

1. Introduction

The one-parameter law of the corresponding states $\Phi(\pi, \varphi, \tau, A) = 0$ based on the van der Waals equation of state (EOS). The first criterion for thermodynamic similarity (CTS) was the critical compressibility factor (CCF) $Z_c = P_c V_c / RT_c$. The CCF values are contained within a range of 0.290-0.270, forcing us to look for other personality characteristics. Several authors drew on the data on the saturated vapor pressure for this purpose. However, no one has obtained a general EOS that would include the newly introduced similarity criterion, the most popular of which was the Pitzer acentric factor ω_p . At the same time, CTS A by L.P. Filippov (LPF) [1] deserves special attention. That convinced the results obtained by us for the new model.

The first form (thermodynamic): $A = 100 \pi$ at $\tau = 0.625$. Here $\pi = P / P_c$, $\tau = T / T_c$, are the reduced pressure and temperature. Recently, it has been shown that the A form is associated with the van der Waals' EOS, which gives reason to consider it as a characteristic of a particular family of equations, which would include the EOS of the vdW. This could be the obtained one-parameter family of equations $\pi = \pi(\varphi, \tau, \beta(\chi), \alpha(\chi), Z_c(\chi), \chi)$ [2], into which it is possible to inscribe many EOS of the vdW-type. The parameter χ has a clear physical meaning (it compares the manifestations of the forces of attraction and repulsion), representing a new similarity criterion, uniquely determines all parameters of the given EOS, including CCF $Z_c = \frac{\chi}{\sqrt{(\chi+1)(\chi-1)+2\chi+1}}$. The expression $Z_c = 0.2563 + 0.0535 \lg A$ was obtained from the experimental data on the properties of substances. **The question** - How are the two criteria related?

The second form (molecular): $A = 4 - 8 \left(\frac{d}{d+\sigma}\right)^2$, σ is the size of the peripheral atom, d is the size of the molecule, $d = 2\rho$, ρ is the chemical's length bond. Let us draw attention

to the unrealized by LPF replacing A with a new parameter $\Omega = \left(\frac{d}{d+\sigma}\right)^2$. Note that then, in the assumed criterion, it would be logical to make the transition to the factor

$$\sigma/d, \Omega = \left(\frac{1}{1+\sigma/d}\right)^2$$

Now we will use the results that we have obtained in modeling the interactions of molecules in the shell model, where σ/d turned out to be the control parameter [3-5].

2. Intermolecular interactions. A polyatomic molecule from of bound atoms. Shell model

Consider the two simplest models for the polyatomic molecule. The first is a rigid structure made of atoms - point centers. The pair centers interaction describes the potential (12-6) L-J. The second model is an active, freely rotating molecule in the spherical shells package form. An atom bound in a molecule characterizes the individual shell's diameter (doubled the length of the chemical bond) and the interaction, which is described by the potential of spherical shells (PSS):

$$U_{S-S} = \frac{A_n P(r)}{r} - \frac{B_n P(r)}{r} \quad U_{S-S}(r, d) = \varepsilon_{S-S} \frac{(3r_m P_m^{(4)} + P_m^{(3)}) \cdot P(r) - (9r_m P_m^{(2)} + P_m^{(1)}) \cdot P(r)}{(9P_m^{(2)} \cdot P_m^{(2)} - 3P_m^{(4)} \cdot P_m^{(3)}) \cdot r}$$

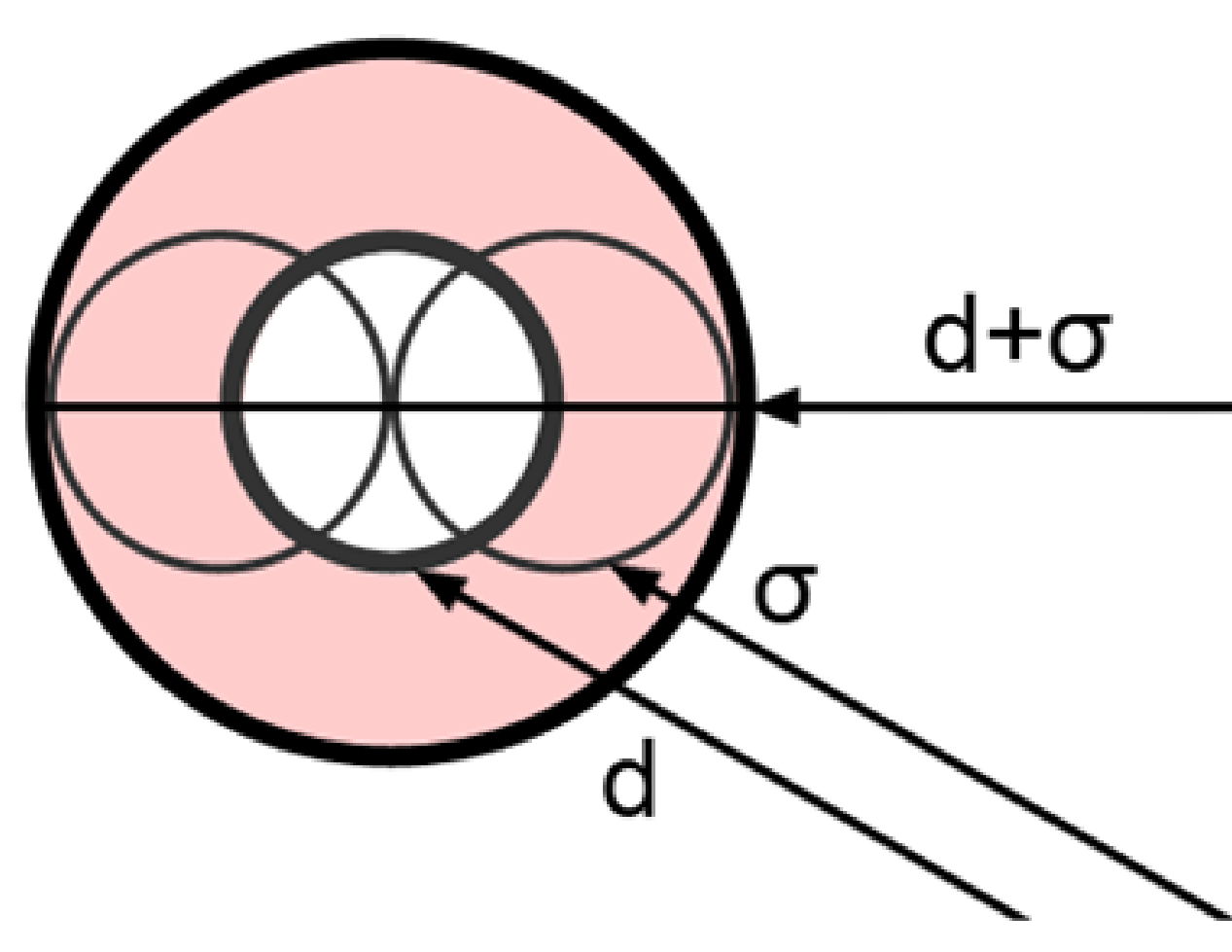
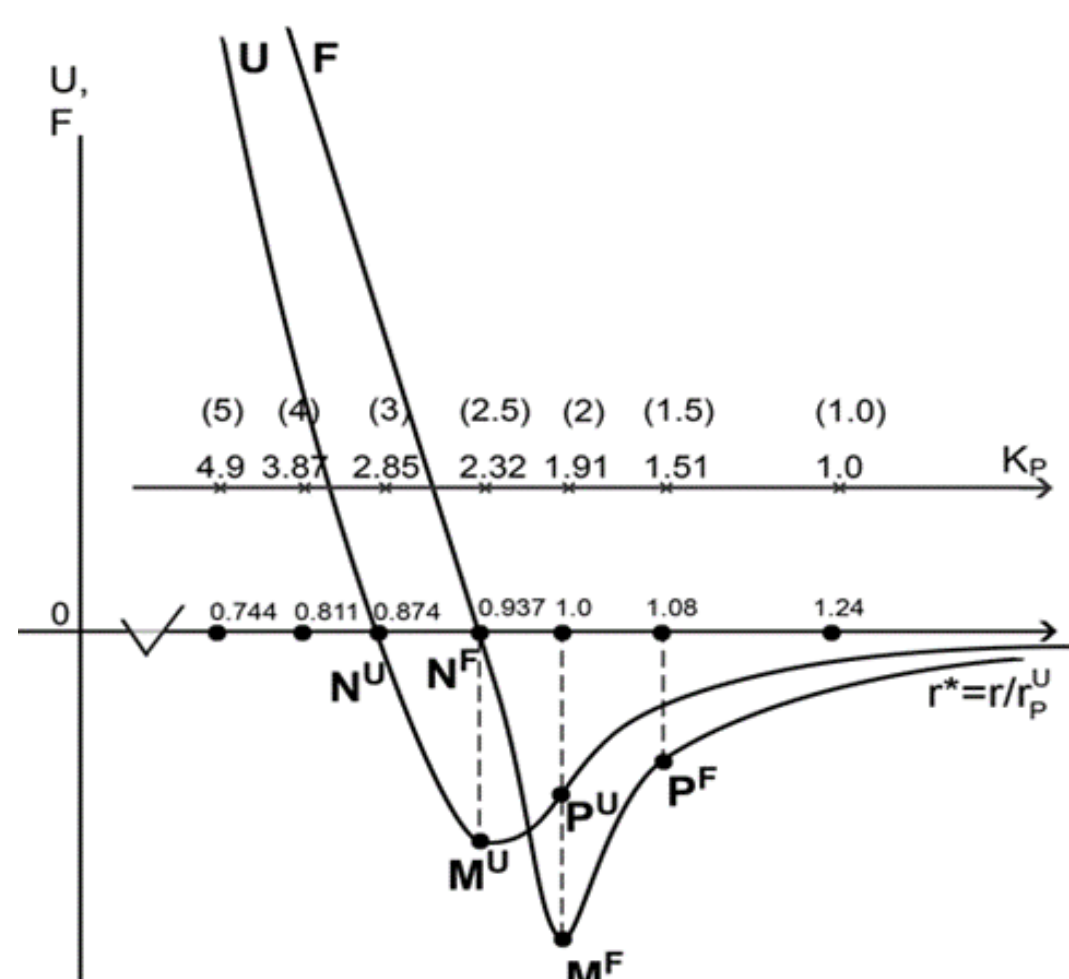
$$r \rightarrow r^* = r/d, \quad P(r) = d^{-N} \cdot P^*(r^*), \quad P^*(r^*) = (r^* + 1)^{-N} - 2r^{*(N)} + (r^* - 1)^{-N}$$

It is shown that the PSS is a one-parameter family of functions, the control factor of which is σ/d . The reduced parameters of the PSS - the coordinates of the singular points of the potential curve (PC), fixing the function's features - are determined solely by this factor. The singular points include the "standard" zero and minimum of the potential curve (PC), as well as the inflection points of the PC introduced by us for the first time in an explicit description. Calculated expressions for parameters obtained and tested. Globular molecules fit best into the model.

For the first time, a similarity between the coordinates of the PC's inflection point and the critical parameters - molar volume and temperature - has been established.

$$V_c = r_p^3, \quad T_c = \varepsilon_p / k$$

The results pose a question - what is the meaning of the factor σ/d ? It is logical to consider it as the most general characteristic of the object as a whole. $g_s = \sigma/d$ was called the "rigidity" of the shell.



Based on the calculated ratios, a chain hierarchy was obtained [6] that connects the effective proper volumes of model objects at 3 singular points (N, M, P^U) PC with the critical molar volume in the form: $V_c = 3b(r_0) = 2.5b(r_m) = 2b(r_p^U)$. The calculations were carried out for the particular case $g_s = 1$. With a more correct forecast, these values will vary - depending on the value of the MIF g_s . (Pay attention to the coefficients - they coincide with those known for the EOS—van der Waals and Diterichi).

Let us recall the central relationship between the critical molar volume and the geometric characteristics of molecules $V_c = 0.792 (d+\sigma)^3$, found by the LPF [1] and fulfilled with an accuracy of 1%. We were able to show that this expression transforms in $V_c = 1.51 b(r_p^F)$. LPF in its expression "groped" for another singular point P^F - the inflection of the force curve. In our model, this point appears as the only one, the coordinate of which does not coincide with the coordinates of three singular points PCs (see the figure on the left). Obviously, the resulting relationship complements the above hierarchy.

Calculations of the ratio of the energy coordinates at the inflection point of the force and PC showed that it depends on the potential (Mie (n-m)) and practically coincides with the **Guldberg number**, which fixes the ratio of the boiling point to T_c equal to 0.66.

This means that the found interaction features (singular points) are manifested in the fundamental properties of a substance, which are formed by the real molecule's general characteristic. **What is this characteristic**, which is reflected in the model by the rigidity of the shell?

Spherical shell model control parameter

Rigidity g_s - as a general characteristic of a dynamic spherical object - was introduced by us based on the representation of a polyatomic molecule in the form of a rotating electron-nuclear system, characterized by two dimensions: d_g (the size of the core formed by the configuration of nuclei) and d_{EH} (the size of the object as a whole, including electron

$$g_s = \frac{d_{EH} - d_g}{d_g}$$

shells):

Using the concepts of another composite model - a molecule as an organized system of atoms - we concretized this characteristic as follows (see the figure on the right):

$g_s = \frac{(d+\sigma) - d}{d} = \frac{\sigma}{d}$, σ is the effective size of a free atom (potential parameter (12-6)), d is the doubled length of the chemical bond of an atom entering the molecule (the diameter of the corresponding shell).

Considering the fundamental nature of the results obtained in the model, we defined the rigidity of the object as **MIF** - its maximum information-intensive factor, reflecting the nuclear-electronic device of a real molecule. Shell rigidity is its analog at the model.

3. Polyatomic molecule. Shell model. Approximating overlapping shells

The formula for the rigidity of a molecule is $g_s^m = 1 / ((nd-1)(1-\beta_a^m))$ [7]. Assumptions: the sizes of all the atomic shells are the same and they overlap equally. nd is the number of atoms in the direction of alignment of the maximum linear size of the molecule. As a rule, it is not equal to the number of atoms in a molecule. Based on a new formula for g_s and for A (g_s) and $Z_c(A)$, we will give a prediction of the SC. Suppose β can vary from 0 to 50%. Let us take into account that an atom in a molecule changes the size σ : $g_s^* = 0.8235 g_s - 0.08$,

$$1) nd=2, \quad g_s^* = \frac{1}{1-\beta_a^2} = \{1, \beta = 0 (g_s = \frac{\sigma}{d} = 1.3) 2, \beta = \frac{1}{2(g_s=2.5)}\}; \quad A = (2.58-3.45); \quad Z_c = (0.279-0.2845)$$

$$2) nd=3, \quad g_s^* = \frac{1}{2(1-\beta_a^3)} = \{0.5, \beta = 0 (g_s = 0.7) 1, \beta = \frac{1}{2(g_s=1.3)}\}; \quad A = (1.44-2.58); \quad Z_c = (0.2656-0.279)$$

For analysis of the data A, we will use the table from [6]. For $nd = 2$ our forecast A: 2.58 - 3.45. Following A values were found in the table: Br₂ -2.58, I₂ -2.75, F₂ - 3.17, Cl₂ - 3.1, N₂ - 3.50, CO - 3.4, HCl -2.6 (6), HBr -3.0 (2) ... All found values belong to this interval. For molecules with $nd = 3$, forecast A: 1.44-2.58. Were found: CO₂ -1.9 (6), N₂O - 2.6, SO₂ - 1.65, MoF₆ - 2.26, WF₆ -1.62; GeCl₄ -1.73, SiCl₄ - 1.71, SnCl₄ - 1.67, CF₄ - 2.19, CCl₄ - 2.06. Analysis of the data gives grounds to carry out such sorting.

Conclusion: the predicted intervals Z_c are very narrow, and the A values are realistic. The above estimates serve as a justification for the concepts of the model built.

Control parameter θ of the molecular level of the IPC model

Let's return to the new CS - the control parameter χ of model. The analysis showed its connection with the value θ : $\sqrt{1+\chi} = \theta$, $\chi = \theta^2 - 1$. All parameters of the IPC EOS are obtained

in the form of simple function θ , including the CCF: $Z_c = \frac{1+\theta+\theta^2}{(1+\theta)^2}$.

The new parameter also turns out to be the governing one for the IPC model [8].

The physical meaning of the parameter θ is also associated with the manifestation of the force, but already at the molecular level. The parameter θ is equal to the ratio of the diameters of two spherical volumes - one of them exhibits a point center, when the attraction does not make allowance in the system, and the second is the resulting volume, which manifests itself

center as a result of the action of both forces: $\theta = \frac{d^{et}}{d^{eff}}$.

It is this molecular level parameter that determines the parameters of the reduced EOS.

4. Conclusion. Hierarchy of similarity criteria

We have two governing parameters of the molecular level, θ , and g_s . Let us compare the results of calculating, carried out in two ways: the first - Z_c as a function of θ , the second

- for the given values of g_s , we will find A and from it Z_c . Conclusion: for the values of g_s close to 1 (this means that the approximation of touching shells is used), there is practical equality $\theta = 1 + g_s^*$. Two control parameters have a similar meaning - the ratio of two sizes - "large" and "small" - for point centers these are imaginary, effective sizes, and for spherical shells - partially "real" (for example, the length of the chemical bond)

$$\theta = \frac{d^{et}}{d^{eff}} = \frac{d + \sigma^{ef}}{d}$$

The established similarity makes it easy to answer the question of how A and the control parameters θ are related. Let us write a new expression for $A = 4 - 8 (1/\theta)^2$.

For the first time in a straightforward model, a chain-hierarchy of similarity criteria built:

The degree of overlapping β of atoms in a molecule, together with the number of atoms that determine the characteristic size of the "molecule" (its "length"), determines the "rigidity" g_s of the object, its maximum information-intensive factor. In turn, the MIF, which forms the nature of the interparticle interaction, determines the parameter θ - the result of the manifestation of the forces of interaction between two model molecules. The value of the parameter θ makes it possible to calculate the control parameter χ , the critical compressibility factor Z_c (or the critical coefficient K_c) and similarity criterion A, which are the control parameters of various equations of state:

$$(\beta_a^m, n) \rightarrow g_s \rightarrow \theta \rightarrow (\chi) \rightarrow Z_c \leftrightarrow K_c \rightarrow A$$

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