SOFT MATTER

BINODAL DIAMETER FOR ATOMIC AND MOLECULAR LIQUIDS IN TERMS OF ENTROPY

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The behavior of the diameter of a liquid–vapor coexistence curve has been studied in terms of the entropy S_d for various classes of liquids, namely, atomic, molecular, polar, and nonpolar ones. The research has been carried out by analogy with the studies of the parameter concerned in terms of the density. It has been shown that the behavior of S_d far from the critical point is governed by the rotational degrees of freedom and the excluded volume effect. An equation of state for relevant liquids which takes the indicated effects into account has been proposed.

1. Introduction

The variety of substance properties stems from the specificity of a particle-to-particle interaction. The latter practically does not depend on the phase state of the substance, provided that no substantial reconstruction of the electron spectrum of the substance takes place at the phase transition associated with structural variations of atomic or ionic positions [1, 2]. Let us consider the case of liquid systems, where, unlike crystalline solids, the symmetry of correlation functions coincides with that of the interparticle interaction (uniformity and isotropy). In this case, it is possible to classify liquids with regard for the kinds of particles that enter into the Hamiltonian of a system as interacting objects. Such a classification has been proposed in works [3, 4] and distinguishes atomic, molecular, ionic, and ion-electronic liquids. In our opinion, being appended by the known principle of corresponding states, such a classification is rather complete. However, it requires some specification, because, even in the simplest case of liquefied inert gases, there can appear effects associated with the for-

mation of bound states and molecular complexes [5]. As a result, there emerges a class of mixed liquids which demonstrate deviations from the law of corresponding states [6]. Note that the same complexes also arise, e.g., in the case of ion-electronic liquids (say, NaCl melts), where the presence of a neutral molecular component substantially modifies both the quantitative and qualitative physical properties of the system [7]. This situation is associated with the fundamental problem of description of thermodynamically incomplete systems, where the Hamiltonian depends, in fact, on the thermodynamic state of the system [8]. Such a situation is typical of ion-electronic systems, because a reconstruction of the electron subsystem, which accompanies a change of the density, gives rise to a modification of the interaction potential. Bearing all that in mind, let us try to analyze those physical quantities, whose behavior is governed by the type of interacting particles and their interaction. For instance, in systems with free charge carriers, the conductivity is sensitive to variations in the electron-ion interaction, but if the metal–insulator transition takes place, another convenient physical quantity should be searched for. As is known from studies of liquid metals, such a sensitive parameter is the asymmetry degree of the phase-equilibrium curve [2]. As a rule, it is characterized by the order parameter diameter

$$\varphi^{(d)}(t) = \frac{1}{2}(\varphi^{(l)}(t) + \varphi^{(g)}(t)), \qquad (1)$$

where $\varphi^{(i)}(t)$ $(i = l, g)$ are the order parameter values in the liquid and gas branches of the coexistence curve, and $t = T/T_c$. In the case of liquids, the density n is usually used as an order parameter.
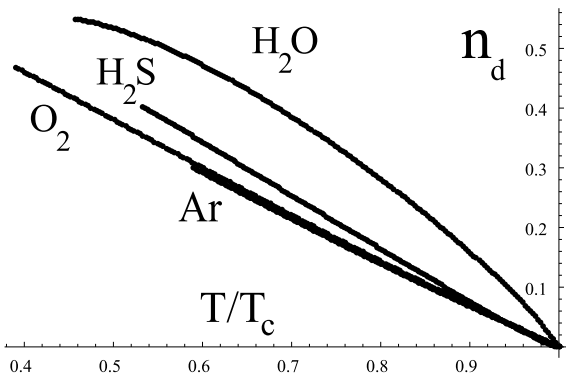
Fig. 1. Coexistence curve diameter in terms of the density for various molecular liquids [11]

Fig. 2. Coexistence curve diameter in terms of the density for molecular liquids C_6H_6 and SF_6 [11]

In this work, the behavior of the binodal diameter has been studied in terms of the entropy S_d for basic classes of liquids and in the temperature interval between the ternary and critical points. The work structure is as follows. In the next section, the peculiarities in the behavior of the diameter of a liquid-vapor coexistence curve in terms of the entropy are considered for atomic and molecular liquids. Section 3 presents a model that considers the excluded volume effects which are generated by quasifree rotations of molecules in the liquid phase. The model is demonstrated to adequately reproduce the behavior of the diameter of a liquid-vapor coexistence curve in terms of the entropy in a wide temperature interval. The behavior of such a diameter for ion-electronic liquids is considered in the next section. Conclusions are formulated in the final section.

2. Behavior of the Coexistence Curve Diameter in Terms of the Entropy

Researches of a liquid-vapor coexistence curve asymmetry have the old story starting from the work by Cailletet and Mathias [9], in which the law of rectilinear diameter was obtained empirically (see also work [10] and the references therein):

$$n_d = \frac{\tilde{n}_l + \tilde{n}_g}{2} - 1 = A\,\tau\,, \qquad (2)$$

where $\tilde{n}_i = n_i/n_c\,(i = l, g)$, n_l and n_g are the densities of the liquid and gas phases, respectively, which are reduced by the critical density n_c. It is clear that this law is approximate, but it is well obeyed practically in the whole interval of temperatures between the ternary and critical points (see Figs. 1 and 2), except for a vicinity of the critical point.

The order parameter diameter is a characteristic of the asymmetry of a coexistence curve. It physically arises
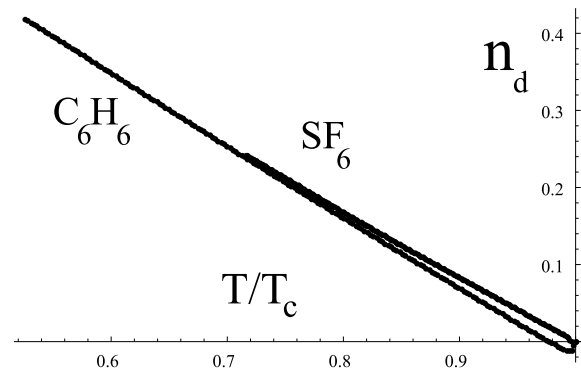
owing to a difference between the characters of thermal motion in the gas and liquid phases. It is clear that an evident characteristic of the coexistence curve is the density which determines the specific volume of a molecule. However, the density is a one-particle correlation function. From such a viewpoint, the choice of entropy as an order parameter is more informative, because the entropy is governed by correlation effects of all orders [12]. We define the the coexistence curve diameter in terms of the entropy in the following way:

$$S_d = \frac{S_l + S_g}{2} - S_c, \qquad (3)$$

where S_c is the entropy at the critical point, and S_l and S_g are the entropies of the liquid and gas phases, respectively. Then a more diverse behavior is to be expected for the diameter than for dependence (2). The analysis of experimental data (see Figs. 3 and 4) confirms this hypothesis.

Really, the diameter of a liquid-vapor coexistence curve in terms of the density is a straight line for atomic and molecular liquids in a wide interval of temperatures. At the same time, the diameter of a liquid-vapor coexistence curve in terms of the entropy is a straight line for one group of molecular liquids and not a straight line for a considerable group of molecular liquids and argon.

The comparison of the S_d-behavior for argon, as a typical representative of atomic liquids, with those for other liquids reveals a correlation between the molecular nonsphericity and a nonmonotonous character of the temperature dependence of S_d. Note that the contribution of rotational degrees of freedom to the entropy is substantial for nonspherical molecules.

The behavior of the binodal diameter in terms of the entropy at a removal from the critical point can be qualitatively explained by a competition of two contributions:
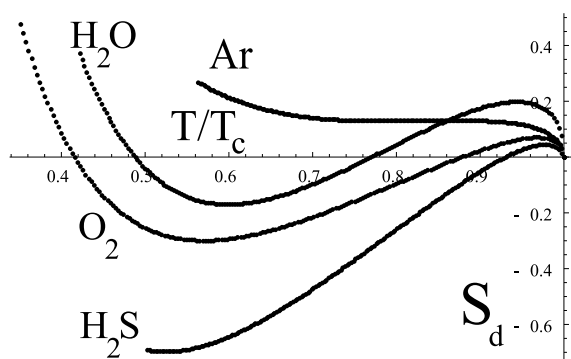
Fig. 3. Coexistence curve diameter in terms of the entropy for various molecular liquids [11]

a growing contribution of the gas phase entropy which approaches the contribution of the ideal gas at low densities,

$$S^{(id)}(T) = c_v^{(id)} \ln \frac{T}{T_c} - \ln \frac{n}{n_c}, \quad c_v^{(id)} = \frac{k}{2}, \qquad (4)$$

and a contribution of the liquid phase which decreases with the temperature reduction because of the liquid density growth. Hence, the nonmonotonous behavior of S_d is a consequence of the counteraction of an increase in the ordering of the liquid phase, as the temperature decreases, against the enhancement of a chaotic character of the gas phase. This conclusion is confirmed by the analysis of the excess entropy $S^{(ex)} = S - S^{(id)}$ and the corresponding diameter $S_d^{(ex)}$. The results of calculations are presented in Fig. 5. As we see, the excess entropy, which is exclusively defined by correlation contributions, really acquires the universal character for liquids of various types.

As was mentioned above, the behavior of the coexistence curve diameter in terms of the entropy reflects variations in the character of rotational motion of molecules in the phase liquid, which accompany a density change. Moreover, due to a crucial role of the heat capacity in the formation of a slope of the diameter S_d, the slope is sensitive to the number of degrees of freedom of rotational motion, which take part in the thermal motion in the liquid phase. On the basis of this fact, a detailed analysis of the behavior of S_d was carried out in work [6] for liquefied inert gases. The observation of a weak nonmonotonous dependence for S_d allowed one to confirm the conclusion about the existence of dimers in the liquid phase of liquefied inert gases and to evaluate the dimerization degree by examining the contribution of dimers to the heat capacity. In the limiting cases of essentially nonspherical multiatomic molecules, such as C_6H_6 and

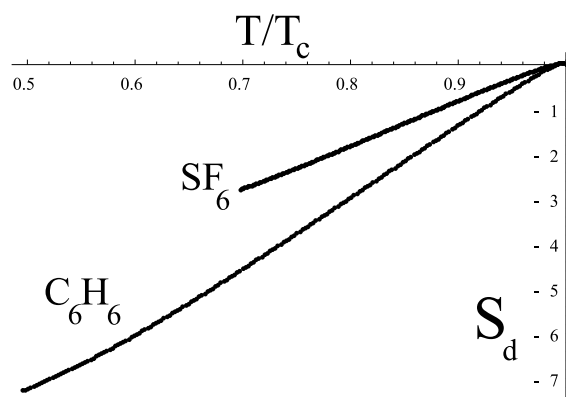Fig. 4. Coexistence curve diameter in terms of the entropy for C_6H_6 and SF_6 [11]

SF_6, the contribution of the liquid phase ordering to the entropy considerably exceeds a corresponding contribution of the configuration disorder to the gas phase entropy (Fig. 4). Whence, one may draw a conclusion that, in the case of such liquids, a considerable contribution to the heat capacity stems from both the liquid phase ordering, owing to a rotational motion restriction, and the excitation of internal molecular vibrations.

To explain the behavior of the binodal diameter in terms of the entropy quantitatively, we use the basic thermodynamic representation of the entropy ($k_B = 1$),

$$S = S_c + c_v \ln \frac{T}{T_c} + f(n) - f(n_c), \qquad (5)$$

where c_v is the specific isochoric heat capacity, and $f(n)$ is the density function which is defined by the equation of state of the substance. Using Eq. (5), we obtain

$$S_d = \frac{c_v^{(l)} + c_v^{(g)}}{2} \ln \frac{T}{T_c} + \frac{f(n_l) + f(n_g)}{2} - f(n_c). \qquad (6)$$

As we see from Eq. (6), the behavior of the coexistence curve diameter in terms of the entropy is governed to a great extent by the dependence of the entropy on the density which is reproduced by the function $f(n)$. It is natural to simulate the behavior of the coexistence curve diameter in terms of the entropy in a corresponding temperature interval on the basis of the Van der Waals equation or a similar one which makes adequate allowance for own particle dimensions. Note that the effect of a liquid phase entropy reduction owing to a deviation of the repulsive potential symmetry from the spherical one – i.e., in fact, due to the nonsphericity of a molecular core – was marked in work [13], where the consideration of this effect based on the modified Carnahan–Starling
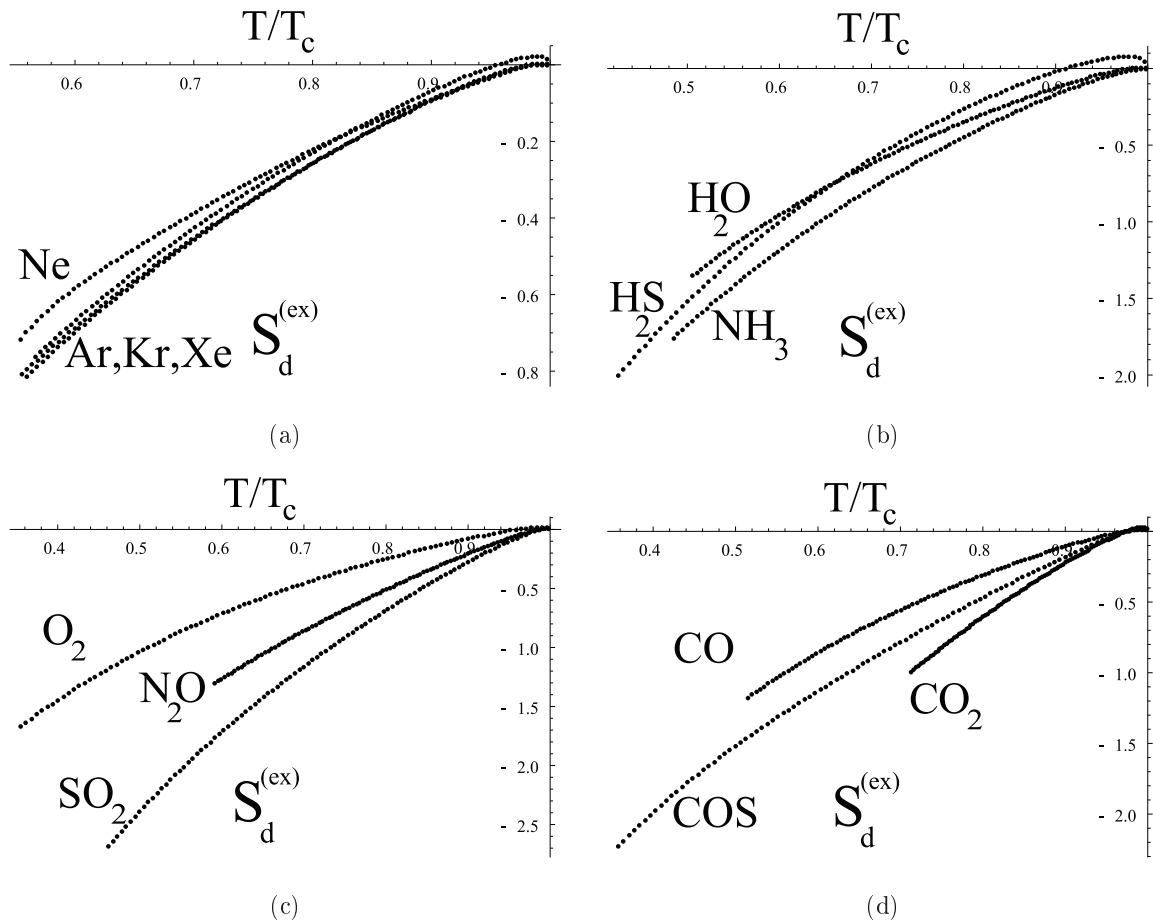
Fig. 5. Coexistence curve diameter in terms of the excess entropy $S_d^{(ex)}$ for (a) atomic (Ne, Ar, Kr, Xe) and molecular (polar and nonpolar) liquids, (b) H_2S, H_2O, NH_3, (c) SO_2, N_2O, O_2, and (d) CO, CO_2, COS, according to the data of work [11]

equation for rigid spherocylinders was confined to the low-pressure range. Since it is the coexistence curve diameter in terms of the entropy that is sensitive to such an effect of a liquid phase entropy reduction, it is of interest to reproduce the behavior of this quantity. In the next section, we formulate a model which quantitatively reproduces the features in the behavior of the binodal diameter in terms of the entropy for atomic and molecular liquids.

3. Model of Compressible Excluded Volume

The equation of state for simple molecular liquids can be represented in the form [14, 15]:

$$p = p_+(n, T) + p_-(n, T), \qquad (7)$$

where p_+ is the the pressure component associated with a repulsive interaction. In the Van der Waals model,

$$p_+ = \frac{p_{id}}{1 - b\,n}, \qquad (8)$$

where $p_{id} = n\,T$ is the pressure of the ideal gas. Another component in Eq. (7), p_-, stems from gravitation, and it can be chosen in the form

$$p_- = -a\,n^2 . \qquad (9)$$

Notice that representation (7) is valid for a wide class of potentials that allow the additive representation as the sum of a short-range repulsion potential and a long-range gravitation potential. As was shown in work [16], the equation of state (7) can be formally represented as the Van der Waals equation,
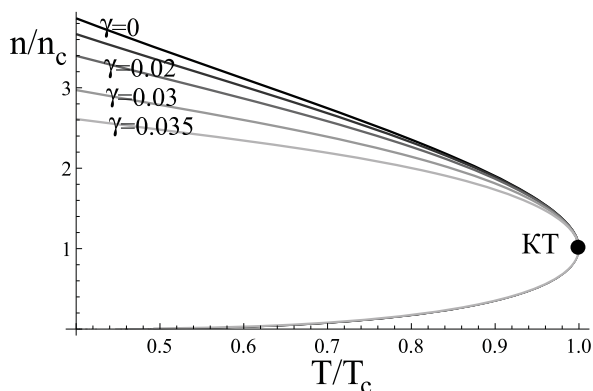
$$p = \frac{n\,T}{1 - b\,n} - a\,n^2 , \qquad (10)$$

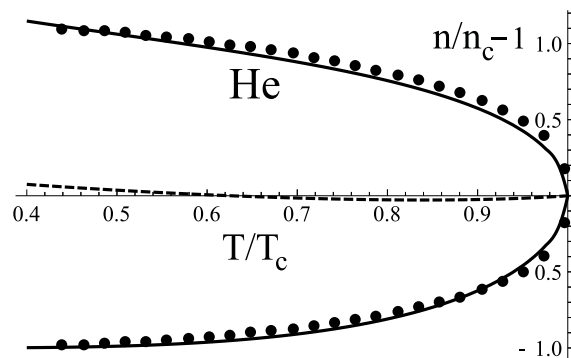Fig. 6. Binodals for model (16) at various values of the parameter γ

Fig. 7. Binodal for helium in the framework of model (16) with $\gamma \approx 0.04$ (solid curve), the diameter (dotted curve), and experimental data (points)

where the parameters a and b look like

$$a = -\frac{2\pi\sigma^3}{3} T \int\limits_{\sigma}^{+\infty} dr\, r^3\, y(r, n, T)\, f'(r, n, T)\,, \tag{11}$$

$$b = b_0 \frac{y(\sigma, n, T)}{1 + b_0\, n\, y(\sigma, n, T)}\,. \tag{12}$$

for spherically symmetric potentials. Here, $b_0 = \frac{2\pi\sigma^3}{3} = 4v_0$, v_0 is the volume of a rigid core of the diameter σ, $f = e^{-\beta v(r)} - 1$ is the Mayer function, $y(r, n, T) = e^{\beta v(r)} g(r, n, T)$ is the so-called void function [15], and $g(r, n, T)$ is the pair distribution function. Actually, the form of p_+ and, accordingly, the meaning of the parameter b are defined by the dependence of a contact value of the pair function at the rigid core distance:

$$p_+ = p_{\rm id}\,(1 + b_0\, n\, y(\sigma, n, T))\,. \tag{13}$$

For instance, in the Carnahan–Starling approximation which well reproduces the behavior of dense liquids [17], the following expression should be used for the determination of the parameter b instead of formula (8):

$$\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} = 1 + n\, b_0 y(\sigma, n, T)\,, \quad \eta = nb/4\,. \tag{14}$$

The solution of Eq. (14) determines b as a function of other parameters, in particular, the pressure. The inclusion of liquids with non-spherical skeletons into consideration makes analytical calculations even more complicated. However, the physical meaning of the parameter b which determines the effective volume per one particle allows a simple physical model, which explains the behavior of the diameter of a liquid-vapor coexistence

curve, to be formulated. According to the aforesaid, let us try the following dependence of the parameter of effective molecular volume b on the density and the temperature:

$$b = \frac{b_0}{1 + \gamma\, p^{\rm (id)}}\,, \quad p^{\rm (id)} = \tilde{n}\, \tilde{T}\,. \tag{15}$$

The physical meaning of relation (15) is very simple, and, concerning the volume accessible to a particle, it is a simple reflection of the fact that the corresponding volume decreases as the pressure increases:

$$v = v_0(1 - \gamma\, p_{\rm id} + \ldots)\,.$$

The fact that we use only an ideal component of the pressure testifies that the correlations in the particle environment, which just determines a volume accessible to the particle, are neglected.

Therefore, the effective parameter b (15) can be used in the corresponding equation of state. Let us use a model, in which the part of the pressure that corresponds to the presence of a rigid core is selected in the Carnahan–Starling approximation. Then, the corresponding free energy looks like

$$F^{\rm (CS)} = F_{\rm id} + T\,\frac{b\, n\,(4 - b\, n)}{(1 - b\, n)^2} - a\, n\,, \tag{16}$$

where $F_{\rm id}$ is the free energy of the ideal gas. In this case, the critical point of the corresponding equation of state has the coordinates

$$\frac{T_c(\gamma)}{T_c(0)} = 1 + t_1\,\gamma + o(\gamma)\,, \quad \frac{n_c(\gamma)}{n_c(0)} = 1 + n_1\,\gamma + o(\gamma)\,,$$

with $t_1 \approx 4.5$ and $n_1 \approx 8.1$. The coexistence curves for Eq. (16) at various values of the parameter γ are given
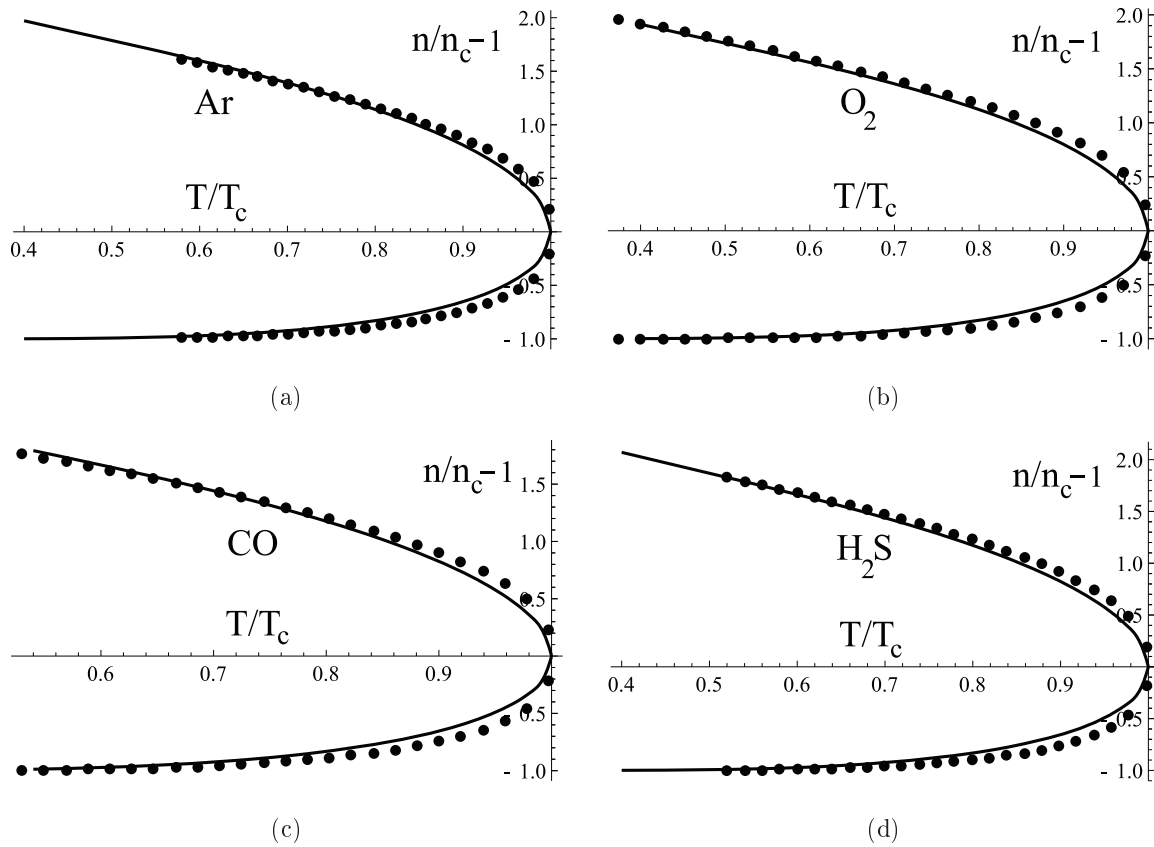
Fig. 8. Calculated binodals for Ar and various molecular liquids in the framework of model (16) with $\gamma \approx 0.03$ (solid curve) and experimental data (points)

in Fig. 6. As follows from the results of calculations, the growth of γ gives rise to a decrease of the degree of binodal asymmetry. This testifies in favor of the parameter γ interpretation as a compressibility, which is quite natural, because the asymmetry of a coexistence curve is associated with the absence of the Ising particle–hole symmetry. Note that, from this point of view, quantum liquids are the most symmetric. Really, as the results of calculations show, the optimum value of the parameter γ for helium equals 0.04 (Fig. 7), whereas $\gamma \approx 0.03$ for argon and the majority of classical molecular liquids (Fig. 8).

The entropy in model (16) is defined in a conventional manner:

$$S = -\frac{\partial F^{(\mathrm{CS})}}{\partial T}. \tag{17}$$

The results of calculations concerning the corresponding diameter for molecular liquids are depicted in Fig. 9.

As we see, the model well reproduces both the coexistence curve in terms of the density and the coexistence curve diameter in terms of the entropy, as well as the heat capacity along the coexistence curve. Note that it is owing to the temperature dependence of the parameter b that the behavior of the heat capacity adequately reproduces experimental results (see Fig. 10). It is clear that the fluctuation effects should be taken into account in a vicinity of the critical point. Really, the behavior of the coexistence curve diameter in terms of the entropy in the fluctuation region demonstrates features [18] which are related to large-scale fluctuations. Note that the line of the coexistence curve diameter in terms of the entropy is shifted (see Fig. 9). This displacement arises due to the fact that S_d is reckoned from the entropy value S_c at the critical point, which corresponds to the critical temperature T_c. Really, on the basis of Eq. (6), we obtain

$$S_d = \left(\tilde{C}_v^{(\mathrm{reg})} + C_v^{(\mathrm{fl})} \right) \ln \frac{T}{T_c} + \dots, \tag{18}$$

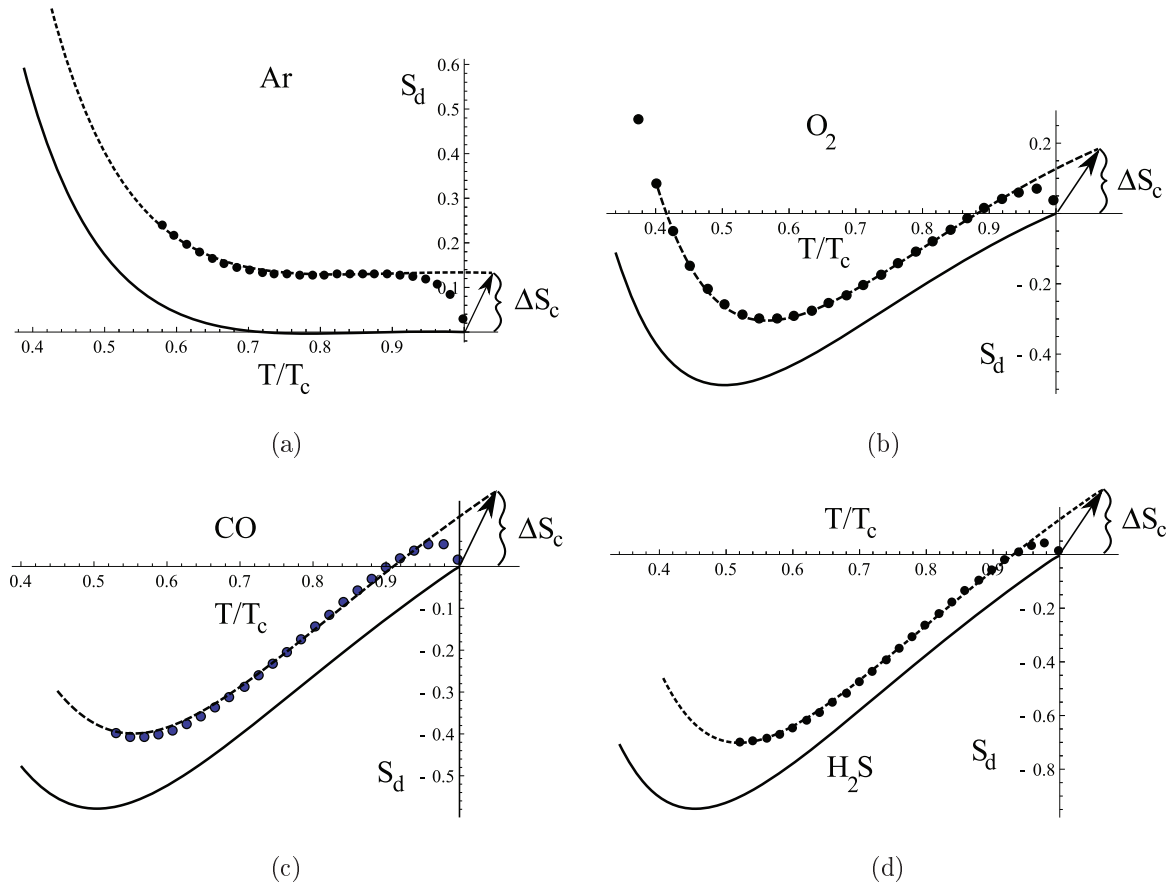$$\tilde{C}_v = \frac{c_v^{(v)} + c_v^{(l)}}{2},$$

Fig. 9. Calculated curves of the coexistence curve diameter in terms of the entropy for model (16) with $\gamma \approx 0.03$ (solid curve) and experimental data (points). Dashed curves correspond to the theoretical result obtained taking the fluctuation shift into account (see discussion in Section 3)

where the terms connected with the dependence on the density are not taken into account. Further calculations give rise to the formula

$$S_d = \tilde{C}_v^{(\text{reg})} \ln \frac{T}{T_c^{(\text{mf})}} + \tilde{C}_v^{(\text{reg})} \ln \frac{T_c^{(\text{mf})}}{T_c} +$$

$$+C_v^{(\text{fl})} \ln \frac{T}{T_c} + \dots \; . \tag{19}$$

Note that the fluctuation component of the heat capacity disappears beyond the fluctuation region. Therefore, the contribution of the mean field S_d becomes shifted along the T-axis, and its value obtains an increment

$$\Delta S \approx \tilde{C}_v^{(\text{reg})} \ln \frac{T_c^{(\text{mf})}}{T_c} \propto \frac{T^{(\text{mf})} - T_c}{T_c}.$$

Such a situation really corresponds to Fig. 9, because the temperature in the mean-field approximation is higher

than the corresponding value obtained with regard for fluctuations [19].

4. Conclusions

The behavior of the coexistence curve diameter in terms of the entropy has been considered for atomic and molecular liquids. The nonmonotonous behavior of the diameter of a binodal in terms of the entropy is demonstrated to be connected with a competition between two contributions to the entropy, each of them being associated with either the entropy or the density. On the contrary, the coexistence curve diameter in terms of the density has a monotonous behavior for those liquids.

In our opinion, ion-electronic liquids are of interest [20]. For alkaline metals, such as Cs and Rb, the behavior of the coexistence curve diameter in terms of the density is qualitatively identical to that for molecular
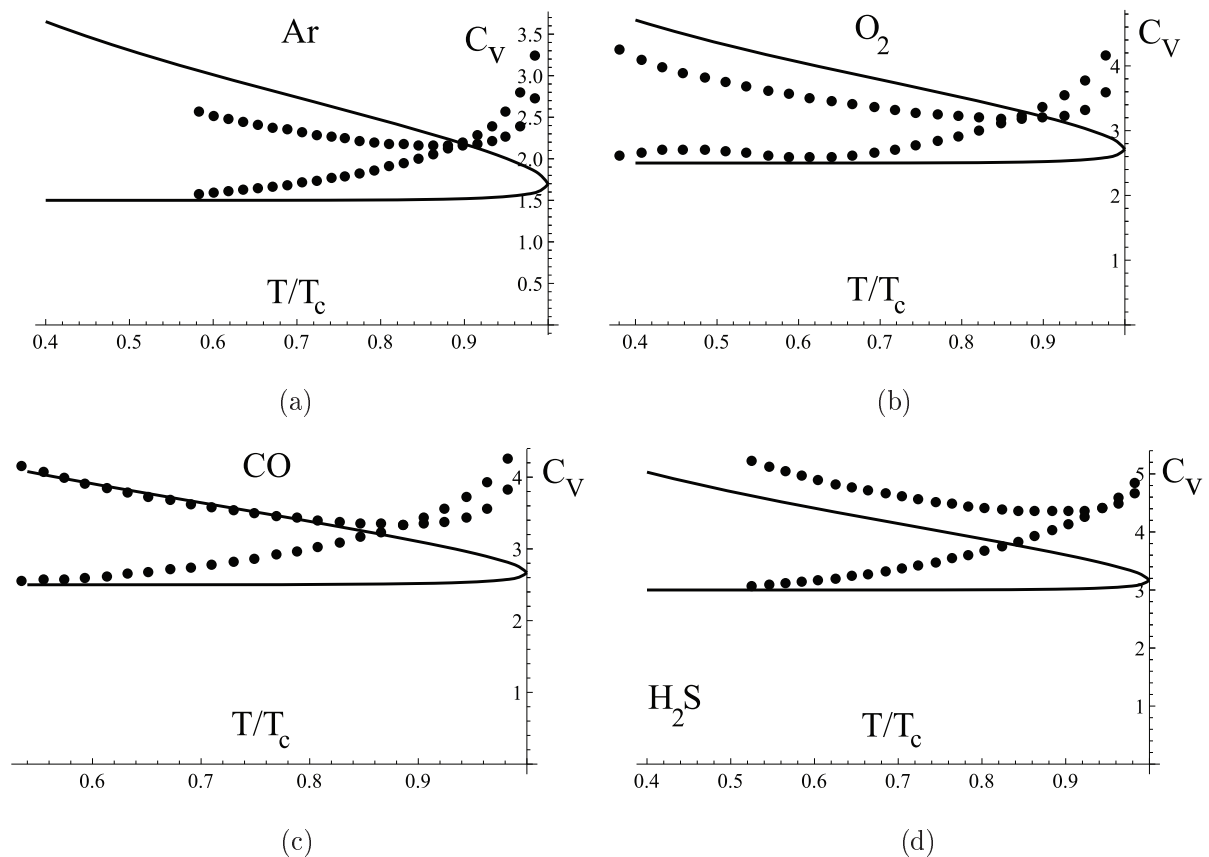
Fig. 10. Heat capacity along a binodal for model (16) with $\gamma \approx 0.03$ (solid curve) and experimental data (points)

liquids, although the corresponding coexistence curve is more asymmetric. At the same time, the coexistence curve diameter in terms of the density for mercury reveals a very nonmonotonous behavior [21]. Note that a number of the model equations of state [21–24] were used for the description of a liquid–vapor equilibrium in liquid metals. However, the consideration in those works was confined to the analysis of a binodal in terms of the density. In our opinion, the verification of those models with respect to their adequate reproduction of the entropy would be expedient, because the entropy is a more sensitive characteristic, in comparison with the density, of structural changes that are responsible for a variation of the electroconductivity character [25]. Such an analysis will be carried out in the paper to follow.

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ДІАМЕТР БІНОДАЛІ АТОМАРНИХ ТА МОЛЕКУЛЯРНИХ РІДИН В ТЕРМІНАХ ЕНТРОПІЇ

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Р е з ю м е

За аналогією з діаметром кривої співіснування рідина–пара в термінах густини для різних класів рідин, а саме: атомарних, молекулярних, полярних та неполярних, досліджено поведінку діаметра кривої співіснування в термінах ентропії S_d. Показано, що на суттєвій відстані від критичної точки рідини поведінка S_d визначається обертальним рухом частинок та ефектом виключеного об'єму. Для відповідних рідин запропоновано модель рівняння стану, яка враховує вказані ефекти.