A new concept for augmented van der Waals equations of state

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ABSTRACT

A novel approach to perturbed equations of state for simple fluids is presented and its advantages over the traditional perturbed hard sphere equations are demonstrated by its application to several model fluids. The approach is based on a short range Yukawa reference which incorporates, in addition to repulsive interactions, also attractive interactions at short separations. The considered models of common interest are the Sutherland, Lennard-Jones, and EXP6 fluids. It is shown that using the proposed approach the reference system captures a good deal of properties of the studied fluids and that an accurate equation of state can be obtained using only the crude mean field (augmented van der Waals) approach.

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1. Introduction

The idea that matter is made up of certain microscopic objects (called atoms or molecules nowadays) which are subject to their mutual interactions was at the time of van der Waals only emerging and several decades away from general acceptance [1]. Nonetheless, van der Waals was convinced that such particles did exist, were real material objects and had thus to have a certain volume. Using then simple physical arguments and intuition he derived his famous 'van der Waals' (vdW) equation of state [2]. The vdW equation provides a qualitatively correct description of the fluid phase, i.e., it yields the critical point and vapor–liquid (L–V) equilibrium envelope but for practical applications is too crude. This would not have been a problem if the equation had been developed within any statistical mechanical scheme so that it would have been clear how to improve its performance. With respect to its purely speculative nature and lack of any understanding of behavior of fluids at the molecular level, the vdW equation was viewed as an interesting and successful attempt without any deeper understanding and a chance to systematically improve it. Nonetheless, it formed a certain basis for developing dozens of empirical equations of state (EOS) used in engineering applications.

Only the development of molecular theories of fluids in the late 1960s, based primarily on results of computer simulations, made it possible to put the vdW equation on a firm theoretical basis by placing it into the framework of perturbation theories. It turns out that the vdW equation is a perturbed hard sphere (HS) equation resulting from the first order perturbation theory using well defined (and justified) approximations. This follows from molecular simulation results performed on various simple fluid models which revealed that their structure (and, in general, the structure of normal fluids) is determined primarily by short range interactions. The straightforward interpretation of this finding was that it was the *repulsive* interaction (i.e., excluded volume) which determined the structure of these fluids. This finding opened the way for non-empirical improvements of the original vdW equation. Unfortunately, this possibility has not been fully acknowledged by the engineering community which continued stubbornly with purely empirical corrections at the level of the original equation. A typical example is adherence to the original vdW expression for the reference HS fluid instead of using the simple but very accurate Carnahan–Starling equation (cf., cubic equations of state). An excuse for the continuous use of such equations may be only a technical reason: when determining the L–V equilibrium, roots of an algebraic cubic equation would have to be determined numerically.

When a rigorous statistical mechanical expansion about a HS reference is followed then the perturbation expansion must be considered, in general, up to the second order if accurate results for thermodynamic properties are to be achieved. The primary reason is that, despite having a very similar structure, the thermodynamic properties of the HS fluid are significantly different from those of more realistic fluids. The evident question is whether

Nomenclature

a	van der Waals coefficient
A	Helmholtz free energy
B_2	second virial coefficient
d	hard core diameter
E	internal energy
g	radial distribution function
N	number of particles
P	pressure
r	distance
r_m	position of the potential energy minimum in parent fluid
u	pair interaction
Δu	perturbation interaction
ΔX	general notation for the perturbation correction to system property

Greek letters

α	softness parameter
β	inverse temperature
ε	potential energy minimum in parent fluid
ε_1	relative strength of the repulsion in a 2Y reference fluid
ε_2	relative strength of the attraction in a 2Y reference fluid
κ	decay parameter for the attraction in a 1Y reference fluid
κ_1	decay parameter for the repulsion in a 2Y reference fluid
κ_2	decay parameter for the attraction in a 2Y reference fluid
μ	chemical potential
ρ	density
σ	zero of potential energy in parent and reference fluids

Super/subscripts

att	attraction
pert	perturbation
ref	reference
rep	repulsion

another model, closer to the system of interest, could be used. For instance, the square-well (SW) fluid for the considered realistic Lennard–Jones (LJ) one. Such attempts were made but, for obvious reasons (e.g., the phase diagram of the LJ fluid cannot be superimposed on that of the SW fluid), without any success.

Considering the perturbation expansion for fluids in general and not only for normal fluids, it is evident that the concept of HS (hard body in general) reference cannot work. Extensive molecular simulations performed in the 1990s on a variety of models, including polar [3,4] and associating [5–8] fluids, showed that the structure of fluids is determined primarily by short range interactions but offered also a more general interpretation: The structure of fluids is determined by the *short range* part of the total interaction which may be both repulsive and attractive. This result justifies attempts to consider the perturbed EOS about a more sophisticated reference system also for simple fluids and the only question is which model may be used to represent the short range interactions in a manageable way.

To find such model one should first answer the question why the HS-based approach has been so successful. Not only because of the availability of accurate analytic results for the HS fluid properties,

but primarily because of the flexibility of the HS fluid. The HS fluid exists only in the fluid phase (i.e., it does not exhibit the L–V phase transition) and this 'defect' makes it possible to change the hard core diameter (and hence the packing density) over a large range of values without imposing serious restrictions on the properties of the considered system and tune thus the results to the wished outcome.

The system that shares with the HS fluid similar properties is the Yukawa (Y) fluid [9]. First, by varying its range parameter Y model can be made short ranged and like HS model existing in a one fluid phase only. Second, as regards available equations for the properties of the Y reference fluid, they also are comparable with those for the HS reference fluid. An analytical treatment of the Y model is available within the mean spherical approximation (MSA) [10] that can be viewed as a counterpart of the common Percus–Yevick (PY) theory in the case of the HS reference system (we remind in passing that for the HS fluid the PY theory is identical to the MSA theory). There are also analytic results for single Yukawa tail developed within the high temperature expansions (HTE) by Henderson, Blum and Noworyta [11], Duh and Mier-y-Teran [12], and Shukla [13] that make it possible to evaluate the thermodynamic properties (the free energy, equation of state and chemical potential) for the Y fluid. By comparison with computer simulation data it has been already shown [13] that the HTE equations work well within broad density and temperature windows. It also possible to combine several Yukawa terms to better reproduce variety of shapes of various potential functions. Even in this case the HTE equations have been developed recently by Guerin [14] for the sum of two Yukawa (2Y) potentials and by Tang et al. [15] for the multi-Yukawa potentials.

Having in mind all the above mentioned properties of the Y fluid and, simultaneously, the problems of HS-based perturbation methods at high temperatures, we have recently formulated a perturbation theory with a short range Y reference [16–18]. A consequence of this choice is that the reference system captures a good deal of the properties of the considered fluid and the correction terms in the perturbation expansion can be confined to the first order only. Moreover, the mean field approximation can be used to evaluate this term to obtain quite accurate results. In this paper we present first the theoretical basis of the method in the next section and the basic formulas of the augmented vdW approach in Section 3. Results of the method obtained for selected model fluids are then shown and discussed in Section 4.

2. General considerations

To keep the theoretical part as general as possible, we consider an arbitrary simple pairwise additive intermolecular potential model $u(r)$. Given the potential u, the perturbation expansion method proceeds then formally as follows:

1. u is first decomposed into a reference part, u_{ref}, and a perturbation part, u_{pert},

$$u(r) = u_{ref}(r) + u_{pert}(r) \qquad (1)$$

The decomposition is not unique and is governed by both physical and mathematical considerations. This is the crucial step of the method that determines convergence (physical considerations) and feasibility (mathematical considerations) of the expansion.

2. The properties of the reference system (thermodynamics and structure) must be estimated accurately and relatively simply so that the evaluation of the perturbation terms is feasible (see below).

3. Finally, property X of the original system is then estimated as

$$X = X_{\text{ref}} + \Delta X \tag{2}$$

where ΔX denotes the contribution that has its origin in the perturbation potential u_{pert}. It is important to stress here that the correction term ΔX is obtained as the average over the reference system.

From the mathematical point of view, the perturbation theory (expansion) is an expansion in powers of u_{pert}. Thus, intuition would tell us that the closer the reference potential u_{ref} is to the original full potential, u, the faster convergence of the expansion should be achieved. However, such a choice would be evidently in conflict with step (2) of the above scheme because the evaluation of the properties of such a reference may be as difficult as of the original one. It is easy to show that the actual form of the reference potential is rather immaterial and that a much weaker condition can do the job regardless of the (relative) magnitudes of the perturbation part u_{pert}: A sufficient condition for the convergence of the perturbation expansion is a similarity (identity) of the *short range* or, in other words, of the *local structure* of the full and reference fluids [19,20]. The entire problem of the perturbation theory reduces then to finding an appropriate model for the reference system, i.e., the model that (i) is simple enough to comply with requirement (2) and, simultaneously, (ii) whose structure would be (nearly) identical to that of the fluid of interest (referred to as the parent fluid henceforth).

To satisfy the above requirement, besides the repulsive interaction part a piece of the attractive interaction must also be incorporated into the reference system. To this end, the interaction must be classified by its range (radius of interaction) rather than its strength/intensity. It is exactly this reason which makes the Y potential a natural candidate for the reference system: it is very convenient to tune its radius of interaction.

When considering the Y fluid as the reference, it is convenient to distinguish two types of fluid models of interest or parent fluid models to which it can be applied. The first type includes the class of fluid models whose repulsive interaction is purely HS repulsion. An example of such models are the Sutherland fluid and the medium and long-range Yukawa fluids. The second class consists of fluid models without any hard core at all. However, the hard-core repulsion can be embedded at some short separation without affecting the properties of the original model (which, in fact, is the usual practice for purely computational reasons). Typical representatives of such class of model fluids are the LJ and EXP6 (modified Buckingham potential) models. The main distinction between the two types of fluids is that only one Y term is sufficient to describe the reference system in the former case of HS-based models while two Y terms are necessary in the latter.

Namely, for the HS-based fluid models of interest we proposed to use for the reference system the hard spheres plus attractive one Yukawa (1Y) potential of the form

$$\frac{1}{\varepsilon} u_{\text{ref}}(r) \equiv \frac{1}{\varepsilon} u_{1Y}(r) \quad = \infty, \qquad\qquad\quad r < d$$
$$= -d \exp[-\kappa(r-d)]/r, \quad r \geq d \tag{3}$$

where d is the hard-core diameter, κ^{-1} determines the range of an attractive tail while ε is the potential depth. Reference potential given by Eq. (3) is characterized by a so far unspecified decay parameter κ and potential depth parameter ε. The idea behind is that the potential depth ε in the reference fluid model is the same as in the parent fluid, while value of κ must yield the attraction range of $u_{\text{ref}}(r)$ that is shorter than that of $u(r)$. To be more specific, to retain the flexibility of the 1Y fluid similar to that of the HS fluid, the range of attraction κ^{-1} should be smaller than one sixth of the hard-core diameter to make the critical point in the 1Y fluid disap-

pear [21]. Since for $\kappa d = 3$ the 1Y fluid critical temperature nearly coincides with the temperature of the LJ triple point, any 1Y fluid with κd between 3 and 6 may thus be an acceptable choice for the 1Y reference in the studies of the LJ-like fluids.

In the case of fluid models of interest determined by continuous potentials a two Yukawa (2Y) model must be used for the reference,

$$\frac{1}{\varepsilon} u_{\text{ref}}(r) \equiv \frac{1}{\varepsilon} u_{2Y}(r) = \varepsilon_1 \frac{r_m}{r} \exp[-\kappa_1 r] - \varepsilon_2 \frac{r_m}{r} \exp[-\kappa_2 r], \tag{4}$$

where r_m is the location of the potential minimum of the parent fluid model (e.g., LJ or EXP6) and ε is its depth. In what follows all distances and length parameters are measured relative to r_m while ε is used as the energy unit. The parameters $\varepsilon_1 > 0$ and $\varepsilon_2 > 0$ are the relative strengths of the repulsive and attractive contributions, respectively, and κ_1^{-1} and κ_2^{-1} are the measures of the range of the corresponding tails of the 2Y reference fluid. To specify the 2Y reference, a relation between the parent fluid and the 2Y fluid must be established. The 2Y potential contains four parameters. Three conditions seem evident: the coincidence of the location r_m and depth ε of the potential minimum of $u_{\text{ref}}(r)$ and $u(r)$ functions,

$$u_{2Y}(r = r_m) = u(r = r_m) = -\varepsilon, \tag{5}$$

$$\frac{du_{2Y}(r)}{dr}\Big|_{r=r_m} = \frac{du(r)}{dr}\Big|_{r=r_m} = 0, \tag{6}$$

and the location of the potential zero at $r = \sigma$ in both parent and reference potential functions,

$$u_{2Y}(r = \sigma) = u(r = \sigma) = 0. \tag{7}$$

Then there remains to impose one more condition on the 2Y potential parameters to complete the set of equations. When doing this one should realize that the goal is not to approximate the given potential model u by a 2Y potential but to use the latter model as a convenient (more appropriate) reference. And this should be done without any *a priori* reference to the properties of the parent fluid. This goal can be achieved in a number of ways. One such possibility is to argue within the spirit of perturbation theories and impose the condition that the second virial coefficients, B_2, of the parent and 2Y fluids, calculated for their repulsive parts only, be as close as possible one to another over a wide range of temperatures. This will further enhance the physical identity of the repulsive interactions in the parent and reference fluids. If necessary, one can also be more specific and account for some specific features of the potential curve. For instance, for the LJ fluid the coincidence of the LJ and 2Y curves in the inflection point of their attractive part may be imposed. The inflection point of the repulsive part of the EXP6 potential can be used similarly. Details of these specific choices are given in Section 4.

3. Augmented van der Waals equation

Provided that the intermolecular potential $u(r)$ of the parent fluid can be written in the form given by Eq. (1), a route to the augmented vdW equation of state (EOS) goes via the expansion of the Helmholtz free energy A in powers of βu_{pert} (denoted further as Δu for simplifying the notation) [22,23],

$$\beta A = \beta A_{\text{ref}} + \beta \langle \Delta U \rangle_{\text{ref}} + \cdots$$
$$= \beta A_{\text{ref}} + 2\pi \beta \rho N \int g_{\text{ref}}(r) \Delta u(r) r^2 dr + \cdots \tag{8}$$

$$= \beta A_{\text{ref}} - N\beta \rho a(T, a) + \cdots \tag{9}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and T is the absolute temperature, ΔU is the total contribution of pair energies $\Delta u \equiv u_{\text{pert}}$ to the total internal energy, $\langle \cdots \rangle$ denotes canonical averaging, N is

the number of molecules, ρ is the number density, and g is the radial distribution function.

Since the potential energy minima in the reference and parent fluids are the same, neglecting the high order expansion terms in (9) is justified. Within the first order expansion the EOS assumes then the form

$$\frac{\beta P}{\rho} = \frac{\beta P_{\text{ref}}}{\rho} - \beta\rho\left[a(T,\rho) + \rho\frac{\partial a(T,\rho)}{\partial\rho}\right], \qquad (10)$$

where P is the pressure. The correction function $a(T,\rho)$ is obtained by averaging over the structure of the reference system, i.e., from the integral involving the reference radial distribution function $g_{\text{ref}}(r)$. In the simplest approximation, the mean field approach, it is assumed that the molecules form a uniform background which implies that $g_{\text{ref}}(r) \approx 1$. This is the route that leads to the augmented vdW approach. Assuming $g_{\text{ref}}(r)$ to be a uniform is rather crude approximation if the reference system is made up of hard spheres, i.e. in the case of the common vdW/HS approach. However, as it will be shown in the next section, the uniformity approximation is fully justified if a more sophisticated Yukawa reference system is chosen, i.e. in the case of the proposed vdW/Y approach. Thus, using mean field approximation, Eq. (10) simplifies to

$$\frac{\beta P}{\rho} = \frac{\beta P_{\text{ref}}}{\rho} - \beta\rho a, \qquad (11)$$

where a is an easily evaluated constant,

$$a = -2\pi \int \Delta u(r) r^2 \, dr. \qquad (12)$$

All other thermodynamic quantities can then be written in a similar way, e.g., the Helmholtz free energy, A,

$$\frac{\beta A}{N} = \frac{\beta A_{\text{ref}}}{N} - \beta\rho a. \qquad (13)$$

the internal energy E,

$$\frac{\beta E}{N} = \frac{\beta E_{\text{ref}}}{N} - \beta\rho a. \qquad (14)$$

and the chemical potential μ,

$$\beta\mu = \frac{\beta A_{\text{ref}}}{N} + \frac{\beta P_{\text{ref}}}{\rho} - 2\beta\rho a. \qquad (15)$$

4. Results and discussion

To demonstrate usability of the presented approach for deriving EOS, we consider two kinds of model systems, namely, one with the purely HS repulsion and the other with a soft repulsion. Although the ultimate goal of the theory is an analytic EOS, we focus here primarily on the methodology to show that the proposed vdW/Y approach may yield better results than the vdW/HS. For this reason in some cases we will also use, in addition to analytic results, also simulation data for the reference fluid to check an accuracy of the vdW/Y approach.

4.1. The hard-core parent fluids

There is only a few HS-based simple fluid models that have been intensively studied over past decades. Most popular among them are the Yukawa fluid of the medium range (decay parameter $\kappa d = 1.8$) [24] and Yukawa fluid of the long range (decay parameter $\kappa d \leq 1$) [25], and the Sutherland fluid [27,26]. We focus here only on the Sutherland (S) fluid defined by the potential

$$\frac{1}{\varepsilon}u(r) \equiv \frac{1}{\varepsilon}u_S(r) = \begin{cases} \infty, & \text{if } r < d, \\ -(d/r)^6, & \text{if } r \geq d, \end{cases} \qquad (16)$$
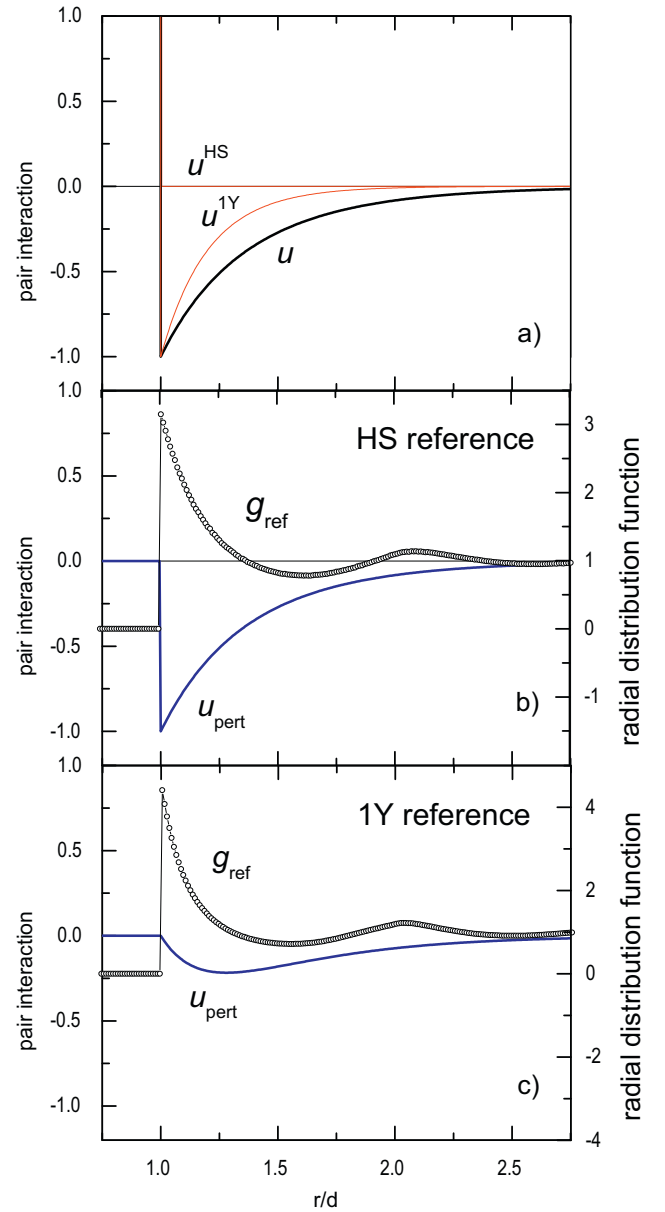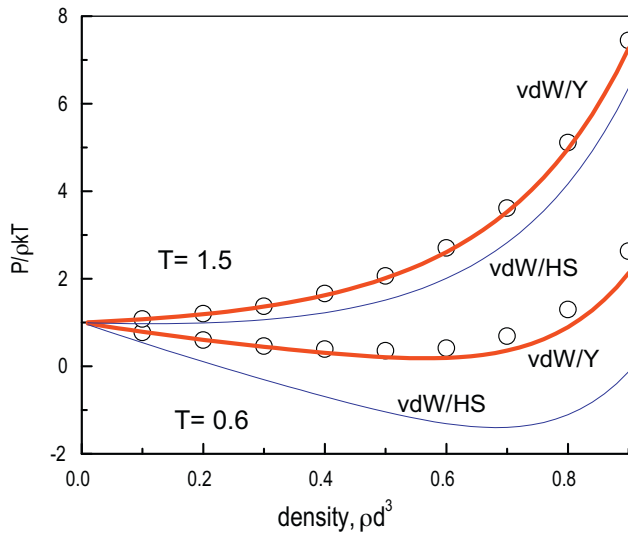

Fig. 1. Pair interaction in the case of the hard-core parent fluid model and its decomposition into the reference u_{ref} and perturbation u_{pert} terms. Part (a) shows the parent fluid model u (thick solid line) and two possible reference fluid models – HS model and 1Y model. Part (b) corresponds to the case of the HS reference fluid and shows the perturbation interaction $u_{\text{pert}} \equiv \Delta u(r)$ for this case and the radial distribution function $g_{\text{ref}}(r)$ of the HS reference system. Part (c) shows the same as part (b) but for the case of the 1Y reference fluid.

where d is the hard-core diameter of the particles, ε is the potential depth.

Following the methodology outlined in Section 2 we choose the 1Y model fluid, Eq. (3), with $\kappa d = 5$ as the reference. In Fig. 1 we show the perturbation potential $u_{\text{pert}} = u_S - u_{\text{HS}}$ for the case of the HS reference

$$\begin{aligned} \frac{1}{\varepsilon}u_{\text{pert}}(r) \quad &= 0, \qquad r < d \\ &= -\frac{d}{r^6}, \quad r \geq d \end{aligned} \qquad (17)$$

Fig. 2. Compressibility factor of the S fluid at two temperatures as indicated at the curves. Symbols correspond to the computer simulation data of Diez et al. [26], thick solid lines show results of the vdW/Y approach, and thin solid lines – results of the vdW/HS approach.

and $u_{\text{pert}} = u_S - u_{1Y}$ for the case of the 1Y reference

$$
\begin{aligned}
\frac{1}{\varepsilon} u_{\text{pert}}(r) &= 0, & r < d \\
&= -\frac{d}{r^6} + \frac{d}{r} \exp[-5(r/d - 1)], & r \geq d.
\end{aligned}
\tag{18}
$$

As we can see from the figure, the inclusion into the reference part of the short range attraction of the same energy minimum ε as in the parent fluid, makes the perturbation interaction $u_{\text{pert}}(r)$ very weak at the short and intermediate distances r. In particular, the perturbation term is exactly zero at the hard-core contact $r/d = 1$, i.e., $u_{\text{pert}}(r = d) = 0$. It means that the perturbation potential $u_{\text{pert}}(r) \equiv \Delta u(r)$ contributes to the correction term a, Eq. (12), primarily at larger separations where the radial distribution function $g_{\text{ref}}(r)$ fluctuates around unity. Consequently, the mean field approximation, $g_{\text{ref}}(r) \approx 1$ is fully justified in the case of 1Y reference fluid. On contrary, when the HS fluid is employed as the reference system then the perturbation interaction $u_{\text{pert}}(r)$ is composed of the entire attraction energy $u_S(r)$ and is the strongest at the hard-core contact $r = d$. Indeed, it has been already shown that with the HS reference the perturbation expansion in the case of the S fluid must be considered to the second order to obtain reasonably accurate results for the thermodynamic functions [26]. The same applies also to the results for the L–V phase diagram of the S fluid [27].

When evaluating thermodynamic properties, both augmented vdW approaches have been followed, i.e., using the HS reference (referred to as the vdW/HS) and the 1Y reference (vdW/Y). The properties of the HS reference have been obtained from the Carnahan–Starling equation [28], for the 1Y reference from the HTE equations [12]. The compressibility factor $P/\rho kT$ for selected isotherms are shown in Fig. 2. As it is seen from this figure, performance of the vdW/HS approach for thermodynamic properties is not satisfactory with increasing density and, especially, when temperature decreases towards the triple point temperature. On contrary, the proposed vdW/Y theory works well for all considered density and temperature conditions. Some small discrepancies can be noticed at very high densities and very low temperatures only. The failure of the vdW/HS theory is even more evident when it is applied to the calculations of L–V equilibrium, see Fig. 3. Although the performance of the vdW/Y is not perfect, it is both quantitatively and qualitatively significantly better than the predictions of the traditional vdW/HS theory. It is also worth mentioning that
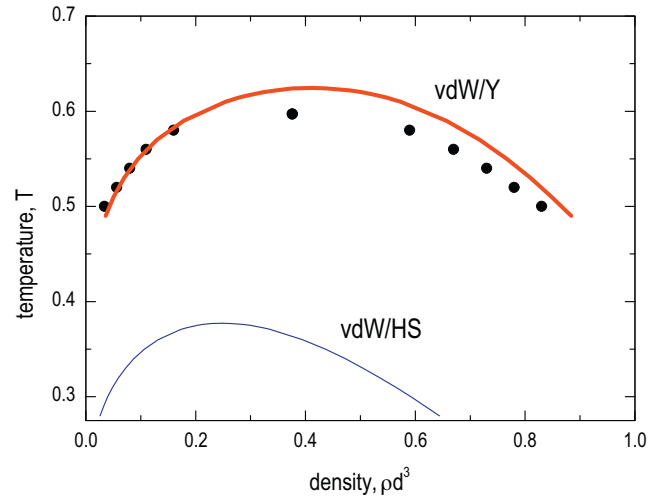
Fig. 3. Liquid–vapor coexisting envelope of the S fluid. Symbols correspond to computer simulation data of Camp [27], thick solid lines show results of the vdW/Y approach, and thin solid lines – results of the vdW/HS approach.

the liquid–vapor envelope obtained within the vdW/Y approach is nearly of the same accuracy as that reported for the S fluid within the second-order thermodynamic perturbation theory by Camp [27] (e.g., see Fig. 7 in Ref. [27]).

4.2. Parent fluid with continuous potentials

Typical examples of this type of fluids are the LJ and EXP6 potential models. Whereas in the case of LJ fluid a number of methods and results are available, to derive analytic expressions for the EXP6 fluid model is not a trivial task and we will therefore focus only on this model also called a modified Buckingham potential,

$$
\begin{aligned}
\frac{1}{\varepsilon} u(r) &\equiv \frac{1}{\varepsilon} u_{\text{EXP6}}(r) = \infty \text{ for } r < r_{\text{max}} \\
&= \frac{1}{\alpha - 6} \left[6 \exp\left[\alpha \left(1 - \frac{r}{r_m} \right) \right] - \alpha \left(\frac{r_m}{r} \right)^6 \right] \text{ for } r > r_{\text{max}}
\end{aligned}
\tag{19}
$$

where r_m is the location of the potential minimum and ε is the depth of the minimum. Parameter α (usually chosen within the range 11–15) determines the softness of repulsion: the repulsion becomes softer with decreasing α. In this study we choose the values of $\alpha = 11.5$.

To determine the 2Y reference for the EXP6 fluid we have followed the methodologies outlined in Section 2. Additionally, we have employed the best fit of the virial coefficients of the respective repulsive parts of the u_{2Y}^{rep} and $u_{\text{EXP6}}^{\text{rep}}$ potentials

$$
\begin{aligned}
u^{\text{rep}}(r) &= u(r) + \varepsilon & \text{for } r < r_m \\
&= 0 & \text{for } r > r_m.
\end{aligned}
\tag{20}
$$

over a wide range of temperatures, $1 < T^* < 20$. The defined in such a way parameters of the descending 2Y potential are: $\varepsilon_1 = 15026.860731$, $\kappa_1 r_m = 9.454846$, $\varepsilon_2 = 227.606845$ and $\kappa_2 r_m = 4.649829$.

Fig. 4 shows the decomposition of the total pair interaction into a reference and perturbation parts in the case of parent fluid with continuous potential. It is supposed that resulting 2Y potential function reproduces the repulsive part of the EXP6 including the region of potential minimum (Fig. 4a), consists of an attractive tail that slightly differs at the intermediate separations from the attractive tail in the EXP6 potential. Namely, the 2Y attraction decays faster, i.e. the $u_{2Y}(r)$ potential is of a shorter range as it is required for the reference potential. As a check of the quality of such a map-
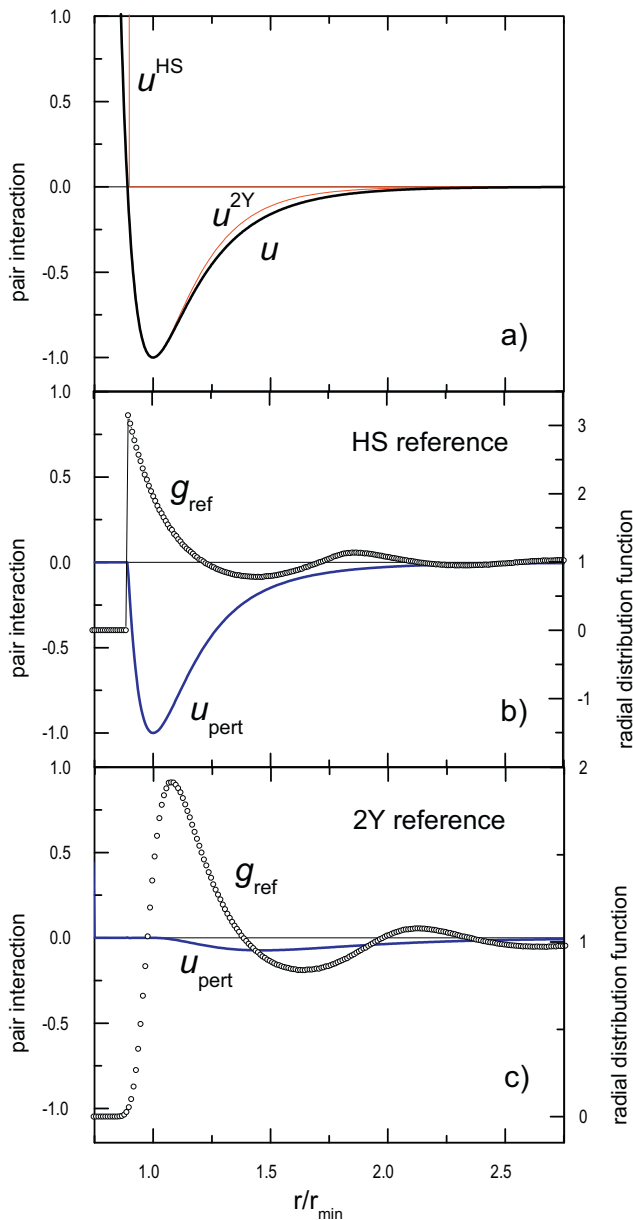
Fig. 4. Pair interaction in the case of the parent fluid model with a continuous potential and its decomposition into the reference u_{ref} and perturbation u_{pert} terms. Part (a) shows the parent fluid model u (thick solid line) and two possible reference fluid models – HS model and 2Y model. Part (b) corresponds to the case of the HS reference fluid and shows the perturbation interaction $u_{pert} \equiv \Delta u(r)$ for this case and the radial distribution function $g_{ref}(r)$ of the HS reference system. Part (c) shows the same as part (b) but for the case of the 2Y reference fluid.

ping, the thermodynamic properties of the only repulsive EXP6 and only repulsive 2Y fluids have been evaluated with the result that they are practically identical although some discrepancies, especially, for the pressure at higher temperatures and densities still exist (see Table 1). Evidently, the HS reference system is a very

Table 1
Computer simulation data for the pressure $P^* = Pr_m^3/\varepsilon$ of the purely repulsive 2Y and EXP6 model fluids.

T^*	ρ^*	P^{rep}_{PEXP6}	P^{rep}_{2Y}
2.00	1.4	24.38 ± 0.01	24.28 ± 0.01
	2.0	90.04 ± 0.01	89.01 ± 0.01
15.00	2.4	326.42 ± 0.01	321.87 ± 0.01

Table 2
Computer simulation data for the pressure $P^* = Pr_m^3/\varepsilon$ of the EXP6 and 2Y fluid models and the pressure difference $\Delta P = P_{EXP6} - P_{2Y}$.

T^*	ρ^*	EXP6	2Y	ΔP^*	$-\{p^*\}^2 a$
2.0	1.4	12.95 ± 0.2	14.933 ± 0.001	-1.983	-1.883
	1.6	24.73 ± 0.3	27.052 ± 0.002	-2.322	-2.460
	1.8	43.22 ± 0.1	45.824 ± 0.004	-2.604	-3.114
	2.0	70.28 ± 0.1	73.045 ± 0.006	-2.765	-3.844
15.0	2.4	294.4 ± 0.5	295.94 ± 0.01	-1.54	-5.536
	3.2	722.0 ± 1.0	721.02 ± 0.02	0.96	-9.841
	3.6	1048.8 ± 2.1	1047.63 ± 0.03	1.17	-12.454
	4.0	1466.0 ± 3.0	1464.90 ± 0.03	1.1	-15.376
	4.4	1978.0 ± 4.0	1982.75 ± 0.05	-4.75	-18.605

Table 3
Pressure, $P^{att} = P - P^{rep}$, of the 2Y and EXP6 fluids, obtained as the difference between computer simulation data for the full potential and for only repulsive part of corresponding potential.

T^*	ρ^*	p^{att}_{PEXP6}	P^{att}_{2Y}	$P^{att}_{EXP6} - P^{att}_{2Y}$	$-(\rho^*)^2 a$
2.00	1.4	-11.43 ± 0.01	-9.347 ± 0.01	-2.083	-1.883
	2.0	-19.76 ± 0.01	-15.965 ± 0.01	-3.795	-3.844
15.00	2.4	-32.02 ± 0.01	-25.93 ± 0.01	-6.09	-5.536

crude approximation for the EXP6 function. For comparison, the perturbation potentials for the case of the HS reference (Fig. 4b) and the 2Y reference (Fig. 4c) are shown as well. In contrast, the 2Y reference potential shows notable differences with parent fluid potential at the intermediate and large separations only, resulting in a rather weak perturbation term $u_{pert}(r)$. As for the coefficient a, in the case of the EXP6 fluid with $\alpha = 11.5$ it can be evaluated analytically yielding the value $a = 0.961\varepsilon r_m^3$.

To assess the performance of the augmented vdW/Y approach based on this 2Y reference two temperatures, $T^* = 2$ and $T^* = 15$, that are within the temperature range encountered in the geochemical applications are considered. Table 2 presents the computer simulation data for the pressure of the parent EXP6 fluid and reference 2Y fluid. As expected the deviations at intermediate separations between the EXP6 and 2Y potential functions lead to some differences, ΔP, in the pressure of two fluids. Our estimates, $-\rho^2 a$, shown in Table 2 as well, indicate that these differences can be easily handled within an augmented vdW/Y approach, similarly as we did it in the case of the S fluid. We note, that deviations between computer simulation data for the pressure difference $\Delta P = P_{EXP6} - P_{2Y}$ and the
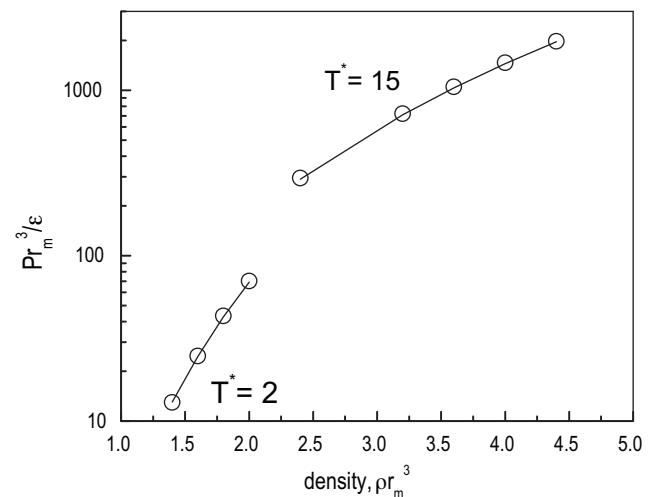
Fig. 5. Pressure of the EXP6 fluid. Symbols correspond to computer simulation data while solid lines represent the results of the vdW/Y approach based on computer simulation data for the 2Y reference fluid model.

analytical prediction $-\rho^2 a$ for this difference at higher temperature $T^* = 15$ originates from the differences between repulsive interactions u_{2Y}^{rep} and u_{EXP6}^{rep} (see Table 1). Indeed, the results in Table 3 show that taking these differences into account makes the vdW/Y approach consistent with computer simulation data. Using computer simulations data for the 2Y reference system, in Fig. 5 we show that augmented van der Waals approach vdW/Y can be developed for EXP6 fluid. We can see, that the simulation data for the pressure of the supercritical EXP6 fluid can be rather accurately expressed via coefficient a.

5. Conclusions

The commonly used augmented vdW equations are based on the hard sphere (hard body) primary contribution to the properties of fluids. This choice suffers from two defects: (i) inaccuracy when only one simple correction term is used, and (ii) limitation to ambient and not too much elevated temperature range only. As an attempt to remove these drawbacks we have formulated an expansion (augmented vdW EOS) about a reference system with soft interactions which incorporates also the attractive interaction at short separations. The method is based on the knowledge of the Yukawa fluid properties and its flexibility.

In this paper we have formulated the methodology of the approach and then presented its implementation in the case of two simple fluids. Particularly the application of the method to the EXP6 fluids extends the applicability of augmented vdW equations to the region of supercritical conditions, i.e. the region where a special theoretical treatment is required and the available results are either only in a numerical form or represent only empirical correlations. The presented results clearly show that the suggested approach may provide a simple and yet quite accurate augmented vdW equation in analytic form able to perform over a very large range of thermodynamic conditions. In other words, to evaluate thermodynamics for EXP6 fluids one needs to calculate (by simulations or theoretically) the properties of 2Y fluid and then employ these data in augmented van der Waals theory.

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