Theoretical equation of state for classical fluids.  
I. Test by perturbation theory

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ABSTRACT. This paper shows how to construct the theoretical equation of state (TEOS) of a classical simple fluid. The theory relies on the mean collisional diameter and range, and maps the thermodynamical properties of the fluid into those of an equivalent square-well (ESW) fluid of appropriate depth $\epsilon$, diameter $\sigma$ and range $R$. It is shown that the ESW has the same pressure as the fluid of interest. Hence the TEOS of any simple fluid takes the form of a SW EOS of the given $\epsilon, \sigma$ and $R$. The theory is applied to a Lennard-Jones (LJ) system in a first-order perturbation. The mapping equations have a physical solution for densities where the SW EOS is accurate; the resulting LJ TEOS agrees very well with the results of computer simulations, and compares favorably with the recent TEOS developed by Song and Mason.

RESUMEN. Se muestra cómo construir la ecuación teórica de estado (ETE) de un fluido simple y clásico. La teoría maneja el diámetro y el alcance colisionales medios y mapea las propiedades del fluido sobre las de un sistema equivalente de pozos cuadrados (EPC) con profundidad $\epsilon$, diámetro $\sigma$ y alcance $R$ apropiados. Se demuestra que las presiones del fluido de interés y del EPC son iguales. Para esto, la ETE de cualquier fluido simple toma la forma de una EE de PC con $\epsilon, \sigma$ y $R$ dados por la teoría. Esta se aplica a un fluido de Lennard-Jones (LJ) en una aproximación perturbativa. El mapeo tiene solución para las densidades en que la EE de PC usada aquí es precisa; la ETE de LJ concuerda muy bien con los resultados de simulación y se compara favorablemente con la ETE recientemente publicada por Song y Mason.

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1. Introduction

Equations of state (EOS) of fluids play an important role in physical theory and applications. For dilute neutral fluids, the problem was essentially solved by the virial expansion of the thermodynamic properties [1], but it is far from solved for dense fluids or liquids. Nevertheless, there have been important successes for some model potentials, as, e.g., the work on hard spheres (HS) and several hard non-spherical particles, which has been recently reviewed by Boublik and Nezbeda [2]. For repulsive and soft interactions there are approximate theories that combine the well-know HS EOS with perturbation methods and the principle of corresponding states [3].

For interactions with an attractive part, the most famous result is the exact derivation of the extended van der Waals EOS obtained by Kac et al. [14], which corresponds to a HS repulsion plus a vanishingly small attraction of infinite range. Approximate results are available for other potentials as, e.g., the adhesive hard-sphere system [5, 6], hard
spheres with electrostatic interactions [7] and the square-well fluid [8]. Some of the latter equations are quite accurate and are used in the theory presented in this paper.

Compared with these slow advances, numeric calculation of thermodynamic properties of not-too-complex fluids by means of statistical mechanics has been very successful. At least for simple fluids, both modern perturbation theory and integral equation techniques allow to calculate the equilibrium thermodynamic properties with an accuracy of the order of computer simulations [9].

The purpose of this work is to present a theory of the EOS of classical fluids and illustrate it for a simple realistic case. The theory is based on simple new concepts of kinetic theory developed by one of the authors and collaborators [10-13], and has already lead to EOS of simple purely repulsive fluids which are exact over the whole fluid density range [14]. An alternative approach to obtain the EOS of fluids from statistical mechanics has been presented recently by Mason and collaborators [15]. In this paper we make an initial comparison between both methods.

The theoretical EOS of a fluid with interaction potential \( u(r) \), is an explicit equation for a thermodynamic property in terms of the state variables. In this work we will obtain the pressure \( P \) as an explicit function of density \( \rho \) and temperature \( T \):

\[
P = P(\rho, T, \Lambda),
\]

where \( \Lambda \) is a set of parameters characterizing the particular fluid of interest. For a theoretical EOS (TEOS) one requires that: a) The dependence of \( P \) on \( \rho, T \) and \( \Lambda \) be derived from statistical mechanics; b) the EOS parameters \( \Lambda \) be well defined as functionals of the potential \( u(r) \); c) the dependency of the EOS parameters \( \Lambda \) on \( \rho \) and \( T \) can be parametrized analytically, and d) the theory should provide the EOS for all fluids in a given class [16].

This article shows how to obtain a TEOS with the above qualities. In Sect. 2 we review briefly the generalized collision frequencies which are essential to the theory. In Sect. 3, these frequencies are used to build the mean diameter \( \langle s \rangle \) and mean attractive range \( \langle l \rangle \) [13]. These quantities allow to write \( P(\rho, T) \) exactly as the pressure of a square-well fluid whose diameter \( \sigma \) and range \( R \) are respectively proportional to \( \langle s \rangle \) and \( \langle l \rangle \). In Sect. 4 we refer to the square-well EOS used here, which is discussed in detail in Ref. [8], and show how the other relevant SW properties are obtained. In order to illustrate the use of this theory, Sect. 5 is devoted to obtain the TEOS of a Lennard-Jones 12/6 fluid. This is done in the simplest way, which relies on a perturbative approximation. The equation thus obtained is compared with empirical EOS for the LJ fluid and with the Song-Mason equation for the same system [15]. The TEOS developed here is quite accurate for \( T \) above 80% the critical \( T_c \), and \( \rho \) smaller than twice the critical \( \rho_c \).

2. Generalized collision frequencies

It is simpler to introduce the collision frequencies in reference to a spherically symmetric discontinuous potential \( u_i(r) \), of the type shown in Fig. 1 [11]. At a step of height \( \delta \epsilon = u(\sigma^+) - u(\sigma^-) \), at \( r = \sigma \), one identifies three types of collisions illustrated in Fig. 1.
Bounces (B), for relative kinetic energy \( e_K < |\delta \epsilon | \), and collisions up-the-step (US) or down-the-step (DS), when \( e_K > |\delta \epsilon | \) and the kinetic energy after the collision is respectively smaller or greater than \( e_K \). The collision frequency for each type of event is written in terms of the mean relative velocity \( \langle v_r \rangle \) and the radial distribution function \( g(r) \) as follows [10-12]:

\[
\nu_B = \pm \pi \sigma^2 \rho (v_r) \delta g(\sigma),
\]

\[
\nu_{US} = \nu_{DS} = \pi \sigma^2 \rho (v_r) g(\sigma^\mp),
\]

where \( \delta g(\sigma) = g(\sigma^+) - g(\sigma^-) \). The signs depend on the sign of \( \delta \epsilon \), and are chosen such that \( \nu_B > 0 \) and \( \sigma^\mp \) is at the top of the step [10-12]. When \( \delta \epsilon \to \infty \), \( \nu_{DS} = \nu_{US} \to 0 \), and \( \nu_B \) reduces to Enskog’s result for the HS collision frequency [17]. These expressions were confirmed by a molecular dynamics simulation [11]. The contribution to the pressure \( P \) from the force at an impulsive step equals the flux of momentum [18, 19]. The contribution to the momentum flux from repulsive bounces from the step at \( r = \sigma \) is found to be

\[
\frac{\beta P_B}{\rho} = \frac{2\pi \nu_B}{3\langle v_r \rangle},
\]

which is identical to the result obtained by the virial theorem of Clausius for the contribution \( P \) of all the forces acting at \( \sigma \). In the kinetic approach, only the bounces contribute to the pressure, because \( P_{DS} = -P_{US} \) and hence \( P = P_B \). This is not so if the effect of the forces is calculated via the virial theorem. In the latter, all forces have contributions of the same sign (which is given by the sign of \( \delta \epsilon \)) and \( P_{DS}' = P_{US}' > 0 \), but are such that the total pressure \( P_B' + P_{DS}' + P_{US}' \) is again identical to \( P_B \) in Eq. (4) [10, 11].

The transition to a continuous potential \( u(r) \) can be made from the impulsive \( u_i(r) \) in Fig. 1 in the limit of infinitely many steps [12, 13]. For collisions at distances \( s < r < s + ds \), the differential frequency for repulsive or attractive bounces, \( d\nu_{R/A}(s) \), follows from (1) when \( \delta \epsilon \to 0 \) and is

\[
d\nu_{R/A}(s) = \pm \pi s^2 \rho (v_r) y(s) \frac{\partial \exp(-\beta u)}{\partial s} ds,
\]

where the (+) sign applies to repulsive (R) and the (−) to attractive (A) parts of \( u(r) \), and \( y(r) = g(r) \exp(\beta u) \).

3. MEAN COLLISION PARAMETERS AND EQUIVALENT SW FLUID

Consider a realistic spherical potential \( u(r) \) with its minimum \(-\epsilon \) at \( r = r_m \). For a pair of particles with \( r < r_m \) and relative energy \( e \) one can define the collision diameter \( s \) as
the smallest distance at which the kinetic energy vanishes, i.e., \( u(s) = e \), so that \( s \) is the distance when a bounce occurs. Hence, the average diameter can be obtained from Eq. (5) as

\[
\langle s \rangle(\rho, T) = \frac{1}{\nu_R} \int d\nu_R s
\]

\[
= \frac{\pi \rho \langle v_r \rangle}{\nu_R} \int_0^{r_m} ds \, s^3 \theta(s) \frac{\partial [\exp(-\beta u)]}{\partial s},
\]

where \( \nu_R \) is the total repulsive frequency, i.e., the integral of (5) for \( s \) between 0 and \( r_m \).

For a pair of particles with \( r > r_m \) and negative energy \( e' \), i.e., for a "van der Walls' dimer", one can also define the collisional attractive range \( l \), where \( u(l) = e' < 0 \). Its average is

\[
\langle l \rangle(\rho, T) = -\frac{\pi \rho \langle v_r \rangle}{\nu_A} \int_{r_m}^{\infty} dl \, l^3 \theta(l) \frac{\partial [\exp(-\beta u)]}{\partial l},
\]

where \( \nu_A \) is the total frequency of attractive collisions. The average collision parameters \( \langle s \rangle \) and \( \langle l \rangle \), and the frequencies \( \nu_A \) and \( \nu_R \) concentrate the information about the collision processes in the fluid, and have been discussed in detail elsewhere [13].

We will now show how to define an equivalent fluid with exactly the same pressure as the system of interest at the same \( (\rho, T) \). This equivalent system has a square-well (SW) interaction of depth \( e_{sw} \), hard-core diameter \( \sigma \) and attractive range \( R \) such that its pressure is

\[
\frac{\beta P_{sw}}{\rho} = 1 + \frac{2\pi \rho}{3} \left[ \sigma^3 y_{sw}(\sigma)e^{\beta e_{sw}} - R^3 y_{sw}(R)(e^{\beta e_{sw}} - 1) \right].
\]
There are several ways to define the equivalent SW fluid. Here we will follow the simplest approach and choose: 1) The SW depth to be identical to that of \( u(r) : \epsilon_\text{sw} = \epsilon \); and 2) the SW diameter and range to be the (renormalized) mean collision diameter and range of the molecules, i.e.,

\[
\sigma = \frac{\nu_r}{\nu_{R_{\text{sw}}}}(s),
\]

and

\[
R = \frac{\nu_A}{\nu_{A_{\text{sw}}}}(l).
\]

Since \( \nu_{R_{\text{sw}}} \) and \( \nu_{A_{\text{sw}}} \) are obtained from Eq. (1), the SW pressure in (8) then becomes

\[
\frac{\beta P_{\text{sw}}}{\rho} = 1 + \frac{2}{3}\langle v_r \rangle \left( \sigma \nu_{R_{\text{sw}}} - R \nu_{A_{\text{sw}}} \right),
\]

which by (9) and (10) gives

\[
\frac{\beta P_{\text{sw}}}{\rho} = 1 + \frac{2}{3}\langle v_r \rangle \left( \langle s \rangle \nu_r - \langle l \rangle \nu_A \right).
\]

Substitution of Eqs. (6) and (7) in (11) then shows that its right-hand side is identical to the desired pressure \( P \) as given by the virial theorem. It is then clear how this approach leads to build the TEOS of the fluid of interest. The pressure is expressed by two components: 1) the SW EOS

\[
P = P_{\text{sw}}(\rho \sigma^3, \beta \epsilon, R/\sigma),
\]

and 2) the quantities \( \sigma(\rho, T) \) and \( R(\rho, T) \) obtained from the mapping Eqs. (9) and (10). The SW EOS will thus be a universal component of the TEOS of all fluids for which the mapping equations have a solution. The latter are written explicitly as

\[
\sigma^3(\rho, T) y_{\text{sw}}(\sigma)e^{\beta \epsilon} = \int_0^{r_m} ds s^3 y(s) \frac{\delta[\exp(-\beta u)]}{\delta s},
\]

and

\[
R^3(\rho, T) y_{\text{sw}}(R)(e^{\beta \epsilon} - 1) = -\int_{r_m}^{\infty} dl l^3 y(l) \frac{\delta[\exp(-\beta u)]}{\delta l}.
\]

At low densities, one can expand the pair distribution functions \( y_{\text{sw}}(r) \) and \( y(r) \) in powers of \( \rho \) so that

\[
\sigma(\rho, T) = \sigma_0(T) + \sigma_1(T) \rho + \sigma_1(T) \rho^2 + \cdots
\]

and

\[
R(\rho, T) = R_0(T) + R_1(T) \rho + R_2(T) \rho^2 + \cdots
\]
Previous evidence indicates that Eqs. (15) are quite convergent and can be safely truncated after a few terms [3, 13, 14, 20, 21]. The results of this work confirm that such is the case. It is interesting that \( \sigma_0(T) \) and \( R_0(T) \), are respectively equal to the \( \rho \to 0 \) limits of the HS diameter in the WCA theory [22], and of the SW range in the SW blip perturbation theory [20].

4. PROPERTIES OF THE SW SYSTEM

The properties of the SW fluid needed in this theory are: an expression for \( P_{sw}(\rho \sigma^3, \beta \epsilon, \lambda) \), with \( \lambda = R/\sigma \), and the values of \( y_{sw}(\sigma) \) and \( y_{sw}(R) \) used in the mapping Eqs. (13) and (14). The first is simply obtained from the SW Helmholtz free energy \( A_{sw} \). It has also been shown that [23]

\[
y_{sw}(R) = \frac{1}{12\eta[\exp(\beta \epsilon) - 1]} \left[ \frac{\partial a_{sw}(\eta, T, \lambda)}{\partial \lambda} \right],
\]

where \( a_{sw} = \beta A_{sw}/N \) and \( \eta = \pi \rho \sigma^3/6 \). Finally, \( y_{sw}(\sigma) \) is obtained from Eqs. (8) and (16).

A paper submitted together with this [8] presents an equation for \( a_{sw} \) which can be used at intermediate ranges \( 1.375 < \lambda < 1.75 \) appropriate for simple fluids [20, 21]. This SW EOS is quite accurate for \( T \sim 0.6T_c \) and \( \rho \leq 2\rho_c \). The reader is referred to Ref. [8] for details. The values of \( y_{sw}(\sigma) \) and \( y_{sw}(R) \) obtained in this way are quite close to the Monte Carlo results of Henderson and collaborators [24, 25] for SW of various \( \lambda, T \) and \( \rho \).

5. THEORETICAL EOS FOR THE LJ 12/6 FLUID

The main question confronting this theory is whether the mapping equations, (9) and (10), or (13) and (11), have solution, i.e., whether the variable-width SW system is flexible enough to represent the properties of the fluid. From the argument leading to Eq. (11), it follows that any solution of the mapping equations will give the pressure of the system with an error which only reflect the accuracy with which the system's r.d.f. is obtained. (This function is the input in Eqs. (13) and (14).) This means that any errors in the SW EOS will not affect the accuracy of the pressure, as long as the mapping equations have real solutions for \( \sigma \) and \( R \). Nevertheless, the inaccuracy of the SW EOS will be reflected in the behaviour of \( \sigma(\rho, T) \) and \( R(\rho, T) \). These questions will be answered and illustrated here by applying this theory to a fluid interacting with the Lennard-Jones 12/6 potential.

To obtain the TEOS of a fluid one needs the r.d.f. for the desired \( u(r) \) and use it in Eqs. (13) and (14) to calculate \( \sigma \) and \( R \) at one state \( (\rho, T) \). At low densities, \( y(r) \) is expanded in a virial series from which the coefficients \( \sigma_0(T), R_0(T) \), etc., in Eqs. (15) are obtained by simple quadrature. This procedure gives the exact low density behaviour of \( \sigma(\rho, T) \) and \( R(\rho, T) \). For the LJ 12/6 fluid, the zeroth-order coefficients are shown in Fig. 2. When \( T^* \to 0 \), both \( \sigma_0 \) and \( R_0 \to r_m \), because at \( T^* = 0 \) all pairs are a distance \( r_m \).
apart. When \( T^* \to \infty \), \( \sigma_0 \to 0 \) slowly and \( R_0 \to 1.5565 \sigma_{LJ} \). The next coefficients \( \sigma_1(T) \) and \( R_1(T) \) were also calculated and behave smoothly for \( T^* > T_c^* \).

At high densities, \( y_{LJ}(r) \) can be obtained from simulations or any of several theories already applied to the LJ 12/6 fluid. In this paper we will follow the simplest approach and calculate \( y_{LJ} \) from first-order perturbation theory. This approach is particularly appealing because the SW fluid is an adequate reference system for the perturbative calculation [26].

In this case

\[
y_{LJ}(r; \rho, T) \approx y_{SW}(r; \epsilon', \sigma', R'; \rho, T),
\]

which, for the LJ system, improves the already good results of the WCA HS perturbation theory [26]. The values of \( \epsilon', \sigma' \) and \( R' \) that define the SW reference in (17) are provided by perturbation theory. In all cases, \( \epsilon = \epsilon' \), but at least two possibilities arise in regard to \( \sigma' \) and \( R' \): The first is to use the same values \( \sigma \) and \( R \) determined by the mapping Eqs. (13) and (14), this assumes that the ESW, which has the same pressure as the fluid of interest, is also a good reference in the perturbation scheme. This choice will be referred to as the "pressure" option. The second choice is to determine \( \sigma' \) and \( R' \) by the common blip procedure which provides a good approximation to the Helmholtz free-energy of the system [20,26]. This will be called the "free-energy" option.

For both options one still needs to calculate \( y_{SW} \). Following the same work [26], \( y_{SW}(r) \) can be parametrized in terms of the well known \( y_{HS}(r) \) as

\[
y_{SW}(r) = L(r)y_{HS}(r),
\]

where \( L(r) \) is a linear polynomial in \( r \) fitted to give the correct values of \( y_{SW}(r) \) at \( r = \sigma \) and \( r = R \). The latter are then obtained from \( a_{SW} \) as described in the previous section.
In the pressure option, one uses approximation (17) and (18) in the coupled set (13) and (14). For the LJ 12/6 fluid, the resulting values for $\sigma^* = \sigma/\sigma_{LJ}$ and $R^* = R/\sigma_{LJ}$ are respectively shown in Figs. 3 and 4 as functions of $\rho^* = \rho \sigma_{LJ}^3$ for several temperatures. The diameter $\sigma$ is remarkably constant for $\rho^* \leq 0.6$, which is the density range where our SW EOS is accurate. Nevertheless, a second solution becomes apparent at higher densities, as is shown in Fig. 5. An analysis of $g_{LJ}(r)$, as obtained in the pressure option, shows that the solution on the top branch grossly misrepresents the known structure of the LJ fluid. Hence, the pressure option gives reliable values of $\sigma$ and $R$ only for densities $\rho^* \leq 0.6$, or slightly larger at high temperatures.

The values of the EOS parameters $\sigma^*$ and $R^*$ for $\rho^* \leq 0.6$ were fitted to fourth-order density polynomials with coefficients $\sigma_n(T)$ and $R_n(T)$, as in Eqs. (15), for $n \geq 1$ and with the exact $\sigma_0(T)$ and $R_0(T)$. The latter guarantee that the second virial coefficient is incorporated exactly and are represented by

$$\sigma_0(T) = \frac{\sigma_{00} + \sigma_{01} T^* + \sigma_{02} T^{*2}}{1 + \sigma_{03} T^* + \sigma_{04} T^{*2} + \sigma_{05} T^{*3}},$$

(19)

$$R_0(T) = \frac{r_{00} + r_{01} T^* + r_{02} T^{*2}}{1 + r_{03} T^* + r_{04} T^{*2}},$$

(20)

with the coefficients $\sigma_{0n}$ and $r_{0n}$ given in Tables I and II. The higher-order density coefficients $\sigma_n$ and $R_n$, $n \geq 1$ are given by polynomials

$$\sigma_n(T) = \sum_{m=0}^{M} \sigma_{nm} T^{*m},$$

(21)

$$R_n(T) = \sum_{m=0}^{M} r_{nm} \beta^{*m},$$

(22)

where $\beta^* = \epsilon/kT$. The coefficients $\sigma_{nm}$ and $r_{nm}$ are also given in Tables I and II, and the order $M$ is implicit in these tables. These simple fits give $\sigma^*$ and $R^*$ as shown in Figs. 3 and 4.

In the free-energy option, $\sigma'$ and $R'$ were obtained by the common blip procedure [26]. The resulting $g_{LJ}(r)$ was used to calculate the right-hand sides of (13) and (14), and this set was solved for $\sigma_A$ and $R_A$. This option reduces the non-linearity of the mapping equations and, as a result, only one solution is found for all densities $\rho^* \leq 1$. The behaviour of $\sigma_A(\rho, T)$ and $R_A(\rho, T)$ is very close to that of $\sigma$ and $R$ for $\rho^* \leq 0.6$.

As was already mentioned, the pressure obtained by this theory will carry any errors made in calculating the r.d.f. on the right-hand sides of Eqs. (13) and (14). Comparing the results for $P$ obtained from the pressure and free-energy options with the empirical LJ EOS of Nicolas et al. [27], one finds that the pressure option is the more accurate of the two in the region $\rho^* \leq 0.6$. The free-energy option is less accurate in this region but is well behaved up to $\rho^* = 1$. 
FIGURE 3. Mean diameter $\sigma^* = \sigma/\sigma_{\text{LJ}}$ of the Lennard-Jones 12/6 particles as function of density calculated by perturbation theory in the "pressure" option. The curves are labeled with the values of $T^*$. 

FIGURE 4. Mean attractive range $R^* = R/\sigma_{\text{LJ}}$ of the LJ 12/6 particles, as a function of density, in the "pressure" option. The labels on the curves give the values of $T^*$. 

Hence, among the simple perturbation approximations here considered, the pressure option is the best, giving explicitly the pressure of the LJ fluid for $\rho^* \leq 0.6$. The resulting LJ TEOS is given by the SW EOS, derived from Eq. (12) as described in Ref. [8], with the mean diameter and range given by Eqs. (19)-(22) and the Tables. The compressibility factor $Z = \beta P/\rho$ thus obtained is compared in Figs. 6 and 7, for several temperatures,
Figure 5. High-density behaviour of the LJ mean diameter in the pressure option, showing the second branch.

Table I. Coefficients in the representation of the mean diameter $\sigma^*$ (The numbers in parenthesis stand for powers of 10).

<table>
<thead>
<tr>
<th>$\sigma_{0m}$</th>
<th>$\sigma_{1m}$</th>
<th>$\sigma_{2m}$</th>
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Table II. Coefficients in the representation of the mean range $R^*$.

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<th>$r_{1m}$</th>
<th>$r_{2m}$</th>
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</table>
FIGURE 6. Comparison between equations of state for the LJ 12/6 fluid at lower temperatures, as labeled. Continuous lines: theoretical EOS from this work; circles: empirical EOS by Nicolas et al. [27]; dashed lines: Song and Mason EOS [15].

FIGURE 7. The same as Fig. 6, but at higher temperatures.

with the empirical equation of Nicolas et al. EOS [27]. The agreement between both is very good at all temperatures and \( \rho^* < 0.6 \). The same figures show the values of \( Z \) obtained from the simpler TEOS of Song and Mason [15]. For \( T^* \leq 5 \) the TEOS here presented is notably more accurate than the Song and Mason EOS in the density range considered, particularly at the lower temperatures. For \( T^* \geq 10 \) both TEOS are indistinguishable.
6. Conclusions

This article shows how to derive a theoretical EOS of simple fluids. This TEOS relies on mapping the system of interest into a SW fluid of suitably defined depth, diameter and range, which are simply related to collisional averages. The mapping equations, (13) and (14), are shown to have solution for the simple LJ 12/6 system in a first-order perturbation approximation. The TEOS obtained within this approximation is shown to reproduce remarkably well the pressure of the LJ system as represented by the empirical EOS of Nicolas et al. [27] for $T^*/T^*_c > 0.8$ and $\rho/\rho_c < 2$. This TEOS compares favourably with the TEOS of Song and Mason [15].

The present application of this theory is limited by the approximate SW EOS used here and by the perturbation approximation used for the system of interest. Both can be tackled by using a SW EOS with a more extended range of application and by using better approximations for the r.d.f. of the fluid of interest.

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