Peculiarities in the behavior of the entropy diameter for molecular liquids as the reflection of molecular rotations and the excluded volume effects

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Abstract

The behavior of the diameter of the coexistence curve in terms of the entropy and the corresponding diameter are investigated. It is shown that the diameter of the coexistence curve in term of the entropy is sensitive to the change in the character of the rotational motion of the molecule in liquid phase which is governed by the short range correlations. The model of the compressible effective volume is proposed to describe the phase coexistence both in terms of the density and the entropy.

1. Introduction

Peculiarities of the asymmetry for the vapor-liquid binodal are the important source of information about different factors influencing its form. It is well known that the asymmetry of binodal is absent for the simplest system known as the lattice gas. From physical point of view it is caused by 1) the absence of the thermal expansion effects (the lattice distance is constant) and 2) the invariance of the energy of system about the transformation: particles ↔ holes. The latter circumstance is evidently violated by 1) the appearance of the soft repulsive core effects and the long-distance attractive interaction between molecules, which are caused by the dispersive

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and electric multipole-multipole interactions, as well as 2) the anisotropic character of interactions for non-spherical molecules. These effects lead to the essential difference in the coefficients of the thermal expansion for liquid and vapor coexisting phases and violate the particle-hole symmetry. One of the simplest characteristics of the asymmetry of the vapor-liquid binodal is its diameter.

If the vapor-liquid binodal is described in the terms temperature-density, its diameter is determined as:

\[ n_d = \frac{n_l + n_v}{2n_c} - 1, \]  

where \( n_i, \ i = l, v, \) are the densities of the liquid and the vapor phases correspondingly and \( n_c \) is the critical density. The number density (or specific volume) is the natural order parameter for the liquid-vapor critical point (CP). In its vicinity the asymmetry of the density diameter is mainly determined by the long-range fluctuations of the order parameter \( \Pi \). Far away from the CP the asymmetry of the diameter of binodal is mainly caused by the hard core effects. This statement follows immediately from the van der Waals (vdW) equation of state, which gives us the reliable qualitative information about the role of main factors in the formation of the EoS. However, the description of the binodal in terms of the density is rather incomplete. The density is expressed via the unary correlation function. Obviously, at such level the rotational degrees of freedom as well as the short range correlations due to nonspherical shapes of the hard core do not manifest themselves in a clear-cut way.

The information about the role these factors can be obtained from the analysis of the entropy diameter:

\[ S_d = \frac{S_l + S_v}{2} - S_c \]  

In general, it includes the part changing similarly to density and the irreducible part, which is caused by the correlation effects of all orders. Due to this the analysis of the asymmetry of the binodal in terms of the temperature-entropy is more informative in comparison with its temperature-density version.

This circumstance becomes evident from the comparison of the temperature dependencies of \( n_d(t) \) and \( S_d(t) \) for several classes of substances: 1) the noble fluids; 2) the simple molecular fluids with the inversion center for
their molecules; 3) the simple molecular fluids without the inversion center for their molecules and 4) the high-molecular fluids. The behavior of $n_d(t)$ and $S_d(t)$ for these of substances is presented in the Fig. 1 and Fig. 2. From the Fig. 1 it follows that the density diameter is the monotonous function of the temperature at least outside the fluctuational region. The temperature dependence for all enumerated substances is close to linear in the wide temperature interval, in connection with this it is called as the law of the rectilinear diameter. In contrast to it the behavior of the entropy diameter is essentially non-monotonous. Such a discussion testifies about the important role of the caloric part of the entropy, which is not reduced to the density effect. On the other hand it gives the additional information about the molecular motion, in the first place, the rotational motion of molecules, which directly contributes to the heat capacity and the entropy. We see that the near critical behavior of the entropy diameter is also stronger expressed.

In [3] the analysis of the behavior of $S_d$ was used to estimate the degrees of the dimerization in the noble fluids near their critical points.

In this paper we investigate the nature of the asymmetry of the binodal in the temperature-entropy terms for molecular substances. The entropy diameter $S_d$ is used as the measure of the asymmetry. We will show that the surprising non-monotonous behavior of the entropy diameter is mainly explained by the rotational motion of molecules. The interconnection between the rotation of molecules and the excluded molecular volume is established. The model equation of state (EoS), taking into account the dependence of the effective excluded volume on pressure, is proposed. Due to this the behavior of $S_d$ as well as the form of the binodal in terms of the temperature-density in the wide temperature interval beyond the fluctuation region near the CP are reproduced self-consistently.

2. The qualitative analysis of the non-monotonous behavior of the entropy diameter

In this section we discuss the main physical mechanisms generating the non-monotonous temperature dependence for the diameter of the entropy. For this purpose we start from the general expression for the specific (per
Figure 1: The density diameter for the molecular fluids: (a) noble; (b) nonpolar; (c) polar; (d) high molecular and anisotropic
Figure 2: The diameters of the entropy for different liquids: (a) noble; (b) nonpolar; (c) polar; (d) high molecular and anisotropic.
particle) entropy \( S \) of arbitrary system:

\[
S = S_c + c_v \ln \frac{T}{T_c} + f(n) - f(n_c). \tag{3}
\]

Here \( S_c \) is the value of the specific entropy at the CP, \( c_v \) is the dimensionless specific heat \((k_B = 1)\), \( f(n) \) is the function which depends on the density only.

From (3) it follows that the diameter of the binodal in terms of temperature-entropy is determined by the expression:

\[
S_d = \frac{1}{2} \left( c_v^{(l)}(t) + c_v^{(v)}(t) \right) \ln \frac{T}{T_c} + \frac{1}{2} \left( f(n_l) + f(n_v) \right) - f(n_c), \tag{4}
\]

where \( c_v^{(i)}, \ i = l, v, \) are the specific heat capacities on the liquid and vapor branches of the binodal.

Since \( c_v^{(l)}(t), c_v^{(v)}(t) > 0 \), the contribution of the first (caloric) term to the diameter of entropy enters with negative sign for all temperatures \( T < T_c \).

The numerical values of the combination \( \frac{1}{2} \left( c_v^{(l)}(t) + c_v^{(v)}(t) \right) \) depend on the number of the degrees of freedom excited in the thermal motion. For the noble gases, having only translational degrees of freedom,

\[
3 < \frac{1}{2} \left( c_v^{(l)}(t) + c_v^{(v)}(t) \right) < 6. \tag{5}
\]

The lower limit corresponds to the case of non-interacting particles, the upper – to the strong interaction between them. For the substances with non-spherical particles the contributions of the rotational degrees of freedom should be taken into account. In this case,

\[
6 < \frac{1}{2} \left( c_v^{(l)}(t) + c_v^{(v)}(t) \right) < 12. \tag{6}
\]

These inequalities are illustrated by Fig. 3. The vibration degrees of freedom for many substances at \( T < T_c \) and, in particular, for all substances enumerated in Fig. 1 and Fig. 2 can be ignored.

The density contribution \( f(n) \) to the entropy obviously increases if the density decreases. Far away from the critical point \( f(n_l) < (<<) f(n_v) \). The resulting sign of \( S_d \) depends on the relation between the caloric and density contributions. To get the qualitative representation about their competition let us consider the ideal gas approximation for \( f(n) \).
2.1. Ideal gas contribution

In the ideal gas approximation we should put

\[ f(n) = -\ln \frac{n}{n_c}. \]  

(7)

This approximation correctly reproduces the tendency in the change of the entropy, caused by the density contribution, for the vapor and liquid branches of the binodal. Therefore, we hope that the expression

\[ S_{d}^{(Q)}(t) = \frac{1}{2} \left[ (c_{v}^{(l)}(t) + c_{v}^{(v)}(t)) \ln \frac{T}{T_c} - \ln \frac{n_l n_v}{n_c^2} \right] \]  

(8)

will correctly reproduce the qualitative peculiarities in the behavior of \( S_{d}(t) \). Here we put additionally

\[ c_{v}^{(v)}(t) = \frac{i}{2} \]

and

\[ c_{v}^{(l)}(t) = c_{v}^{(v)}(t) + \Delta c_v \]  

(9)

where \( i = i_{tr} + i_r \) is the sum of the translational and rotational degrees of freedom. Of course the value \( i \) is determined only in low density vapor phase where the interaction contribution to the specific heat is negligible. With the increasing density this contribution increases (see Fig. 3). In accordance with Fig. 3 we put

\[ \Delta c_v \approx \begin{cases} 
1, & \text{for Ar}, \\
2, & \text{for } H_2S, \\
5, & \text{for } H_2O.
\end{cases} \]  

(10)

Substituting the estimates (9) and (10) for the specific heat to (8) and the experimental values of \( n_l \) and \( n_v \) we find that 1) at \( i = 3 \), that is characteristic for argon-like liquids, the diameter of entropy is a monotonous function of temperature and 2) the non-monotonous behavior of \( S_{d}(t) \) is observed for \( i \geq 5 \). These results are in full qualitative agreement with experimental results presented in Fig. 2.

Here it is relevant to pay attention on the position of the roots of the equation \( S_{d}^{(Q)}(t) = 0 \). It has two different roots: \( t_l \) and \( t_h \), \( t_l < t_h \). One of them, \( t_h \), coincides with the CP: \( t_h = t_c = 1 \). Another root \( t_l \) is close to
Figure 3: The specific heat along the gas branch of the binodal for the number of molecular liquids: 1 - Ar, 2 - O$_2$, 3 - H$_2$S, 4 - NH$_3$, 5 - H$_2$O, 6 - SO$_2$. The dashed lines correspond to $i = 3$, $i = 5$ and $i = 6$ respectively.

the corresponding experimental values. For example, for O$_2$ Eqs. (8) and (9) with $i = 5/2$ and $\Delta c_v = 3$ gives:

$$t_l = \begin{cases} 
0.42, & \text{for } S_d^{(Q)} = 0, \\
0.42, & \text{for } S_d^{(\text{exp})} = 0.
\end{cases} \quad (11)$$

At the same time, the equation $S_d^{(\text{exp})} = 0$ has three roots: $t_l, t_u$ and $t_h = 1$. The roots $t_h$ for equations $S_d^{(Q)} = 0$ and $S_d^{(\text{exp})} = 0$ are trivial, since the diameter of the entropy vanishes at the CP because of its definition. For O$_2$ the intermediate root $t_u = 0.88$. The appearance of this root for the equation $S_d^{(\text{exp})} = 0$ is connected with the influence of the critical fluctuations.

2.2. The manifestation of critical fluctuations

The critical fluctuations manifest themselves in two relations: 1) they shift the position of the CP ($T_c^{(mf)} \rightarrow T_c = T_c^{(mf)} - \Delta T_{fl}$, $\Delta T_{fl} > 0$), determined in the framework of some mean-field approximation and 2) they renormalize the value of the entropy at the CP: $S_c^{(mf)} \rightarrow S_c = S_c^{(mf)} - \Delta S_{fl}$, $\Delta S_{fl} > 0$. In consequence of this at the comparison of $S_d^{(\text{exp})}$ and
$S_d^{(Q)}$, which can be considered as the simplest mean-field approximation, we should take into account that the normalized temperatures are different. We have

$$S_d^{(mf)} \left( \frac{T}{T_c} \right) \approx S_d^{(mf)} \left( \frac{T}{T_c^{(mf)}} - \Delta T_{fl} \right) \approx S_d^{(mf)} \left( \frac{T}{T_c^{(mf)}} \right) + \Delta S_{fl}, \quad (12)$$

where

$$\Delta S_{fl} = c_v^{(mf)} \cdot \frac{\Delta T_{fl}}{T_c^{(mf)}} \approx c_v^{(mf)} \cdot \frac{\Delta T_{fl}}{T_c} \quad (13)$$

is the fluctuation contribution to the entropy at the CP.

Let us consider the application of Eqs. (12), (13) to the description of the diameter of the entropy outside the fluctuational region for noble gases. For the comparison of $S_d^{(ex)}(t)$ corresponding to the experimental data with $S_d^{(Q)}$, it is necessary to shift the latter curve 1) upward on the distance $\Delta S_{fl}$ and 2) along the temperature axis on $-\Delta T_{fl}$. These operations will be carried out everywhere below. As a result, the height of the plateaus (see Fig. 2a) is determined by the second term in Eq. (12). At the same time it means that the caloric contribution into $S_d^{(mf)}$ is practically compensated by the density dependent term in the temperature interval $0.65 \leq T/T_c \leq 0.95$.

2.3. The diameter of the entropy for the van der Waals model of the liquid and vapor branches of the binodal

In this subsection we consider the temperature dependence of the diameter of the entropy if the binodal is modeled by the van der Waals equation of state.

$$P = \frac{n T}{1 - b n} - a n^2. \quad (14)$$

The values of $n_l$ and $n_v$, which follows from (14) should be substituted in (8). Near the critical point we have

$$\frac{n_{l,v}}{n_c} = 1 \pm B_0 |\tau|^{1/2} + A |\tau| + ..., \quad (15)$$

where $\tau = \frac{T - T_c}{T_c}$. From (14) it is easy to get:

$$B_0 = 2, \quad A = 0.4. \quad (16)$$
Substituting Eq. (15) into Eq. (4) with (7) in the whole temperature interval for liquid states we obtain:

\[ S_d^{(Q)}(T) = \left( c_v^{(id)} + \frac{1}{2} \Delta c_v \right) \ln \frac{T}{T_c} - \ln (1 - \lambda |\tau|) \],

(17)

where \( \lambda = B_0^2 - 2A \). For the van der Waals EoS \( \lambda = 3.2 \). The same procedure applied to the EoS with the Carnahan-Starling contribution:

\[ p = nT \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - a n^2 \]

(18)

where \( \eta = n b/4 \), leads to (17) with \( \lambda \approx 3.7 \). The comparison of the experimental data for \( H_2S \) and the results obtained from Eq. (17) is on Fig. 4. The fitted value of the parameter \( \lambda \approx 1.8 \) is almost as twice as smaller than the corresponding values which have been obtained above within simplified model (7) and (15). This simple treatment allows to conclude that the non-monotonic dependence of \( S_d \) can be get qualitatively as the consequence of the interplay between two opposite tendencies: increase of the configurational chaos of the gaseous phase and the entropy decrease of the liquid phase with lowering the temperature. In Section 3 we propose the model EoS describes the behavior of the entropy diameter more adequately (see Fig. 7 below).

2.4. The excess entropy

In connection with said above it is appropriate to use the excess entropy:

\[ S^{(ex)} = S(T, n) - \frac{i}{2} \ln \frac{T}{T_c} + \ln \frac{n}{n_c} \],

(19)
in which the ideal gas contribution is subtracted. In accordance with its definition \( S^{(ex)} \) includes the fluctuation contribution in the vicinity of the critical point and the effects caused by the interactions between translational and rotational degrees of freedom. It means that \( S^{(ex)} \) is expected to be greater in absolute value for the liquid phase in comparison with the vapor phase. This statement is naturally confirmed by Fig. 5. In correspondence with this we redefine also the diameter of the entropy

\[
S_d \rightarrow S_d^{(ex)} = \frac{1}{2} \left( S_{l}^{(ex)} + S_{v}^{(ex)} \right) - S_c^{(ex)}.
\]

(20)

It is behavior is presented in Fig. 6. The latter is monotonic excluding small interval near the critical point where the fluctuation effects lead to the appearance of singularities [6]. The slope of \( S_d^{(ex)} \) is the source of the important information about the combination of coefficients describing the attraction and repulsion between molecules.

Here we want to note the following peculiarities of the temperature dependence of \( S_d^{(ex)} \) for different liquids. We see that the characteristic values of slopes of \( S_d^{(ex)} \) for noble gases are essentially smaller in comparison with those for molecular liquids. Besides, the values of \( S_d^{(ex)} \) for different noble gases are very close that is in good agreement with the Principle of Corresponding States. The difference between noble gases and molecular liquids has also natural explanation: the intermolecular interactions in molecular liquids are stronger than in noble gases.
Figure 6: The behavior of the diameter of the excess entropy.
It is also essential that the slopes of $S^{(ex)}_d$ for molecular liquids of different types are close to each other i.e. the molecular sizes, electrostatic multipole moments and H-bonds are responsible only for fine details. Such a situation reflects the fact that the behavior of $S^{(ex)}_d$ is determined by the averaged intermolecular potential [7, 8]. After averaging on the rotational degrees of freedom the effective intermolecular potential reduces to argon-like one which in general is the state dependent quantity [9, 10]. The noticeable deviations from the predictions made with the help of averaged potential are observed only in the narrow vicinity of the critical point and in supercooled states of liquids. As an example, for water the contribution of the orientational correlations can reach several percents [11].

3. Effective volume model

In this Section we propose the model of the effective volume which allows to include on the phenomenological level the effects of the nonsphericity of the particles. As shown in [12–14] the form of EoS (22) with $a$ and $b$ as constants is adequate in the vicinity of the triple point. But they fail to reproduce the behavior for $S_d$ even for noble gases like Ar, Kr and Xe where the interaction is obviously spherically symmetrical. For the molecular fluids with anizotropic hard core potentials like N$_2$ and O$_2$ using vdW-like EoS which is based on the effective spherically symmetrical interaction can be justified [8]. Therefore we can use the simplest geometrical representation of the shape of the excluded effective volume as a sphere.

Nevertheless such a fine property as the behavior of $S_d$ was not studied. In additions the specific heat for the model EoS’s of type (22) with $b = \text{const}$ does not depend on the density. As a result the diameter of the entropy as well as the behavior of the specific heat along the coexistence curve is not reproduced even qualitatively. To overcome this deficiency one should consider the parameter $b$ as the function of the thermodynamic state.

In this Section we propose simple model which account for the rotational degrees of freedom of the non spherical molecules through making the parameter $b$ state dependent quantity. The correspondingly modified EoS of Carnahan-Starling is proposed. The first consequence of such a modification is more correct reproducibility of the liquid branch of the binodal. The second is the correct description of the entropy diameter and satisfactory agreement with the specific heat data outside the fluctuational region. Note
that van der Waals himself and Kamerling-Onnes did attempts to make the vdW parameter \( b \) pressure dependent \([14][17]\).

From what has been said above it is clear that one can model the influence of the density on the rotation as the restriction of the angular configuration space available for the molecule in a cell formed by its neighbors. The change in the available space for free rotation of the molecule can be described by the dependence of the volume parameter \( b \) on the density and the temperature. In such an approach the change of the excess entropy of the liquid phase with the density (see Fig. 6) can be reproduced.

Basing on the physical interpretation of \( b \) as the available free volume we propose the following model:

\[
b = \frac{b_0}{1 + \gamma x}, \quad x = \frac{p^{(id)}}{p^{(vdW)}}, \quad p^{(id)} = nT, 
\]

where \( p^{(vdW)} \) is the vdW critical pressure and \( \gamma \) is the adjustable parameter. From the physical point of view the model (21) states that the volume available for a particle decreases if the pressure increases:

\[
v = v_0 \left( 1 - \gamma \frac{p_{id}}{p_0} + \ldots \right).
\]

This qualitatively conforms with the pressure dependence of the free volume which can be obtained from the molar refractivity data \([18]\). The conception of the effective free volume in the liquid state theory is widely used. A lot of modifications for the repulsive pressure contribution which use temperature dependent effective core diameter \( \sigma(T) \) have been proposed \([18][21]\). Usually, the \( P-V-T \) data are used for the determination and the interpretation of the effective free volume and in particular the soft core diameter \( \sigma(T) \). The analysis of the influence of the core softness on the entropy and the specific heat are more scarce \([22]\).

To justify the model (21) we use the generalized vdW EoS approach \([23][24]\). This approach allows to define the free volume in rigorous manner for the molecular systems with the spherically invariant interactions. It is based on the fact that for a wide class of the potentials the EoS for simple molecular fluids is \([24]\):

\[
p = p_+(n, T) + p_-(n, T),
\]

where \( p_+ \) is the pressure contribution due to hard core repulsive interactions and \( p_- \) is the contribution of the attractive long range part of the potential.
Two contributions in (22) can be represented in the vdW-like form [23]:

\[ p_+ = \frac{nT}{1 - bn} \]  
\[ p_- = -an^2. \]  

(23)  
(24)

The vdW coefficients \( a(n, T), b(n, T) \) are in general the functions of the thermodynamic state [26]. The function \( b(n, T) \) is determined by the contact value of the cavity function:

\[ b = b_0 \frac{y(\sigma, n, T)}{1 + b_0 n y(\sigma, n, T)} , \]  

(25)

in accordance with the basic representation for \( p_+ \) [23]:

\[ p_+ = p_{id} \left( 1 + b_0 n y(\sigma, n, T) \right) , \]  

(26)

where \( b_0 = \frac{2\pi\sigma^3}{3} = 4v_0 \) and \( \sigma \) is the diameter of the hard core, \( y(r, n, T) = e^{\beta v(r)} g(r, n, T) \) - the cavity function, \( g(r, n, T) \) - pair distribution function. Here \( p_{id} = nT \) is the ideal gas pressure. E.g., for the Carnahan-Starling (CS) model of \( p_+ \) the function \( b \) is determined as:

\[ b = \frac{1}{n} \left( 1 - \frac{(1 - \eta)^3}{1 + \eta + \eta^2 - \eta^3} \right) , \quad \eta = n b_0 / 4 . \]  

(27)

In [26] it is shown that in the high density regime \( n > n^*(T) \), when the parameter \( a(n, T) \) becomes negative \((a(n^*(T), T) = 0)\), the approximate EoS has the form

\[ p \left( 1 - b_f n \right) = nT \]  

(28)

and the free volume of a molecule \( b_f \) can be written as:

\[ b_f = v \left( 1 - \frac{p_{id}}{p} \right) . \]  

(29)

Comparison (21) with (29) justifies the model of compressible volume as the simple approximation for (29).

Note that the structure of (24) is determined by the form of the EoS (22) due to separation of the hard core effect. Indeed, the ideal gas term in (24) is the zeroth approximation if \( b \rightarrow 0 \). But as noted in [27] the parameter \( b \)
Figure 7: The comparison of the results for the binodal and the diameter of the entropy for \( H_2S \) calculated within proposed model of compressible volume Eq. (21) with \( \gamma \approx 0.03 \) (solid lines) and the common assumption \( b = const, \gamma = 0 \) (dashed lines). The points are the experimental data.

is rather the excluded volume than the size of the molecular core although there is correlation between these quantities [18]. Therefore we can extend [26] by introducing the compressibility of the excluded volume \( b \) into any model for \( p_+ \), in particular for CS approximation (26). The corresponding pressure term has the form:

\[
p_+ = p_+^{(CS)} \left( 1 + \frac{n}{b} \left( \frac{\partial b}{\partial n} \right) \right),
\]

(30)

where \( p_+^{(CS)} \) is the repulsive pressure term in CS approximation, which now corresponds to the limit of incompressible effective volume \( \frac{\partial b}{\partial n} \rightarrow 0 \) in analogy with (26). In accordance with Eq. (30) and the identity \( p = -\frac{\partial F}{\partial V} \), we arrive to the following free energy consistent with Eq. (30):

\[
F = F_{id} + T \frac{b n (4-b n)}{(1-b n)^2} - a n,
\]

(31)

where \( F_{id} \) is the free energy of the ideal gas:

\[
\frac{F_{id}}{T} = -c_v \ln T + \ln n.
\]

The comparison of the calculation the binodal using (21) with \( \gamma = 0 \) (standard incompressible volume) and \( \gamma = 0.03 \) are presented in Fig. 7. Note
that the curve for $S_d$ with $\gamma = 0$ was shifted for matching the characteristic minimum of these curves (see Fig. 4). The influence of the compressible proper molecular volume $b$ on the binodal is shown in Fig. 6. As expected only the liquid branch (upper curve) is sensible to the dependence of $b$ on the parameters of the state. The difference between the liquid branches of the binodal with $\gamma = 0$ and $\gamma = 0.03$ increases with increase of the density. At $t \leq 0.5$ the role of the compressibility of the proper volume becomes very essential. For the model (31) the equation of state (EoS) as well as vapor-liquid phase equilibrium can be obtained. The results of the calculations are shown on Fig. 8 and display good correlation with the experimental data. The difference between the proposed model of compressible volume and the standard model with $b = \text{const}$ is illustrated on Fig. 7.

Similar results are obtained for other liquids with linear molecular geometry ($i = 5$) and low dipolar moments like $N_2$, $F_2$, $N_2O$, $COS$ for which the difference between low temperature values of the specific heat in coexistent phases does not exceed 2.

The liquids with polyatomic molecules $i = 6$ with hydrogen groups, like $H_2S$, $NH_3$ and $CH_4$ also show satisfactory correspondence with the data. For their homologs where the hydrogen atoms are substituted by some other element, e.g. $SO_2$, $NF_3$, $CF_4$ the model is less accurate in representing the behavior of $S_d$. It should be noted that in cases like $NH_3$ and $H_2O$ one could expect the greater deviations because of the strong associative properties of these liquids [28]. The main source of error for such liquids comes from the absence of the proper density dependence of the heat capacity contribution due to dipole-dipole interactions which is clearly seen from the comparison of the behavior of the gas branch of the heat capacity (see Fig. 11).

Note that in cases of $SO_2$, $NF_3$, $CF_4$ the parameter $\gamma$ takes the value $\gamma \approx 0.025$, which is smaller than that for their hydrated analogs $H_2S$, $NH_3$, $CH_4$. It correctly represents the meaning of $\gamma$ as the compressibility of the free volume. Indeed, from the physical point of view it can be explained based on the fact that the hydrogen group has lesser moment of inertia and thus supports almost free rotation of the molecule in a cell, which result in greater compressibility. Therefore for the molecules like $SO_2$, $NF_3$, $CF_4$ the influence of the neighbors is significant. For such liquids with polyatomic molecules further improvement can be reached with the help of the modification of the
Figure 8: The calculated binodal (solid) for the model (31) with (21) and $\gamma \approx 0.03$ and the binodal for different molecular liquids (dots)
Figure 9: The diameter of the entropy for different molecular liquids for the model \( \text{(31)} \) with \( \gamma \approx 0.03 \). The fluctuational shift for \( S_d \) is shown.
Figure 10: The specific heat along the binodal (solid) for the model (31) with (21) and $\gamma \approx 0.03$. The dots are the experimental data, the solid curves are the model EoS.
particle-in-a-cell approach [27, 29], where the contribution of the molecular motion in a cell formed by the neighbors to the specific heat is taken into account (see Fig. 11). Also the molecular shape could be taken into account using the extension of the CS approximation for the nonspherical molecules [30–32].

4. Discussion

In this work the main attention is focused on the behavior of the diameter $S_d(t)$ of the vapor-liquid binodal in term of the temperature-entropy for different molecular liquids. It is shown that $S_d(t)$ for low molecular substances with non-spherical molecules has the surprising non-monotone behavior. It is essentially different from that for the diameter $n_d(t)$ of the binodal in the terms of the temperature-density. The latter is a monotonous function of the temperature excepting, maybe, the narrow vicinity of the critical point. Such a difference is connected with more complicated physical nature of the entropy. It is the sum of the two independent contributions: one of which is proportional to the density and the second is formed by the irreducible many particles correlations as well as the rotational and vibration degrees of freedom. At the same time the peculiarities of the diameter $n_d(t)$ of the binodal is mainly determined by the thermal expansion effects, which are very different for liquid and vapor phases.

In the work it is shown that for low molecular liquids the non-monotone behavior of $S_d(t)$ is caused in the first place by the rotational motion of non-spherical molecules. The molecular motion influences also on such important molecular characteristics as the excluded volume in the equation of state for a system. Due to this the behavior of the entropy diameter is strongly connected with the EoS. The modified van der Waals EoS with the excluded volume, which is dependent on the external pressure is proposed. The corresponding generalization of the ideal gas expression for the entropy is given too. It was shown that the diameter of the entropy and the vapor and liquid branches of the binodal are self-consistently and successfully described on the same basis. In connection with this we want to emphasize that the self-consistent reproduction of the $PVT$-data and the diameter of the entropy is the weight criterion for the modeled EoS.

Our consideration of these questions leads to necessity to construct the rigorous statistical theory for the description of the rotational motion of
Figure 11: The calculated (solid) binodal, specific heat and the diameter of the entropy for the model (31) with (21) and $\gamma \approx 0.025$ for different molecular liquids with $i = 6$. The fluctuational shift for $S_d$ is shown.
molecules and, in particular, for the clear establishing of the $P, T$-dependence for the excluded volume in an EoS.

The many-particles contributions to the entropy are especially important for liquid metals, first of all for Cs, Rb and Hg. Here the difference in the interparticle interaction is caused by the strong reconstruction of their electronic subsystem. Therefore the analysis of the temperature dependence of $S_d(t)$ for them is also very important.

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