On round dates, acute issues and solving problems of low-parametric equations of state by logical abduction

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Abstract. Within the framework of a simple molecular thermodynamic model, the problems of comparing equations of state (EOS) and the choice of analogs in three sets are analyzed: equations based on the model of interacting point centers, van der Waals type equations, and Martin equations derived from volume translation. A method for the selection of EOS was proposed and approved by calculating the critical isotherms Ar and C4F8. According to the results of the PV calculations, the selected EOSs turned out to be better than known those of Peng-Robinson, Martin, Redlich-Kwong. On the basis of a new characteristic of the equation, a parameter comparing the configuration contributions, a method has been proposed for choosing EOS-analogs in different families. An explanation is given for the impossibility of describing equally well with one equation two states with a reduced density of 2 and 3/2. The results obtained for the EOS of the new model confirm its adequacy in full accordance with the method of abduction.

1. Introduction
Low-parametric equations of state (EOS) are still in demand – as a calculation tool due to its simplicity and economy and as a research tool that can be associated with the molecular fundamental level. Therefore, obtaining new, improving known and choosing the most optimal, as well as EOS-analogues – still remain relevant. Our research relates to all the components of a big problem.

1.1. About round dates
The famous van der Waals EOS (vdW) soon (2023) will turn 150 years old. The equation is a two-term, two-parameter, cubic. It is still emphasized that the van der Waals model is a more general concept than the EOS, since it includes molecular representations. By the middle of the past, the 20th century, it was supplanted by multi-constant equations. Interest concerning low-parametric EOS has been revived by the work of [1] Redlich–Kwong. Their cubic, two-member, two-parameter EOS, which turned out to be more successful in the calculations, will celebrate its 70th anniversary in 2019. Hundreds of unconnected empirical modification of the two EOS, are now known as EOS vdW-type.

EOS Clausius after a year and a half it will be 140 years. Cubic, two-member, three-parameter (first). After 100 years after the appearance of the original equation, interest in Clausius’ EOS
revived J. Martin. The following year, the EOS \cite{2} in functional form by Clausius, modified by Martin on the basis his own idea of volume translation \cite{3}, will be 40 years old.

Given that the age of many EOS is quite respectable and, it would seem, they have been thoroughly studied, there are questions that are not answered and cannot be obtained on the standard approach.

1.2. About issues
In the system approach, the thermal EOS should be considered as a manifestation of the molecular $\mu$-model, on the basis which it is built. On the $\mu$-model of the authors, only van der Waals spoke. His chief excellence (he thought so), since ideas about molecules in the form of rigid spheres, attracted to each other, were used by him when the existence of molecules was not yet proven.

At the same time, the authors of the new EOS, which essentially are empirical modifications of the vdW EOS, declare that the meaning of the two parameters $a$ and $b$ of their equations is the same as that of the vdW. In other words, they shift the responsibility for the physics of the model to van der Waals. As a result, the main drawback and problem of the vdw-type EOS is today considered to be precisely the unmanifested connection with the micro level. Moreover, manyf questions have accumulated to the vdw-type EOS. At least require an answer: a question about the correct meaning of the first contribution to a vdw-type EOS, the problem of the third parameter is its meaning and the implications of introducing a new EOS, the correct meaning of parameter $b$ in the Redlich-Kwong EOS, and an explanation why its value is two times less what gives the “correct” formula of the vdW \cite{4}, the question of Abbott \cite{5} about the meaningless numbers that define a successful EOS.

Separately, there is the problem of comparing and choosing the optimal EOS, as well as the search for EOS-analogues. Recently, we connected to the analysis of the EOS model of Martin, who paid much attention to this particular problem \cite{2}. In this regard, we add a list of questions without an answer. We include in it the fact that it is impossible to describe with one cubic EOS equally good states with a reduced density (in units of $\rho_{cr}$) 2 and 3/2. Moreover, if one state is described well, then the error in describing the second one may be 100% or more. This is emphasized by Martin \cite{2} and noted by Prauznitz \cite{4}.

1.3. Method of logical abduction
The situation is entirely consistent with the method of logical abduction \cite{6}. There is a van der Waals model of hard spheres and a set of vdw-type EOSs. There are questions that are impossible to get answers. Requires a new hypothesis, a new model. And if she allows to answer these questions, she is counted as adequate – as the next step in the extraction of knowledge.

In this paper, we present some of the results obtained in the development of a new molecular thermodynamic model, with an emphasis on the problems outlined above.

Analysis of many EOS has led to the conclusion that the model of the vdW is not the simplest. The simplest model is the point centers (PC), the interaction of which is described by central potentials. There is a problem of obtaining a EOS based on the model of interacting point centers (IPC). We succeeded in using a minimum of information about the EOS of non-interacting spheres and PCs and the generally accepted assumption that a pair of rigidly repelling PCs separated by a distance $d$ is equivalent to a pair of contiguous but non-interacting hard spheres of the same diameter.
2. The new model – EOS based on the molecular model of interacting point centers

For lack of space, we present here only a few basic relations of the IPC model. All the details are in our works (see on the site http://www.csmos.ru). The first of the IPC EOS [7] reflects the following character of the interaction of the point center – rigid repulsion and optimized attraction (the condition of weakness is removed):

\[ P = \frac{RT}{V} + \frac{RTb}{V(V-b)} - \frac{a}{V(V+c)}. \]  

(1)

\( V \) is the volume of the system, which is fully accessible to the PC when there is no interaction between them: \( V = V_f \) (no/int). The first contribution is the equation of noninteracting point centers, the other two are configurational, related to taking into account repulsion and attraction of PC.

In the new three-term EOS IPC, all three parameters have a meaning associated with the manifestation of intermolecular forces. The introduced parameter \( \chi = c/b \), comparing the manifestations of the forces of attraction and rigid repulsion of the PC with respect to the available volume, turned out to be the only controlling parameter of the thermodynamic level [8], since it determines all three parameters of the reduced EOS and \( Z_C \), converting the original three-parameter equation into a one-parameter EOSs family:

\[ \beta = b/V_C, \quad \sigma = c/V_C, \quad \alpha = a/RT_C V_C, \quad Z_C = P_C V_C/RT_C, \]

\[ \beta = \frac{1}{\chi} \left( \sqrt[3]{1+\chi} - 1 \right), \quad \alpha = \frac{\chi}{\chi^2 + 1} \left( \sqrt[3]{(\chi + 1)(\chi - 1)} + 2\chi + 1 \right), \]

\[ \sigma = \left( \sqrt[3]{(\chi + 1)} - 1 \right), \quad Z_C = \frac{\chi}{\sqrt[3]{(\chi + 1)(\chi - 1)} + 2\chi + 1}. \]  

(2)

From this it follows: the parameters \( \alpha, \sigma, \beta \) and \( Z_C \) cannot be considered as independent values.

3. On the inclusion in the physically justified model of the IPC EOS of vdw-type

At first, two sets – a vdw-type EOS and an IPC model, were considered separately. However, information on unrelated to each other, the accumulated over many years, has become a problem of its use. It turned out that many vdw-type EOS can be reformatted into IPC EOSs [9]. And it is especially easy to do this for the EOSs, the first contribution of which has the form \( RT/(V-b) \), to which we return the true meaning of the EOS non-interacting hard spheres; and further from non-interacting spheres (on the left, (3)) go to the model of rigidly repelling PCs (on the right, (3))

\[ \frac{RT}{V-b} = \frac{RT}{V} + \frac{RTb}{V(V-b)}. \]  

(3)

And finally, we bring the attractive contribution to a unified form, which is characterized by the EOS IPCs: \( a/V(V+c) \). In this case, the parameter \( c \) can be constant or depend on the density.

On the meaning of the parameter \( c \) note the following. When deriving the EOS in the IPC model, the concepts of two effective spherical volumes \( b \) are used [10]. One of them, \( b^h \), shows a center when the system does not take into account (or does not manifest) attraction (as in EOS (3)) and the second, \( b^{ES} \), is the resultant effective volume that manifests itself in a point center as a result of repulsion and attraction. That it is included in the resulting EOS (1). Consequently, their difference is the result of the manifestation of attractive forces, it determines the value of the parameter \( c \)

\[ c = b^h - b^{ES}. \]
As a result of the transition between models (from spheres to centers), all the parameters of the reformulated EOS acquire a certain meaning, and we get a group of vdw-type EOS belonging to a physically based IPC model. In this case, they are no longer independent EOSs, but represent the equations of one family, the difference between which at the macro level is determined by the difference in the ratio of intermolecular forces, which is ensured by different values of $\chi$.

The new parameter $\chi$ is determined directly by the form of the EOS of the condition: $c = \chi b$. Consider the case when $\chi$ is a constant. The Redlich-Kwong EOS meets this condition. The transition to the IPC family for it means the form in which the parameter $\chi = 1$. This gives the ratio for the parameters of the resulting EOS (1): $\chi = c/b = 1$, where $c = b - b^{ES}$, and in the denominator, the value of the parameter $b = b^{ES}$. As a result, we get $b/b^{ES} = 2$. Conclusion: the relation noted by Prauznitz in [4] is a EOS property, it will be such not only for argon.

4. Comparison and selection of the optimal EOS

Until recently, our interest was focused on the analytical capabilities of the IPC model. For all the above questions, we received answers. Recently, a check was started on the design capabilities of the model, during which it was shown that the new IPC EOSs not only turn out to be “better than” Martin, but also open another interesting opportunity when comparing the quality of simple equations.

4.1. Method of selection of the EOSs IPC

The first important result in the IPC model are formulas for the parameters of the EOS, determined by a single value of the parameter $\chi$. The fact that they form a consistent set allows us to build on their basis a method of choice in the IPC family of EOSs with a specific value of $Z_C$. Algorithm of actions: by the known value $Z_C$ of a particular substance, we find the value of the parameter $\chi$. Using the restored value, using the formulas (2), we calculate three parameters of the selected EOS.

For lack of space, we only mention another variant of the technique, when $c$ depends on the density and the parameters of the general EOS [11] are determined by a set of two generating numbers $k$.

4.2. Approbation of the technique

From the known value of $Z_C = 0.291$, we found that the parameter $\chi = 3.3$. The following parameters correspond to it: $\beta = 0.18973$, $\sigma = 0.62615$, $\alpha = 1.53374$. The given EOS IPC for the critical Ar isotherm

$$P_R = \frac{1}{0.291V_R} \left[ 1 + \frac{0.18973}{V_R - 0.18973} - \frac{1.53374}{V_R + 0.62615} \right].$$

The result of the calculation according to the EOS (4) and deviations in percent of the EOS selected by Martin reference in [2] are in table 1, column 3. Here are the results for Martin EOS, who chose as the best translated EOS for argon (in the form given relative to critical parameters)

$$P_R = \frac{T_R}{Z_C V_R - 0.082} - \frac{27/64 T_R^{0.55}}{(Z_C V_R + 0.043)^2}.$$

Comparison in [2] showed that the best calculations for the two-member EOS (5) coincide with the results for the Redlich-Kwong EOS. That is why it is included in the table.
Table 1. The results of comparisons for the critical isotherms of different EOS. Argon

| $V_R$ | $P_R$ | $\Delta, \%$ | $\Delta, \%$ | $\Delta, \%$ | $\Delta, \%$ | $\chi_P$ | $\chi_P$ | $\chi_P$ | $\chi_P$ |
|-------|-------|-------------|-------------|-------------|-------------|---------|---------|---------|---------|
|       |       | ES (4)      | ES [11]     | ES (5)      | $R - K w$   | $R - K w$ | 0.08    | 0.06    | [11]    |
|       |       | (3; -1)     | (3; -1)     | (3; -1)     | (3; -1)     | (3; -1)  | (3; -1) | (3; -1) | (3; -1) |
| 1     | 2     | 3           | 4           | 5           | 6           | 7       | 8       | 9       | 10      |
| 100   | 0.03395 | -0.335      | -0.144      | -0.03       | -0.03       | 4.79    | 5.1     | 7       | 7.25    |
| 20    | 0.16209 | -1.09       | -0.86       | -0.12       | -0.13       | -0.15   | 4.6     | 6.2     | 6.2     |
| 5     | 0.54073 | -0.66       | -5.29       | -0.13       | -0.15       | -0.5    | 4.0     | 5.4     | 5.3     |
| 2.5   | 0.82428 | -3.54       | -7.81       | +0.49       | +0.5        | 3.2     | 4.2     | 4.0     | 4.7     |
| 1.25  | 0.99556 | -1.4        | -0.18       | +0.37       | +0.38       | 3.0     | 3.97    | 3.8     | 3.8     |
| 10/9  | 0.99946 | -0.81       | -0.02       | +0.06       | +0.06       | 2.67    | 2.8     | 3.7     | 3.57    |
| 1     | 1.0000  | -0.009      | -0.066      | +0.29       | +0.38       | 2.67    | 2.8     | 3.7     | 3.57    |
| 10/11 | 1.0000  | +1.23       | +0.017      | +1.7        | +1.9        | 2.6     | 3.5     | 3.3     | 3.44    |
| 10/12 | 1.0058  | +2.99       | -0.05       | +4.8        | +5.4        | 2.5     | 3.3     | 3.14    | 3.34    |
| 10/14 | 1.0685  | +6.5        | -2.2        | +16.0       | +18.0       | 2.1     | 2.9     | 2.76    | 2.76    |
| 10/16 | 1.3426  | -0.42       | -13         | +24.0       | +30.0       | 1.8     | 2.56    | 2.43    | 2.43    |
| mean abs. dev., % | 1.67 | 2.6 | 4.3 | 5.78 |
| mean abs. dev., % | 3.3 | 5.4 | 5.25 | 7.3 |

The ratio $\chi_P$ of the configuration contributions of the four EOS: 1.56 1.97 1.88 1.34

Explanation of the two parts of the table 1. Part 1. Column 2 – calculation by the EOS, selected by Martin as a reference; Columns 3, 4, 5, 6 – calculation for two IPC EOSs, Martin and Redlich-Kwong EOSs – the absolute deviations of the reduced pressure values from the reference EOS calculated for the studied EOSs. Part 2. Columns 7–10 – the ratio of configurational contributions (attraction to repulsion) of different EOS for different values of density.

From table 1 can be seen that the EOSs from the IPC family selected by the methodology proposed by us turn out to be better or not worse than Martin’s (5) EOS, which he defined as “the simplest and best among the two-terms EOSs”. Similar calculations were also carried out for $C_4F_8$ and the IPC EOS also turned out to be the best (1.33%), beating even the Peng-Robinson EOS (2.67%) [12].

5. New feature – the basis for comparing the EOS and the choice of analogues

Formally, we will make the same transition to the EOS IPC for the two-component EOS Martin as for a vdw-type EOS. Let us turn to Martin’s EOS, which he also applied to argon ($t = 0.06$, $Z_C = 0.2912$)

$$P_R = \frac{T_R}{Z_C V_R - 0.06} - \frac{27/64 T_R^{0.55}}{(Z_C V_R + 0.065)^2}. \quad (6)$$

We write the EOS (6) in a three-term form, transforming the first contribution, so that the configuration contributions are allocated to the EOS. For the critical argon isotherm, we write:

$$P_R = \frac{1}{Z_C V_R} \left[ 1 + \frac{0.06}{(Z_C V_R - 0.06)} - \frac{27/64}{Z_C V_R(1 + 0.065/Z_C V_R)^2} \right]. \quad (7)$$

When the EOS (Martin or vdw-type, two-component in the original) is written in the form corresponding to the IPC EOS, it is possible to use the structure of three-term EOS, by entering the value comparing the configuration contributions to pressure

$$\chi_P = \Delta P(attr)/\Delta P(rep). \quad (8)$$
The new parameter was calculated by the results of calculations [12] (see table 1, part 2). We note close intervals of the obtained values for two EOSs from different families: 7–3.7–1.9 and 7.25–3.57–1.88. As for the third EOS (5) \((t = 0.082)\), which, as was shown, almost coincides with the Redlich–Kwong EOS, the parameter intervals are \((5.1–2.8–1.34)\) and \((4.89–2.67–1.56)\) for the EOS Redlich–Kwong. The number in the middle is the value of the parameter EOS at the critical point. It can be seen that the equations studied were divided into two distinct pairs, but within each pair, they are very close. It turns out that by coincidence or non-coincidence of this parameter, it is possible to determine the degree of closeness of the EOS, i.e. find EOS analogues. The solution of such a problem of choice, obviously, can significantly save time and money, because will exclude from consideration deliberately “distant” from analogous EOSs of various families, for which also carry out calculations in order to compare the EOS and select the best.

6. Why one EOS cannot equally well describe states with a reduced density of 2 and 3/2

In conclusion, we will give our explanation of the known fact. Let us turn to the molecular level of modeling and draw the results we obtained for two simple models, point centers and spherical shells. The capabilities of the model of shells making transitions between the potentials of two families.

The interaction of the point center describes the central potentials of the Mie \((n – m)\). For the shell model, we managed to isolate the control parameter [13], called rigidity. In the PCu (potential curve) description, the PCu inflection point [14] was explicitly entered and we managed to relate the coordinates of the two singular points (SP) – points of inflection PCu and the critical point [15] \(V_C = (r_p^U)^3\). The established relationship gave reason to believe that the PCu adequately models the energy of the interaction, which made it possible to introduce into consideration the corresponding force curve (FCu). Table 2 shows the results of calculating the ratio of the force of attraction to the repulsive force for the model potential Mie \((n – m)\) at the inflection point of the PCu for the index \(n\) values that are considered the most likely \((m = 6)\) for polyatomic molecules.

| \(n\) | 11  | 12  | 13  | 17  | 18  | 20  | 22  | 27  | 34  | 48  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \(\varsigma\) | 1.71 | 1.86 | 2   | 2.57 | 2.7 | 3   | 3.28 | 4.0 | 5   | 7   |

Let us compare those results for “force” molecular level data, with those which were obtained at the EOS level for \(\chi_p\). There is a complete coincidence of intervals (7–2).

The FCu is also characterized by a number of singular points, most of which coincide with the SPs of the PCu, but there is one new, fixing the bend of the FCu itself.

We write the decomposition of the potential function \(U(r)\) into a Taylor series in the vicinity of two singular inflection points of the PCu and FCu

\[
U(r_p^u + x) = U(r_p^u) + U'(r_p^u)x + U''(r_p^u)x^2/2 + \ldots 
\]

\[
U(r_p^f + x) = U(r_p^f) + U'(r_p^f)x + U''(r_p^f)x^2/2 + \ldots 
\]

Since different contributions fall out in the decomposition (derivatives of different orders vanish at different SPs), the form of the potential and the interaction forces in the neighborhood of the \(r\)-coordinates of these points will differ. We associate with these \(r\)-coordinates –
intermolecular distances – the effective dimensions of model object. The corresponding volumes of these objects also form a series: $b(r_0)$, $b(r_m)$, $b(r_u)$, $b(r_f)$. For the inflection point, $P_u$ effective volume is $b(r_u) = (4/3)\pi(r_u^3/2)^3$. From the above relation of the critical molar volume and the coordinates of the PCu inflection point follows the equality: $V_C = 1.91b(r_p)$. The inflection point of the FCu and its $r$-coordinate were empirically “groped” in the works of LP Filippov. He found [16] a ratio that, with an error of 1%, holds for many different molecules $V_C = 0.792(d + \sigma)^3$. We found in [17] that this corresponds to the ratio for SP $P_f$ FC: $V_C = 1.51b(r_p)$.

Let us estimate the reduced volume of states determined by average intermolecular distances equal to the coordinates of the points of inflection of the PCu and FCu:

$$V_R(P_u) = b(r_u)/(V_C = 1.91b(r_p)) = 1/1.91 \approx 1/2,$$
$$V_R(P_f) = b(r_f)/(V_C = 1.51b(r_p)) = 1/1.51 \approx 2/3.$$

As follows from (9) and (10), the forces in the vicinity of these SPs are different. Consequently, it is impossible to describe these two states equally well with one EOS, as noted by Martin and Prauznits The results presented first here and obtained recently [18], connect the models of two levels and make it possible, by molecular information, to elucidate many of the acute questions that exist for a low-parametric EOS.

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