Potential curves companions and the forecast of critical parameters

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Abstract. Here, new results obtained by modeling intermolecular interactions are presented. A third special point, the inflection point, is introduced in the potential curve (PC) description. General relations are obtained that refer to the coordinates of the minimum and inflection by the PC – and the indices n and m, that determine the shape of individual contributions to Mie potentials (n-m). The new approach applies to 10 globule molecules in the analysis of potentials restored from data on the properties of substances (second virial coefficient and viscosity) using standard methods. The analysis revealed several problems, the source of which turned out to be data characteristics for WF_6 molecules. As a result, a new concept has been introduced of PC – companions, which characterize each object. Calculations of the coordinates of the inflection points of PC companions and their comparison with critical parameters showed that one of them (PC with a large value of n) better predicts the critical temperature, and the other (PC with a lower value of n) predicts a critical volume. The results obtained, of fundamental interest, raise new questions.

1. Introduction

A significant part of the difficulty in determining the properties of substances by theoretical and computational methods is associated with the description of the energy of intermolecular interaction (IMI) [1]. The practical impossibility of accurately calculating the energy of the IMI of polyatomic molecules requires the use of model potential (MP) concepts.

MPs have two forms of implementation - the potential function (PF) and potential curve (PC) forms. MPs should convey the asymptotic behavior of molecules' interaction, that is, the predominance of repulsion at close distances and attraction at long distances. MP parameters are determined by various properties of substances (ie, second virial coefficient, transport properties, and crystal properties). The parameters that determine the shape of the PC are identified quite rarely. At the same time, the assumption that the use of macroscopic-level information is the only viable method is a consequence of the insufficiently effective use of known information about molecules and the IMI.

The sought MP should simultaneously simulate the interaction energy of real molecules and be a manifestation of the properties of model objects (ie, the characteristics of the model object should determine its shape and parameter values). It follows from what has been said that the PC is considered to be mapped onto the U - r plane of the true potential energy surface of molecules. If we assume that the PC obtained by such a transition is an adequate model of the IMI, we can assume that much more attention should be paid to the description of the shape of the PC, the determination of its parameters,
and their relationship with the fundamental properties of the substance than has been observed throughout the literature to date. Our work is devoted to these questions. It was this that became the basis for the search for correlations between the “fundamental” properties of substances and the coordinates of the “fundamental” features of intermolecular curves. What are these features, and how should they be connected with the PC and its form? Our analysis uses the simplest molecular model of interacting point centers. Within its framework, we have obtained new results, which are presented in this work.

2. The simplest models of molecules and IMI. PC singular points

2.1. Zero and minimum - two “standard” singular points of the PC

We restrict our consideration to the most straightforward PF, \( U(r, A, B) \), consisting of two terms — one of them describes repulsion, the other describes the attraction of model objects. The PC intersects the \( r \) axis at the point of zero \( N(r_0) \) and has a minimum point \( M \) with coordinates \( r_m, \varepsilon_m \). At these two singular points (SP), fixing zero and a minimum of the PF, the conditions are satisfied:

\[
N(r_0, \varepsilon_0): \quad U(r_0) = \varepsilon_0 = 0, \\
M(r_m, \varepsilon_m): \quad U(r_m) = -\varepsilon_m, \quad U'(r_m) = 0, \quad (\text{extremum PF}), U''(r_m) \neq 0 \quad (1)
\]

This equation represents the coordinates of singular points - PC parameters: \( r_0 \) is the effective diameter of the collisions, \( r_m \) is the equilibrium distance between the centers (van der Waals diameter), \( \varepsilon_m \) is the minimum depth, the binding energy of the molecules in the dimer. Using condition (1), we can express the coefficients A, B of the potential function in terms of the \( \varepsilon \)- and \( r \)-parameters of the PC.

2.2. Point centers and central potentials

The simplest model of any molecule is the point center that does not have geometric characteristics. Central potentials describe the interaction of a pair of centers. The most popular to date is the central Mie potentials \((n-m)\), represented by inverse functions:

\[
U(r) = \frac{a}{r^n} - \frac{b}{r^m}, \quad (2)
\]

when \( n > m > 3 \), \( r \) is the distance between the centers of objects, and \( a \) and \( b \) are coefficients.

Expressing them based on (1) through the coordinates of point M, we get:

\[
U(r) = \varepsilon_m \frac{n}{m} \left[ \frac{m}{n} \left( \frac{r_m}{r} \right)^n - \left( \frac{r_m}{r} \right)^m \right] \quad (3)
\]

The family of functions (3) with a fixed value \( m = 6 \) is named after Lennard-Jones, who first actively applied them in his works.

2.3. Inflection point - the third singular point of the PC

The PC has another SP; namely, the inflection point \( P(r_p, \varepsilon_p) \), in which, by definition [2]:

\[
U''(r_p) = 0, \quad U'''(r_p) \neq 0, \quad U(r_p) = -\varepsilon_p. \quad (4)
\]

Some authors mention [3] about the existence of an inflection point, but we do not know whether it has been explicitly described in the context of IMI. This is understandable - an increase in the number of adjustable parameters does not facilitate the task of determining them, all the more so since it is not clear what the physical meaning of these parameters is.

We use conditions (4) and obtain a new expression for the Mie potentials \((n-m)\):

\[
U(r) = \frac{\varepsilon_p}{n(n+1) - m(m+1)} \left\{ m(m+1) \left( \frac{r_p}{r} \right)^n - n(n+1) \left( \frac{r_p}{r} \right)^m \right\}. \quad (5)
\]

3. The equation of connection parameters

An introduction to the description of the inflection point \( P \) opens up new possibilities. The new coordinates allow us to enter several “relative parameters” – form factors (FF) and, with their help,
describe in some detail the shape of the PC of any family. In a previous publication [4], we introduced the following FF - steepness \( (r_p/r_m) \), curvature \( (r_p^2/r_m) \), relative depth \( (\varepsilon_p/\varepsilon_m) \), width, as well as the degree of asymmetry.

For MP Mie (n-m) expressions for the FF are easily obtained in the form of functions of indices n and m. We assume that the two expressions (3) and (5) obtained for the same MP Mie (n-m), will differ only in the form of the coefficients. The equality of the FFs in equations (3) and (5) implies the equality of the corresponding MP coefficients; once transformed, we can obtain general relationships relating the parameters of the potential (coordinates of the singular points M and P) with the indices that determine the form of contributions. We call these the coupling equations (CE). We give one option (6)

\[
\frac{\varepsilon_p}{\varepsilon_m} \frac{r_p}{r_m} \left( \frac{n+1}{n+1+m} \right) \left( \frac{n+1}{m+1} \right)^{m-1-n} = 1
\]

From (3) and (5), we can also obtain expressions for the FF that connect them with the indices

\[
\Phi_R = \frac{r_p}{r_m} = \left( \frac{n+1}{m+1} \right)^{m-n}, \Phi_E = \frac{\varepsilon_p}{\varepsilon_m} \left( \frac{n+1}{m+1} \right) \left( 1 + \frac{m}{n+1} \right)
\]

(7)

In (6), we select the part depending on the indices n and m, and denote it by \( \Phi(n, m) \):

\[
\left( \frac{n+1}{n+1+m} \right) \left( \frac{n+1}{m+1} \right)^{m-1-n} = \Phi(n, m)
\]

(8)

Consider the following options (6), which have different implications.

Option 1. CE (6) can be written as the product of the factors of the shape of the PC:

\[
\left( \frac{\varepsilon_p}{\varepsilon_m} \right) \left( \frac{r_p}{r_m} \right) \Phi(n, m) = 1
\]

\[
\left( \frac{\varepsilon_p}{\varepsilon_m} \right) \left( \frac{r_p}{r_m} \right) = 1 / \Phi(n, m)
\]

(9a) (9b)

Option 2. CE (6) can also be expressed in terms of the ratio of the values obtained by multiplying the parameters, which are considered as the ratio \( S_P/S_M \) of two "areas" of rectangles built on the coordinates of the singular points:

\[
\left( \frac{\varepsilon_p}{\varepsilon_m} \frac{r_p}{r_m} \right) \Phi(n, m) = 1
\]

\[
\left( \frac{\varepsilon_p}{\varepsilon_m} \frac{r_p}{r_m} \right) = 1 / \Phi(n, m)
\]

(10a) (10b)

Let us analyze two selected options (6). Table 1 summarizes the results of the calculations of two FFs and the ratio of areas. Index \( m = 6 \).

| N  | \( \varepsilon_p/\varepsilon_m \) | \( r_p^2/r_m \) | \( \Phi(n, m) \) | \( \Phi_E \Phi \Phi(n) \) | \( S_P/S_M=1/\Phi(n, m) \) |
|----|-----------------|----------------|-----------------|-----------------|--------------------|
| 139| 0.911028        | 1.022780       | 1.073213        | 0.999999        | 0.9318             |
| 99 | 0.892886        | 1.029007       | 1.083939        | 0.999999        | 0.9188             |
| 69 | 0.871921        | 1.037225       | 1.105731        | 0.999999        | 0.9044             |
| 54 | 0.857154        | 1.04388        | 1.117608        | 0.999997        | 0.8947             |
| 48 | 0.850038        | 1.047421       | 1.123156        | 0.999999        | 0.8905             |
36  0.833002  1.057068  1.135665  0.999998  0.8805
24  0.811225  1.073281  1.148537  0.999999  0.8707
18  0.798654  1.086770  1.152135  0.999999  0.8679538
17  0.79654  1.08965  1.152137  0.999999  0.8679523
16  0.794453  1.092786  1.151851  0.999999  0.8682
14  0.790466  1.099953  1.150119  1.000000  0.8695
12  0.786984  1.108683  1.146113  1.000001  0.8726

As the index n increases, the ratio $\varepsilon_p/\varepsilon_m$ monotonically increases, and $r_p^n/r_m$ decreases to 1 in both cases as n tends to infinity. The fascinating behavior of the function $\Phi (n, m)$ is noteworthy. With the growth of the index n to 17, it grows, reaching an absolute maximum, and then decreases. In another description, this means that the ratio of the areas at this “point” are reversed - if, before that, the relation of the $S_p$ to $S_m$ was reduced, then from this point the relation will increase.

It seems very logical and refreshing based on a new approach – taking into account the “inflection of the PC” to analyze the results obtained in the framework of the concept of semi-empirical potentials (i.e., with a standard approach to modeling the IMI).

4. Results and discussion

4.1. Application of the criterion to potential n-6

Let us turn to the work [5], the results of which related to the IMI energy modeling for globular molecules and were included in the information-computational knowledge base of the transport properties of rarefied gases and gas mixtures. As objects, quasi-spherical molecules with tetra- and octahedral symmetries of CCl₄ and WF₆ type were chosen. To model the properties of systems of similar objects, the number of which is large, it is vital to have adequate potential for interparticle interaction. The authors worked with two families of potentials. The first is a four-parameter potential for which parameters depend on temperature. The second family is a three-parameter MP Mie (n-6), the parameters of which are the coordinates of the minimum, and the index n, the repulsive contribution index responsible for the shape of the PC, which reconstructed from the second virial coefficient and viscosity data. Note that these data are usually considered separately, and two sets of parameters are obtained for a given apriori MP (12-6). According to the results, preference is given to a simpler three-parameter family than to a four-parameter family. The data obtained is presented in the form of a table, which shows a list of objects located following the structure - first molecules with tetrahedral symmetry, then hexafluorides.

An analysis of results presented in [5] was carried out according to the methods we propose. We exclude further fitting of the parameters found by the properties of the substances. We introduce the inflection point in the description of the PC. For the indices n obtained in [5], we calculate the form factors using formulas (7) and the functions $\Phi (n, 6)$ using (8).

The results of our calculations and analysis are presented in table 2, which also opens a list of objects. However, the list is different to those seen in [5]. Let us explain what caused this. The authors (as is customary) define the index n as a value that determines the shape of the PC’s repulsive branch. In our approach, Mie potentials have the value of n as the characteristics of the interaction of objects, their most common properties are manifested. The same applies to the value of $\Phi$, in which both indexes – n and m – manifest themselves on the one hand, and both forms factor. Therefore, the molecules are ranked by the value of $\Phi$ and index n. An increase in the values of the function $\Phi$ from 1.1296 to 1.1518 corresponds to a decrease in the index n from 41.6 to 19.1. This is the case for all objects and is violated only for WF₆. On a systematic assessment of the $\Phi$ value, WF₆ should be located between molecules.
with \( n \) values equal to 25.8 and 19.4 (see the separate last line supplementing table 2). However, the value \( n = 14.9 \) predicted for it in [5] is far from the found interval and does not fall into it.

4.2. The coordinates of the inflection point

Using the calculated FF and the parameter values and the coordinates of the M point from [5], we calculate the coordinates of the inflection points of the predicted PCs.

Compare \( \varepsilon/p/k \) with the critical temperature \( T_k \) (both in degrees Kelvin). In 5 out of 10 cases (they are indicated in bold in the last columns), the calculated \( \varepsilon/p/k \) values are very close to \( T_k \) (absolute deviations in % range from 0.4 to 3.0 and are indicated in brackets next to the values). In a model with an inflection point, this finding means that the parameter \( \varepsilon_m \) has been found adequately. Thus, a basis appears in criterion (6) to replace \( \varepsilon/p/k \) with \( T_k \). In this case, the idea arises to associate with the critical volume the second coordinate of point P.

After calculating \( r_p \) and comparing \( r_p^3 \) with the critical volume \( V_k \), we see that in all cases, \( r_m \) values from [5] give \( r_p^3 \) smaller than \( V_k \). The only case of practical coincidence of the two quantities is WF₆. It should be noted that the course of the FF change has been violated here - it changes to the opposite concerning all other objects (which can be tracked in column 5). This finding corresponds to an increase in the parameter \( r_p \). It follows from the foregoing that this particular case deserves more detailed analysis, but in general, the \( r_p \) value needs to be adjusted by increasing it.

| Molecule | \( r_m \), K | \( r_m \), \% | \( n_1 \) | \( \varepsilon/p/k \), \% | \( \Phi(n)_/p/8(n) \) | \( T_k \) | \( \varepsilon/p/k \) |
|----------|-------------|-------------|----------|-------------------------|------------------------|----------|-------------------------|
| CF₄      | 267.1       | 4.49        | 41.6     | 1.0520                  | 1.1296                 | 8.6      | 1.1291                  |
|          |             |             |          | 0.84147                 | 0.78397                |          | 105.4                   |
|          |             |             |          |                        |                        |          |                          |
| SF₆      | 336         | 5.243       | 30.9     | 1.0628                  | 1.14135                | 10.63    | 1.115887                |
|          |             |             |          | 0.8244                  | 0.783517               |          | 179.2                   |
|          |             |             |          |                        |                        |          |                          |
| MoF₆     | 568.9       | 5.32        | 27.6     | 1.0673                  | 1.1449                 | 11.58    | 1.11077                 |
|          |             |             |          | 0.8183                  | 0.78633                |          | 183.3                   |
|          |             |             |          |                        |                        |          |                          |
| C(CH₃)₄  | 481.8       | 5.98        | 27.3     | 1.0678                  | 1.14526                | 11.7     | 1.11016                 |
|          |             |             |          | 0.8177                  | 0.78635                |          | 260.3                   |
|          |             |             |          |                        |                        |          |                          |
| UF₆      | 637         | 5.42        | 26.7     | 1.0687                  | 1.14589                | 11.92    | 1.10097                 |
|          |             |             |          | 0.81657                 | 0.7870                 |          | 194.3                   |
|          |             |             |          |                        |                        |          |                          |
| SiCl₄    | 620         | 5.93        | 25.8     | 1.07015                 | 1.1468                 | 12.28    | 1.10735                 |
|          |             |             |          | 0.8148                  | 0.787426               |          | 255                     |
|          |             |             |          |                        |                        |          |                          |
| WF₆      | 425         | 5.57        | 20.6     | 1.08233                 | 1.1511                 | 14.9     | 1.0965                  |
|          |             |             |          | 0.804174                | 0.7922                 |          | 219.7                   |
|          |             |             |          |                        |                        |          |                          |
| CCl₄     | 700         | 5.60        | 19.4     | 1.08309                 | 1.1517                 | 15.8     | 1.093445                |
|          |             |             |          | 0.80163                 | 0.794945               |          | 223                     |
|          |             |             |          |                        |                        |          |                          |
| SiF₄     | 205.5       | 5.19        | 19.3     | 1.0833                  | 1.15185                | 16       | 1.0928                  |
|          |             |             |          | 0.804148                | 0.794495               |          | 177(?)                  |
|          |             |             |          |                        |                        |          |                          |
| Si(CH₃)₄ | 445.5       | 6.36        | 19.1     | 1.08385                 | 1.151866               | 16.02    | 1.09227                |
|          |             |             |          | 0.80099                 | 0.794495               |          | 326                     |
|          |             |             |          |                        |                        |          |                          |
| *WF₂*    | 425         | 5.57        | 14.9     | 1.0965                  | 1.1511                 | 20.6     | 1.08233                 |
|          |             |             |          | 0.7922                  | 0.804174               |          | 227.8(2)                |
|          |             |             |          |                        |                        |          |                          |

4.3. Companion PC

As a result of the two outlined steps above, both FFs will change. However, in order for the criterion value to remain the same (that is, at least for it not to become worse), the value \( \Phi(n_1) = \Phi(n_2) \) must be kept. The question is whether it is possible to find such other values of the index \( n \) for which the equality \( \Phi(n_1) = \Phi(n_2) \) will hold and whether it will be possible to find PC “companions” for those defined in
The found values of the index \( n_2 \) are shown in column 7, are in ascending order, which is violated only for \( \text{WF}_6 \). For it, the value \( n_2 = 20.6 \) was obtained, which should rise, disrupting the order, between the values 12.28 and 15.8.

For the newly-found PC companions, FFs were calculated, and based on them, and the parameters from [5], the coordinates of the inflection point \( P \) were found. Let us start with \( r_p \). In 4 cases out of 7, the values of \( r_p \) were obtained, which practically coincided with \( V_k \). Let us once again draw attention to the line of information for \( \text{WF}_6 \), which "breaks" the correct course of all quantities and interchanges the indices \( n_1 \) and \( n_2 \), as well as the associated FFs (this has already been done in table 2). The order will be restored wherever it is violated. As for all other molecules, the companion curve will give the best value for the critical volume.

We conclude that the authors of [5] on the properties of substances in the only case of \( \text{WF}_6 \) found specifically the PC companion. As for the coordinate \( \varepsilon_P \) in two cases – \( \text{UF}_6 \) and \( \text{CCl}_4 \) – a good forecast has become even better. Moreover, the absolute deviations in percent change is as follows: 3% by 0.7, 0.9% by 0.0. In the remaining cases, the discrepancies with the critical temperature recorded by the first set of FFs corresponding to the values of \( n_1 \) has slightly increased, observing the decreasing trend.

As a result, for the same substance, we have two PC companions with \( n_1 > n_2 \), one of which (\( n_1 \)) gives a better forecast of the critical temperature, and the second PC (\( n_2 \)) better predicts the critical volume. Here we recall the preliminary calculations of the functions \( \Phi (n, m) \) and the "critical" value of the index \( n = 17 \) found there (table 1). In table 2, the interaction potential for the last substance in the list is characterized by the values \( n_1 = 19.1 \) (decreasing row) and \( n_2 = 16.02 \) (growing row). It is for \( n = 17 \) that for some objects become equal to FF, since now it is a single PC (figure). It is interesting to find such objects. Such a finding takes us to the area of unsolved problems associated with the selection or prediction of substances according to their intermolecular interactions.

![Figure 1. The index n behavior for two companion PCs.](image)

In the meantime, the following holds. For the selected molecule, two PC companions can be found with the same values of \( \Phi (n, m) \). Many questions arise. Including this one - is this fact a kind of justification for the separate restoration of parameters from different properties? Do two PC companions describe two states of matter – rarefied gas and denser fluid? Moreover, is there, and is it possible to
find a single PC, the coordinates of the inflection point that exactly and simultaneously coincide with critical parameters?

So far, we have considered one option for analyzing the results obtained in a standard way, within the framework of the new model. Note the following. If 20 years ago, we had not found a connection between the coordinates of the inflection points at two levels of description – the critical isotherm and PC – (and it was found [4, 6, 7]), it would still have manifested itself as a result of our analysis.

5. Conclusion

This year marks the 150 year anniversary of the Periodic Table of the Elements of Mendeleev. Anyone familiar with the System of Elements creation history knows the story about multiple shuffling of cards during the data systematization and objects classification. Our analysis of the Mie potentials (n=6), obtained by the standard method in [5] for globule molecules, also came down to shifting the “cards.”

We will not draw analogies with the Periodic Table, but suggest that an entirely new concept of PC companions would not have been introduced if there had been not one revealed discrepancy in the data on the IMI potential for WF_6, reconstructed from the properties of the substance of these molecules.

We take into account that when restoring the parameters and index n, the authors of [5] used the results of more than one work; their number varies from 6 for MoF_6 to 103 for SF_6. At the same time, the technique, conventionally called “critical”, which was the result of introducing the inflection point of the PC into the description, makes it possible to obtain an adequate description on the basis of knowledge of one value of the index n, which is usually associated with the potential shape. Moreover, if it were possible to solve the problem of choosing n for Mie potentials based on the general characteristics of model molecules, which are manifested in their interaction (i.e., in the form of a PC), this finding would be a significant resource economy. With this in mind, we took the first steps [8] concerning the possibilities of a more realistic model of spherical shells compared to point centers. The first results in the direction of choosing the shape of a PC based on molecular information only have been obtained and presented in [9, 10].

Note that the results obtained require a deeper understanding of the specialists involved in the development of models at two levels, both - molecular and thermodynamic.

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