text{int})} = S - S^{(\text{id})}, \quad S^{(\text{id})} = \frac{3}{2} \ln \frac{T}{T_c} - \ln \frac{n}{n_c},$$

with the help of the vdW EOS, shows that the slope of the $S_d$ increases with account of the dimers (see remarks about Eq. (14)). The comparison of the experimental data for Ne and Ar, Kr, Xe supports this conclusion (see Fig. 9). In order to clarify some qualitative details of the temperature behavior of $S_d$ we will discuss the dimerization of the heavy noble fluids in more details in the next Section. The behavior of $S_d$ in the fluctuation region we will discuss after this.
V. THE DEGREE OF THE DIMERIZATION FROM THE CHEMICAL EQUILIBRIUM

First let us make some general conclusions about the temperature behavior of Eq. (5) along the binodal. For the description of the dimerization let us introduce the quantity

\[ R_{\text{dim}} = \frac{\tilde{n}}{\tilde{n}_1}, \quad \tilde{n} = \frac{n}{n^{(c)}}, \quad \tilde{n}_1 = \frac{n_1}{n_1^{(c)}}, \]  

where \( n \) is the total density (dimers and monomers) and \( n_1 \) is the number density for monomeric fluid.

For high enough density in liquid branch for the substances of interest \( R_{\text{dim}} \) will be close to unity far away from the critical point. It is seems to be natural that with increasing the density the dimerization becomes negligible.

At \( T = T_c \) according to the definition \( R_{\text{dim}} = 1 \). The monotonous change of \( R_{\text{dim}}(T) \) between these boundary values shows the quantitative similarity between substances and thus the validity of the PCS. In contrast to this the nonmonotonic behavior for \( R_{\text{dim}}(T) \) along the binodal signifies the qualitative difference in the process of thermal expansion.

According to what has been said above the dimerization takes place at low enough densities near the critical point. The formation of the dimers lead to the flattening of the binodal thus increasing the difference in the densities of the coexisting phases. The increase of the density in liquid phase far from the critical point makes the dimerization impossible both from the energetic and configurational point of view. In such a case one expects the nonmonotonous behavior of \( R_{\text{dim}}(T) \) along the binodal in liquid phase.

Here we calculate the dimerization degree for the heavy noble fluids using the chemical equilibrium for the dimerization process:

\[ \text{monomer} + \text{monomer} \rightleftharpoons \text{dimer} \]

Let us introduce the degree of association \( a \):

\[ n_1 = (1 - a) n_0, \quad n_2 = \frac{a}{2} n_0. \]  

where \( n_2 \) is the number density of the dimers and \( n_0 = n_1 + 2n_2 \) is the total number density of atoms. The equation of chemical equilibrium for \( a \) is:

\[ \frac{a}{(1 - a)^2} = 2n_0 \exp \left( \frac{2\mu_1^{(ex)} - \mu_2^{(ex)} + E_{\text{diss}}}{T} \right) \]
where \( E_{\text{diss}} \) the dissociation energy of the dimer (in calculation \( E_{\text{diss}} = 0.97T_c \). The excessive chemical potentials are:

\[
\mu_{i}^{(ex)} = \left. \frac{\partial F^{(ex)}}{\partial n_i} \right|_T,
\]

where \( F^{(ex)} \) is the excessive free energy is the difference of the total free energy \( F \) and the ideal part \( F^{(id)} \):

\[
F^{(ex)} = F - F^{(id)}.
\] (18)

In its turn \( F^{(ex)} \) can be decomposed

\[
F^{(ex)} = F^{(hc)} + F^{(int)},
\]

where \( F^{(hc)} \) is the hard core contribution and \( F^{(int)} \) is the contribution due to van der Waals interaction. Further we will use the quantities reduced to the vdW values of the critical parameters for monomeric fluid. The interaction term \( F^{(int)} \) we take in standard binary form:

\[
F^{(int)} = -\frac{9}{8} \left( \bar{n}_1^2 + \lambda \bar{n}_1 \bar{n}_2 + \gamma \bar{n}_2^2 \right).
\] (19)

Assuming the similarity of the interparticle interactions (see Eq. (1)) for monomers and dimers, within the vdW approximation and \( \lambda \) and \( \gamma \) are determined as following:

\[
\lambda \approx \frac{U_{12}}{8U_{11}} \left( 1 + \frac{\sigma_2}{\sigma_1} \right)^3, \quad \gamma \approx \frac{U_{22}}{U_{11}} \left( \frac{\sigma_2}{\sigma_1} \right)^3,
\]

where \( U_{11}, U_{12}, U_{22} \) are the interaction constants for ”monomer-monomer”, ”monomer-dimer” and ”dimer-dimer” correspondingly. In the order of magnitude \( \lambda \gtrsim 1 \) and \( \gamma \gtrsim 2 \).

The hard core contribution is taken in vdW form with account of the mutual influence of excluded volume for the monomers and the dimers:

\[
F^{(hc)} = -T \left[ n_1 \ln \left( 1 - \frac{n_1}{3} - \frac{b_1 n_2}{3} \right) + n_2 \ln \left( 1 - \frac{b_2 n_2}{3} - \frac{b_1 n_1}{3} \right) \right].
\] (20)

Here \( b_1 \) and \( b_2 \) are the specific volumes per dimer (in units of the monomer volume) in environment of the monomers and the dimers correspondingly. As the calculations show that the account of the dimerization leads to the broadening of the binodal in \( n - T \) coordinates (see Fig. 10).

The ratio \( R \) is shown in Fig. 11. The comparison with the experimental data of \( R_{Ne} \) for the pair of substances \( Xe \) and \( Ne \) as the vdW fluids with dimers and without them
FIG. 10: The binodals for vdW EOS (dashed) and for vdW with account of the dimerization (bold) correspondingly. It shows that the mean field approach is adequate at least qualitatively (see Fig. 11).

The nonmonotonic behavior of $R_{Ne}$ as it follows from Fig. 5 takes place in close vicinity of the critical point. The formation of the dimers becomes impossible if the specific volume becomes less that $2v_0$ (in reduced coordinates $\tilde{n} \approx 1.5$). Simple estimate shows that it occurs exactly at the temperature $T \approx 0.95 \div 0.97 T_c$. In the proposed mean field description $R_{dim}$ changes in broader region, $\tilde{n} \approx 2$ (see Fig. 11). Such a discrepancy can be attributed to the inadequate account of the hard core effects which mainly governs the destruction of the dimers when the density increases. The use of more appropriate approximation for the hard sphere contribution, e.g. Carnahan-Starling, decreases the value of $R_{dim}$ beyond the fluctuation region. The behavior of $S_d$ in the mean field region, $T/T_c < 0.9$, depends on the short range correlations. Obviously the difference in the character of such short range correlations is responsible for the different behavior of the rectilinear diameter of the entropy $S_d$ which is clearly shown on Fig. 8 for the heavy ($Ar, Kr, Xe$) and light noble fluids. As has been noted above the existence of the dimers is not possible in this region. But the stronger short range correlations, as compared to those in lighter ones, should be expected in the heavy noble gases as the remnants of the near critical point dimerization.
VI. THE RECTILINEAR DIAMETER ANOMALY

The asymptotic behavior of the rectilinear diameter of the density in the fluctuational region is as following:

\[ n_d = \frac{n_l + n_g}{2n_c} - 1 = D_{2\beta} |\tau|^{2\beta} + D_{1-\alpha} |\tau|^{1-\alpha} + D_1 |\tau| + o(\tau), \quad D_1 < 0. \]  

(21)

It contains \(|\tau|^{2\beta}\)-term \([19, 20, 21]\). The ground for introduction of such a term as the sequence of the choice of the order parameter predicted firstly within the canonical formalism approach \([20, 22]\). Note that according to \([23]\) the ratio of the leading singularity amplitudes for the temperature dependence of the rectilinear diameter is “almost” universal:

\[ \frac{D_{1-\alpha}}{D_{2\beta}} \simeq a^{1-\alpha-2\beta} \frac{l_s(0)}{g_s^2(0)} < 0. \]  

(22)

where \(a\) is the nonuniversal factor. The quantities \(f_s\) and \(g_s\) are universal functions:

\[ f_s(x) = f_s(-x), \quad g_s(x) = \frac{d f_s(x)}{dx}. \]

They are determined by the asymptotic thermodynamic potential

\[ \Phi = |A_2|^{2-\alpha} f_s \left( \frac{A_1}{A_2^{\beta+\gamma}} \right) + \ldots \]

in isomorphic variables \(A_1\) - conjugated field-like variable and \(A_2\) - temperature-like variable.

The temperature behavior of the rectilinear diameter strongly depends on the interplay between the values of \(D_i\). Basing on the experimental data shown in Fig. 7 it seems natural to assume that \(D_1 > 0\). From the physical interpretation of the \(n_d\) it is clear that the
repulsive terms in pressure decrease the absolute value of $D_1$. Since the $2\beta$ singularity is the strongest one the non monotonous behavior of the density rectilinear diameter takes place if $D_{2\beta} < 0$. In order this behavior manifests clearly there should be $D_{1-\alpha} < |D_{2\beta}|$ which according to Eq. (22) means that $a < 1$. The parameter $a$ depends on the choice of the initial order parameter. This explains the fact that $2\beta$ singularity amplitude varies greatly depending on the order parameter chosen. This usually is interpreted as the division of the order parameters into more and less symmetrical ones, e.g. like density $\rho$ and volume $v$ [24].

Even if $D_{2\beta} > 0$ the $2\beta$ singularity can be masked by the interplay of linear and “$1 - \alpha$” terms $D_1 \approx |D_{1-\alpha}|$ if $D_{2\beta}/|D_{1-\alpha}| \ll 1$ ($a < 1$, see Eq. (22)). In particular from the results of [24] it follows that $D_{2\beta}/D_{1-\alpha} \approx -0.1$ with $D_{2\beta} > 0$. Note that in [25] the data for the liquids with different degree of the binodal were analyzed, namely SF$_6$ as typical molecular liquid and alkali metals Cs, Rb.

If $D_{2\beta} > 0$ and in addition $(1 - \alpha)|D_{1-\alpha}| \gtrsim D_1$ then essentially nonmonotonous behavior for the rectilinear diameter takes place. There is minimum at

$$\tau_{\text{min}} \approx \frac{1}{\alpha} \ln \frac{(1 - \alpha)D_{1-\alpha}}{D_1}$$

and the maximum

$$\tau_{\text{max}} \approx \left( \frac{2\beta}{1 - \alpha} \frac{D_{2\beta}}{D_{1-\alpha}} \right)^{\frac{1}{1 - 2\beta - \alpha}}.$$

The location of this maximum is very close to $T_c$ ($|D_{2\beta}/D_{1-\alpha}| < 1$) and can be measured only if $(1 - \alpha)|D_{1-\alpha}| \approx D_1$. The clear example of such situation is given by rectilinear diameter for the binodal of Hg [26]. The data used for light noble fluids here does not allow to distinguish between this case and the situation with $D_{2\beta} < 0$.

The values of the amplitudes $D_{2\beta}$ and $D_{1-\alpha}$ are the same for the substances which belong to the same class of corresponding states (eg. Kr and Xe). As is shown in [23] $D_{2\beta}$ and $D_{1-\alpha}$ have opposite signs. The coefficient $D_{2\beta}$ can be either positive or negative depending on the details of the intermolecular interactions. Taking into account the results of the previous section we can conclude that for molecular liquids as well as in liquid metals [26] where the clusterization takes place in near critical region the coefficient $D_{2\beta}$ is positive. The same is true for the entropy diameter and any other order parameter for which the Landau-Ginsburg functional contains the odd power terms.

The situation with the rectilinear diameter for lighter noble fluids suggests two possibilities. The first one is that the amplitude $|D_{1-\alpha}| > (\gg)D_{2\beta} > 0$ but $(1 - \alpha)|D_{1-\alpha}| \gtrsim D_1$
and the binodal is quite symmetrical. The second is that $a < 1$ so that $D_{1-\alpha}(\ll) < -D_{2\beta}$.

The data for $N e$ also conform with such a proposition. Note that helium has "almost" symmetrical binodal ($|D_1| \ll 1$) in comparison with other noble liquids. Obviously this can be attributed to the quantum corrections to the equation of state which gives the additional repulsive contribution to the pressure. Thus one can expect that in $He$ the coefficient $D_{2\beta}$.

From here we can make the following conclusion concerning the sign of the amplitude $D_{2\beta}$. The dimerization influences the character of the short range correlations. If the dimerization is negligible then one can expect that $D_{2\beta} < 0$. For the systems where the dimerization takes place $D_{2\beta} > 0$. This leads to the qualitative difference in the behavior of the rectilinear diameter $n_d$ observed.

Here we perform the analysis of the critical asymptotic of the rectilinear diameter for the entropy

$$S_d = S_{2\beta} |\tau|^{2\beta} + S_{1-\alpha} |\tau|^{1-\alpha} + S_1 |\tau| + o(\tau).$$

The first contribution is caused by the corresponding term of the density diameter and the quadratic density contribution in Eq. (11). Note the term $\propto |\tau|^{1-\alpha}$ is generated by the density diameter and the specific heat terms according to Eq. (11). Note, that as follows from the representation (8) $S_{1-\alpha} < 0$. In contrast to the coefficients $D_{1-\alpha}$ which is generated by the asymmetry of the Hamiltonian, the coefficient $S_{1-\alpha}$ does not vanish in symmetrical case, e.g. in the Ising model, and correspondingly:

$$S_{1-\alpha} = S_{1-\alpha}^{(sym)} + S_{1-\alpha}^{(asym)}. \quad (24)$$

It is obvious that the symmetrical part $S_{1-\alpha}^{(sym)}$ is generated by the heat capacity singularity.

As follows from Eq. (11), $S_{1-\alpha} < 0$. In order to distinguish between the $\tau^{2\beta}$ and $\tau^{1-\alpha}$ terms for rectilinear diameter we subtracted the analytic background terms outside the critical region. The coefficients $s_k$ of the polynomial

$$S_d^{\text{reg}} = \sum_{k=1}^{5} s_k \left( T_c/T - 1 \right)^k$$

have been determined with the help of the experimental data in the region $T/T_c < 0.75$.

The results of calculation of the ratio $S_{2\beta}/S_{1-\alpha}$ are placed in Table and they confirm the conclusion of the canonical formalism about its universal character. Small variations in this ratio in dependence on the specific fluid are explained by the difference between
TABLE II: The ratio $\frac{S_2}{S_1^{\alpha}}$ for the noble gases.

|   | $H_2$ | $Ne$ | $Ar$ | $Kr$ | $Xe$ |
|---|-------|------|------|------|------|
| $S_1^{\alpha}$ | -0.28 | -0.30 | -0.31 | -0.34 | -0.33 |

canonical temperature variable $A_2$ and the reduced temperature $\tau$. Besides we neglected the symmetrical in $S_1^{(sym)}$ since it is proportional to the fluctuation correction of the heat capacity. The results allow to conclude that $S_1^{(sym)}$ is smaller that the term generated by the asymmetry of the Hamiltonian.

VII. DISCUSSION

In this work it is stressed that the leading role in the understanding of the difference and similarity in the thermodynamic behavior of fluids belongs to the PCS. The main result of the present work is the clear demonstration of that fact, that noble gases do not rigorously follow the PCS principle of corresponding states [1].

As was shown from the analysis of the density and the entropy the deviations from PCS are observed 1) for liquid phase near the critical point and 2) and for gaseous phase in the whole region of their existence. The latter is especially important circumstance, which directly indicates the main cause of such deviations. It is the dimerization processes in noble gases. The most essentially the dimerization manifests itself in gaseous phase far away from the critical point, where the doubled fraction volume per molecule $2\nu$ is noticeably more than the own volume for a dimer. The degree of the dimerization here reaches 10%. In liquid phase due to the geometrical restriction for the existence of the dimers the temperature interval where the dimerization effects in nobel fluids take place is rather narrow due to the closeness of the dissociation temperature $T_{diss}$ to the critical one $T_c$ ($T_{diss} \approx 0.96 T_c$). Nevertheless they are quite noticeable in the temperature behavior of the entropy and the specific heat. The analysis of the experimental data with taking into account of the dimerization effect for the liquid phase in near critical region give the estimate $\lesssim 5\%$ for the degree of dimerization. Note that these effects can not be adequately described with the standard two parametric vdW-like EOS.

The density and the entropy diameters are the fine characteristics of the EOS. From
our analysis it follows that widely used vdW and Bertlo EOS are not able to describe the formation of the plato in the temperature dependence of $S_d$ for the heavy noble fluids. At the same time the density binodal is reproduced quite correctly.

The analogous situation is characteristic for liquids with nonspherical molecules, first of all, for benzene and water. In these cases the behavior of the entropy diameter is essentially nonmonotonic. This circumstance for water is expected since the association processes in it are considerably more expressed than in noble gases. In [27] it was shown that the degree of the dimerization near the critical point is close to unit ($a \approx 0.9$). At removing from the critical point the associates in liquid water becomes more complicated. So their influence on the fine details of density and the entropy of water is considerably more expressed. Strong correlations in liquid benzene lead also to considerable changes in the behavior of $S_d$. The specific structure manifest itself also in kinetic properties such as viscosity.

As shown in the work, the dimerization radically influences the behavior of the density rectilinear diameter. From the analysis of the last for $He$, $H_2$ and $Ne$ it follows that $D_{2\beta}$ is negative or takes the small positive value, essentially less than $D_{1-\alpha}$. Note, that the using of the experimental data from [25] allows to get the following estimate for their ratio: $D_{2\beta}/D_{1-\alpha} = -0.1$.

It is necessary to emphasize that in accordance with the canonical formalism reasons the signs of $D_{2\beta}$ and $D_{1-\alpha}$ should be opposite. This very important conclusion could not be got with the help of theory developed in [21, 28]. This question will be discussed in separate paper.

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