Problems of low-parameter equations of state

G G Petrik

1 Institute for Geothermal Research of the Dagestan Scientific Center of the Russian Academy of Sciences, Shamilya 39A, Makhachkala, Dagestan 367030, Russia

E-mail: galina_petrik@mail.ru

Abstract. The paper focuses on the system approach to problems of low-parametric equations of state (EOS). It is a continuation of the investigations in the field of substantiated prognosis of properties on two levels, molecular and thermodynamic. Two sets of low-parameter EOS have been considered based on two very simple molecular-level models. The first one consists of EOS of van der Waals type (a modification of van der Waals EOS proposed for spheres). The main problem of these EOS is a weak connection with the micro-level, which raise many uncertainties. The second group of EOS has been derived by the author independently of the ideas of van der Waals based on the model of interacting point centers (IPC). All the parameters of the EOS have a meaning and are associated with the manifestation of attractive and repulsive forces. The relationship between them is found to be the control parameter of the thermodynamic level. In this case, EOS IPC passes into a one-parameter family. It is shown that many EOS of vdW-type can be included in the framework of the PC model. Simultaneously, all their parameters acquire a physical meaning.

1. Introduction
The problem of deriving the physically reasonable equation of state (EOS) presents a fundamental problem of thermophysics and molecular physics. Obviously, the solution of such a difficult problem should start with the simplest molecular models and EOS. In this respect, the low-parametric EOS with a number of parameters from 2 to 5 are of special interest. The problem of deriving the physically substantiated EOS in this case may be solved by linking its parameters with the parameters of the underlying molecular model.

The paper considers two sets of the low-parameter EOS. The first ones are the known independent empirical modifications of van der Waals EOS, the main shortcoming of which is considered to be the weak connection with the micro-level [1]. In practice, it is limited to the fact that many authors of the new equations "shift responsibility to van der Waals" for the physics of the model, that is for underlying their EOS molecular model.

The second group of EOS we have derived independently of the van der Waals ideas based on the simplest molecular model of interacting point centers (IPC) [2, 3]. For the first time, all parameters of the EOS IPC have sense and related to the manifestation of the intermolecular interaction forces. For the first time, the control parameters of two levels (thermodynamic and molecular), defining the properties of the model system, are highlighted and comprehended. The analytical possibilities of the new model allow including many EOS of vdW-type in its framework and presented as particular cases of equations belonging to the same one-parameter family.
2. Simple models of two-levels. Selection and rationale
The search for physically sound EOS implies a system approach to modeling on two levels: molecular and thermodynamic. The two simplest models of the molecular level are point centers, which do not have geometric characteristics, and rigid spheres having their own volume and shape. A realistic model must take into account the interaction of objects. At the thermodynamic level, they must be corresponded by two simplest general EOS, including contributions to pressure, determined by attraction and repulsion of the objects. If there is no interaction, the general EOS goes into a particular case of EOS for non-interacting point centers or spheres. Overview of the reported papers shows that there is no general EOS for interacting point centers. It is known only for non-interacting PC (EOS for an ideal gas, Clapeyron - Mendeleev, \( p = \frac{RT}{V} \)). For rigid non-interacting balls, an empirical EOS with a covolume (Dupree, Abel, Noble, \( p = \frac{RT}{V - b} \)) is known. There is also no general EOS for interacting spheres. The similarity of situations for spheres and PC is limited by this.

There are many EOS of vdW-type [4-6] considered to be their empirical modifications for spheres. They are widely used for calculations. The model of point centers seems should also generate plenty of equations. But there are no publications. We show here how to close the gap and derive a EOS based on a simple model of PC. However, before turning to the first results for the new PC model, let us dwell on the unresolved problems of the EOS of vdW-type. The part of these problems connected evidently with contradictions in the notions of the famous van der Waals model, originally laid by its author, and existing in contemporary papers.

3. Comparative analysis of the van der Waals model presentations
3.1. The main provisions of the original van der Waals model [7,8]
The objects are rigid spheres. Their interaction: attraction, weak enough to not affect the translation of the spheres. The repulsion was not taken into account (van der Waals did not guess about it). (Conclusion: the nature of the interaction determines a very specific model). The main task for the vdW EOS was to take into account that the interacting objects have their own volume:

\[ (P + \frac{a}{V^2})(V - b) = RT \]

In this case, the pressure is determined by two contributions: the first one takes into account the fact of the presence of volume in the hard spheres, the second - their weak attraction:

\[ P = \frac{RT}{V - b} - \frac{a}{V^2} \]  \hspace{1cm} (1)

The meaning of the parameters: \( b \) (the attribute of the object) is related to the intrinsic volume of the sphere, \( a \) is "cohesive", and it is responsible for the attraction. If the interaction (attraction) is absent, the attribute must be preserved and the vdW EOS passes into the EOS for the non-interacting spheres (with a covolume):

\[ P = \frac{RT}{V - b} \]  \hspace{1cm} (2)

3.2. Generally accepted ideas about the EOS of vdW-type and the models underlying them
Similar to the vdW EOS, these equations are cubic ones; as a rule, binomial, and low-parametric (from 2 to 5). Many of them can be written in the form

\[ P = \frac{RT}{V - b} - \frac{a}{V(V + c)} \]  \hspace{1cm} (3)

The second contribution to the pressure in both (3) and (1) is due to the attraction of the spheres. As for the first contribution of these equations, it is now believed to be related to the repulsion of the spheres. They show that in the limit EOS (1) passes into the EOS of an ideal gas (namely, non-interacting points!). It is believed that the basis of these equations is the same model as van der Waals' one "the simplest and physically clear" (see the conclusion above). (With the system approach: the
authors, introducing additional parameters in the EOS, that is changing the properties of the model of the thermodynamic level, should connect and explain them by changes in the molecular model. Here there is the main cognitive problem of the EOS of vdW-type. The parameters $a$, and $b$ are given the same sense as in the van der Waals model. For the new third parameter $c$ "there is no sense". Because it is related to other characteristics of the model, uncertainty also arises in their relation. As a result, the big problem of the EOS of vdW-type is considered to be their weak connection with the micro-level. (As a counterexample, they usually refer to the virial equation, in which the expansion coefficients are related to the intermolecular interaction of pairs, triples, and others).

4. Problems of low-parametric EOS of vdW-type

The weak unmanifested relation of the EOS of vdW-type to the micro-level generates many issues, the answers to which are not available in the extensive literature. For example, a number of questions that form the problem of parameters: what is the true number of parameters in the "two-parameter" EOS; whether they are constants of the substance identity or reflect the nature of intermolecular interaction forces; to which leads the requirement of the constancy of the parameters of the EOS; what is the meaning of the third parameters of various EOS.

The issues concern both the general aspects of the problem and a number of specific equations. Why does the EOS of vdW poorly describe the properties of rarefied gases? Is it correct to interpret the first contribution to the vdW EOS (and vdW-type) as repulsive for the spheres? Could it be that just the assumption of attraction weakness gives a certain meaning to the parameters of vdW EOS? What is the meaning of the parameter $b$ in the Redlich-Kwong EOS and why is its value almost half the value given by the van der Waals formula? Why are the values of the critical factor compressibility ($C_{FC}$) $Z_C$ calculated from the EOS should be greater than their experimental values by 15-25%?

The list of questions can be continued. They prefer not to discuss them. Answers can not be received, till there is no physical meaning in these EOS. At the same time, only answering the questions, we can expect progress in solving the problems of the EOS of vdW-type. This situation stimulates the search for a model where the repulsion and attraction of objects are more adequately reflected. A new approach to the old problems is needed. However, hundreds of works performed in the standard way, suggest that the scientific authority of the Nobel laureate, namely van der Waals, clearly restrains the new approach.

5. Features of a new model of interacting point centers

Van der Waals, ahead of his time, had assumed the existence of molecules in the form of objects with a shape and a volume, and, supposing a certain character of attraction, he built his own equation of state. Almost a century and a half passed, during which the van der Waals model was "responsible for the physics" of many low-parameter EOS.

Now we offer a new approach involving minimum information about real molecules, and realize the capabilities of the IPC model. The objects are simpler than spheres. The point centers do not have their own volume, and their effective volume is determined by the distance between them, which is the result of the manifestation of repulsion and attraction forces. Each of the forces contributes to the change of the distance (therefore, in the effective size), resulting in a change in the available (free) for the PC volume.

But their interaction is not the same as in van der Waals model. We are taking into account the availability of an optimized attraction (the condition of weakness is removed) and hard repulsion. The nature of the repulsion and the form of the associated contribution to the EOS of IPC are determined on the basis of the assumption now adopted at the molecular level. Its essence lies in the fact that in the approximation of tangent shells, a pair of rigidly repelling centers separated by a distance $d$ and a pair of non-interacting rigid spheres of the same diameter are equivalent.
The transfer of the assumption to the thermodynamic level, to the language of the EOS and the transition from PC without interaction \((\text{no int})\) to PC with repulsion determined the form related contribution \(\Delta P\) (rep):
\[
\frac{\text{RT}}{V} + \frac{\Delta P (\text{rep})}{V} = \frac{\text{RT}}{V} (\text{hsp / no int}) \quad \Delta P (\text{rep}) = \frac{RTb}{V(V-b)}
\]

Involving the ideas of similarity in the manifestation of forces allowed justifying the form of the attractive contribution:
\[
\Delta P (\text{attr}) = \frac{a}{V(V+c)}
\]
Parameters \(b\) and \(c\) have the meaning of changes in the volume accessible to the PC, caused by the action of repulsion and attraction forces. The possibilities of the new EOS IPC are discussed in the next section.

6. The IPC model. EOS and control parameter of the thermodynamic level
6.1. IPC with optimized attraction and hard repulsion
Three-term and three-parameter cubic EOS IPC (for one mole, the designations of variables are standard) has the form [2,3]
\[
P = \frac{RT}{V_f (\text{PC / no / int})} + \frac{RT\Delta V_f (\text{rep})}{V_f (\text{no / int})V_f (\text{rep})} - \frac{a}{V_f (\text{no / int})V_f (\text{attr})}
\]

Here the subscript \(f\) for \(V\) fixes that it is free, available for PC, volume. The first contribution to the pressure is the EOS for potentially non-interacting PC, the other two are configuration ("structure") ones associated with the account of repulsion and attraction between the PC. For simplicity we use an equivalent entry in the form
\[
P = \frac{RT}{V} + \frac{RTb}{V(V-b)} - \frac{a}{V(V+c)} , \quad (4)
\]
where \(V\) is the volume of the system fully accessible to PC when there is no interaction between them: \(V = V_f (\text{no / int})\). For the first time, all three parameters of the EOS (4) \(b\), \(c\), and \(a\) make sense. Two of them are integral characteristics. They are equal to the changes in the volume available for PC, caused by the action of forces: attraction \(c = -\Delta V_f (\text{attr})\) and repulsion \(b = \Delta V_f (\text{rep})\). The third parameter \(a\) (we do not call it cohesive) is related to \(c\), but different from it because of the difference in the nature of the forces. (An analogy with exponents in the potential Mi (m-n)). The meaning of the parameters \(b\), and \(a\) is different in two models. (For the time being, we consider only \(P(V)\)-dependence of the attractive contribution, eliminating the temperature contribution, since this question requires a separate analysis).

6.2. The control parameter \(\chi\)
The three parameters \(b\), \(c\), and \(a\) of the EOS IPC, which make sense, create new opportunities. It is logical to assume that the state of the model "substance" is determined by the ratio of the manifestations of the attraction and repulsion forces. Based on it, we introduced the parameter
\[
\chi = \frac{c}{b}, \quad \chi = \frac{-\Delta V_f (\text{attr})}{\Delta V_f (\text{rep})}
\]
In the EOS IPC (4) we make the transition to the values given in terms of the critical parameters: \(\varphi = V / V_o, \quad \zeta = T / T_o, \quad \pi = P / P_o, \quad \beta = b / V_o, \quad \sigma = c / V_o, \quad a = a / (RTV_f), \quad \chi = \sigma / \beta\). Investigating the given EOS, we have obtained expressions for all parameters in the form of functions of the parameter \(\chi\) [9]
\[
\beta = \frac{1}{\chi} (\sqrt{\chi + \chi} - 1), \quad \alpha = \frac{\chi^2}{(\sqrt{(\chi + 1)(\chi - 1) + 2\chi + 1})(\sqrt{(\chi + 1)(\chi - 1) + 2\chi + 1})}
\]
\[
\sigma = (\sqrt{\chi + \chi} - 1), \quad Z_c = \frac{\chi}{\sqrt{(\chi + 1)(\chi - 1) + 2\chi + 1}}
\]

(5)
As a result, the three-parametric EOS IPC (4) becomes a one-parameter family of equations. This can be considered as confirmation of the one-parameter law of the corresponding states in the framework of a very simple model. The quantity $\chi$ was called the control parameter of the thermodynamic level [10].

7. Connection of EOS vdW-type and EOS IPC

7.1. Transformation of EOS vdW-type with undefined parameters in the EOS IPC

After the control parameter of the model is found, and its meaning is established, let us search a method for $\chi$ determining. One can consider it as an adjustable parameter, but the relation with molecular interaction dictates a different direction of analysis. Let us investigate what values are possible for $\chi$ and how to use the information accumulated for EOS vdW-type. Although there are no control parameters in original EOS vdW-type, it turned out that information on $\chi$ can be found by the form of the equations themselves.

Many EOS vdW-type can be included in the IPC model [3, 9,10,11]. It is turned to be especially easy done for the largest group of equations (see (3)), whose first contribution has form \( RT/(V-b) \). We return to it the original meaning of the EOS with the covolume, namely non-interacting spheres. We will apply the same assumption about the relation between spheres and the EOS with rigid repulsion, as in the derivation of EOS IPC. As a result of the transition from one molecular model to another (now from spheres to PC), all the parameters of the reformulated EOS acquire a certain meaning. Consequently, we obtain the known EOS vdW-type, but belonging as particular cases to the physically justified PC model of the same one-parameter family. They differ by values and forms of the parameter $\chi$, that is difference in the manifestation of intermolecular forces. Thus, their main defect, the weak connection with the micro-level, is eliminated.

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

(6)

7.2. EOS of vdW-type with $\chi = \text{const}$ in the IPC model

This condition is met by three EOS. For EOS vdW, $\chi = 0$ ($c = 0$, which corresponds to the van der Waals assumption of weak attraction forces and absence of their influence on intermolecular distances). For the Redlich-Kwong EOS, $\chi = 1$ ($c = h$, the manifestations of forces are balanced that corresponds to the most energetically favorable state. There are many indications [5] that this is the most suitable for describing properties under moderate thermobaric conditions). Another little-known Wong – Prauznits EOS [12] has $\chi = 0.2$. There is an issue for the new EOS IPC, if they should have so small values of the control parameter? Calculations show that values $\chi$ from the range of (2-7) distinguish in the family EOS (6) equations with realistic CFC $Z_c$ values of 0.31 - 0.26. The problem of such EOS has several important aspects, related just to the domain of definition of the parameter $\chi$ and of meaning of parameter b.

7.3. EOS of vdW-type with $\chi = \kappa_1 + \kappa_2 b \rho$ in the IPC model

The constraints related to the condition $\chi = \text{const}$ were revealed when studying the properties. This demanded further optimization of the model. An analysis of a number of EOS of vdW-type (Peng - Robinson, Clausius, Patel - Teia, Harmens - Knapp, Schmidt - Wentzel, and others) showed that the parameter $c$ now depends on the molar volume. (Let us recall the search by van der Waals for the dependence of his parameter $b$ on the density). The "structured" EOS IPC takes the form [13]

\[
P = \frac{RT}{V} + \frac{RTb}{V(V-b)} - \frac{a}{V(V+b(k_1 + k_2 \rho b/V))}, \quad \chi_V = c/b = \kappa_1 + \kappa_2 \rho b
\]

$k_1, k_2$ are certain numbers. After transformations, we obtain the cubic equation for $\beta$

\[
\beta^3(k_2 - k_1(k_2 + k_1)) - 3\beta^2(k_1 + k_2) - 3\beta + 1 = 0
\]

The expressions obtained show that all the EOS parameters are determined by specifying a pair of numbers $k_1$ and $k_2$, which we call generating ones. Assigning values to them (plus the density of the system), determines the value of the control parameter $\chi$.

7.4. The possible explanation of the structure of the parameter $\chi$ and meaning of numbers $k_1, k_2$
We continue the search for the physical meaning of $\chi$. Translational and vibrational motions are possible for a point center. Suppose that when forming the parameter $\chi = c / b$ (in this case, the parameters refer to a single object, this can be easily shown in the average-field approximation), both types of motion should appear: $\chi = \chi_{\text{trans}} + \chi_{\text{vibr}}$. It can be assumed that for a state close to ideal gas, $\chi_{\text{vibr}} = 0$ and the total change in volume is the result of the translational motion of the PC, $\chi_{\text{trans}} \neq 0$. At high density and low temperatures translational motion is practically absent, and then $\chi_{\text{trans}} = 0$, and $\chi_{\text{vibr}} \neq 0$. Under intermediate conditions, both types of motion contribute to parameter $\chi$. These arguments help to decipher the expression for $\chi = \kappa_{1} + \kappa_{2} b \rho$, where two numbers $k_{1}$ and $k_{2}$ are obviously related to the two degrees of freedom for PC ((in the standard approach they have no sense)). In this context, for example, a number of facts related to the EOS of vdW can be explained.

8. Conclusion
We do not provide answers to all the questions to the EOS of vdW-type, but many of them have been obtained. The results show that the simple model of IPC and equation of state based on it are very informative. At the same time, the EOS is not general one due to rigid repulsion of PC. In addition, the PC is a primitive object itself. Naturally, this can determine the direction of optimization of the model. The combination of it with the results that we have obtained in the modeling of intermolecular interactions [14] is especially promising. We have found a factor connected with the geometric characteristics of the object, which models a polyatomic molecule with a shell package, and have shown that it determines the nature of spherical shells interaction. These are the following after PC objects in terms of complexity, with which more adequate low-parameter EOS should be associated.

References
[1] Anderko A 2000 Experimental Thermodynamics V (Edited by Sengers J V, Kayser R F, Peters C J and White H J, Jr Elsevier) 75-126
[2] Petrik G G and Gadzhieva Z R 2007 Vestnik DNC RAN 27 5-12 in Russian
[3] Petrik G G 2009 Monitoring. Nauka i tekhnologii 1 45-61 in Russian
[4] Vukalovich M P and Novikov I I 1948 Uravneniya sostoyaniya real'nykh gazov (M.) in Russian
[5] Uehjles S 1989 Fazovey ravnovesiya v kimicheskoy tekhnologii: V 2-ch. (M.: Mir) in Russian
[6] Anderko A 1990 Fluid Phase Equilibria 61 145-225.
[7] Kipnis A Ya and Yavelov B E 1985 Iogannes Diderik Van-der-Vaal's (L.: Nauka) 309 in Russian
[8] Van der Waals J D 1873 Over de continuiteit van den gas-en Vloeistofoestand doctoral dissertation Leiden Holland
[9] Petrik G G 2010 Monitoring. Nauka i tekhnologii 3 84-97 in Russian
[10] Petrik G G and Gadzhieva Z R 2010 Monitoring. Nauka i tekhnologii 1. 67-78 in Russian
[11] Petrik G G 2012 Fiziko-himicheskie aspekty izucheniya klasterov, nanostruktur i nanomaterialov Mezhvuzovskij sbornik nauchnyh trudov (Tver’:Tverskoy gosudarstvennyj universitet) 4 235-247
[12] Wong J O, Prausnitz J M 1985 Chem. Eng. Commun. 37 41-53
[13] Petrik G G 2010 Monitoring. Nauka i tekhnologii 2 79-92 in Russian
[14] Petrik G G and Todorovskij B E 1988 Zhurnal fizicheskoy khimi 62 12 3257- 63 in Russian