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Citation: J. Chem. Phys. 137, 204102 (2012); doi: 10.1063/1.4767065
View online: http://dx.doi.org/10.1063/1.4767065
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v137/i20
Published by the American Institute of Physics.

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An asymptotically consistent approximant method with application to soft- and hard-sphere fluids

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(Received 3 August 2012; accepted 29 October 2012; published online 26 November 2012)

A modified Padé approximant is used to construct an equation of state, which has the same large-density asymptotic behavior as the model fluid being described, while still retaining the low-density behavior of the virial equation of state (virial series). Within this framework, all sequences of rational functions that are analytic in the physical domain converge to the correct behavior at the same rate, eliminating the ambiguity of choosing the correct form of Padé approximant. The method is applied to fluids composed of “soft” spherical particles with separation distance \( r \) interacting through an inverse-power pair potential, \( \phi = \epsilon (\sigma / r)^n \), where \( \epsilon \) and \( \sigma \) are model parameters and \( n \) is the “hardness” of the spheres. For \( n < 9 \), the approximants provide a significant improvement over the 8-term virial series, when compared against molecular simulation data. For \( n \geq 9 \), both the approximants and the 8-term virial series give an accurate description of the fluid behavior, when compared with simulation data. When taking the limit as \( n \to \infty \), an equation of state for hard spheres is obtained, which is closer to simulation data than the 10-term virial series for hard spheres, and is comparable in accuracy to other recently proposed equations of state. By applying a least square fit to the approximants, we obtain a general and accurate soft-sphere equation of state as a function of \( n \), valid over the full range of density in the fluid phase. © 2012 American Institute of Physics.

[http://dx.doi.org/10.1063/1.4767065]

I. INTRODUCTION

The virial equation of state (VEOS, virial series) describes the dependence of pressure on density via a series expansion about the ideal-gas limit,¹ and is given by

\[
Z \equiv \frac{P}{\rho kT} = 1 + \sum_{j=2}^{\infty} B_j \rho^{j-1},
\]

where \( Z \) is the compressibility factor, \( P \) is the pressure, \( \rho \) is the number density, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. The virial coefficients \( B_j \) are functions of \( T \) and the physical parameters describing the intermolecular potential. Specifically, the \( j \)th coefficient is given in terms of integrals over the positions of \( j \) molecules.² \( B_3 \), for example, requires integration over the variables describing the second and third molecules’ positions relative to the first molecule. For illustration, the first two coefficients are written

\[
B_2 = -\frac{1}{2V} \int f_{12}dr_1dr_2,
\]

\[
B_3 = -\frac{1}{3V} \int \int f_{12}f_{13}f_{23}dr_1dr_2dr_3,
\]

where \( f_{ab} \) is the Mayer \( f \)-function, \( f_{ab} = \exp(-\phi_{ab}/kT) - 1 \), and \( \phi_{ab} \) is the intermolecular potential between molecule \( a \) and molecule \( b \) with separation distance \( r_{ab} = |r_a - r_b| \). Here, we examine the classical pair-wise additive and spherically symmetric repulsive soft-sphere potential, defined by

\[
\phi_{ab} = \epsilon (\sigma / r_{ab})^n,
\]

where \( \epsilon, \sigma, \) and \( n \) are positive parameters, which characterize the energy, size, and “hardness” of the spheres, respectively. Note that when \( n \to \infty \), Eq. (3) becomes the hard-sphere potential, and \( \sigma \) is interpreted in this limit as the hard-sphere diameter.

Standard quadrature methods are ineffective in calculating the multidimensional integrals that connect the virial coefficients to molecular interactions. Each increment in the order of the virial coefficient introduces integration over additional spatial variables for description of the new molecule’s relative position, as well as (for non-spherical molecules) any other variables required to describe orientational and internal degrees of freedom. Moreover, the number of integrals involved in calculating virial coefficients increases rapidly and non-linearly with the order \( j \) of the coefficient. For example, the calculation of \( B_7 \) and \( B_8 \) requires the evaluation of 171 and 2606 Ree-Hoover cluster integrals, respectively, where each cluster integral represents a collection of nested integrals.³ The Mayer sampling Monte Carlo (MSMC) approach is an effective way to compute these integrals, using importance...
Coefficients for $n = 4$ and 7 are taken from Tan and Barlow.\textsuperscript{16} All $\bar{n}$ for $n = 24, 50,$ and 80 are also taken from Wheatley.\textsuperscript{7} All $B_j$'s for hard-spheres ($n = \infty$) are taken from Chisholm and McCoy,\textsuperscript{9} which also reports $B_9 = 0.4884(5)$ and $B_{10} = 0.313(1).$ All other values are newly generated by the authors.

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<th>$n$</th>
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The soft-sphere model, with a potential given by Eq. (3), has only one effective parameter, $\epsilon \sigma^n$. As a consequence, each virial coefficient can be evaluated at any temperature, through the relation $B_j = \bar{B}_j \epsilon^{n(3/\pi)^j} \sigma^{-j}$. However, this can lead to a poorly converging series, as emphasized by Wheatley.\textsuperscript{7} In this section, we explore possible uses of this poor convergence and its dependence on the hardness $n$. This analysis enables us to resolve convergence issues and develop a general equation of state that is accurate for all $n$, given in Sec. III C.
We begin by examining the properties of the soft-sphere virial series for three representative cases: \( n = 4 \) (poor convergence), \( n = 6 \) (mild convergence), and \( n = 12 \) (good convergence). Convergence is ranked according to: (i) for a fixed \( \rho \), the rate at which \( Z \) approaches a limiting value as more terms are added in the virial series; (ii) the extent of \( \rho \) over which such limiting values exist, allowing the series to converge. For soft-spheres, the virial series is currently (at most) given as an 8-term expansion. For a series with so few terms, standard convergence measures such as the root-test or ratio-test are not expected to provide reliable estimates for the radius of convergence.\(^9\),\(^10\) As discussed later (Sec. III D), the radii of convergence of Taylor series of approximants to the virial series can be obtained explicitly; these hint at the dependence of the “actual” radius of convergence of the virial series on \( n \) (for small \( n \)).

Truncations of the virial series for \( n = 4, 6, \) and 12 are shown, respectively, in Figs. 1–3, where \( Z \) is plotted versus the reduced density \( \bar{\rho} = \rho \sigma^3 [\epsilon/(kT)]^{3/n} \). In the figures, the reduced freezing density, \( \bar{\rho}_f \), is indicated, taken from Hoover et al.\(^12\) (\( n = 4 \)) and Tan et al.\(^8\) (\( n = 6, 12 \)). The fluid regime, defined as \( 0 \leq \bar{\rho} \leq \bar{\rho}_f \), is the range over which the virial series can (at best) be used to extract meaningful thermo-physical properties. It is clear from Fig. 1(a) that VEOS8 gives a poor description of the \( Z(\rho) \) behavior for \( n = 4 \). As the order of the virial series is increased for the \( n = 4 \) fluid, the series does in fact converge, but in a very small region near \( \bar{\rho} = 0 \), which is relatively far from \( \bar{\rho}_f \). This can be seen in the magnification given in Fig. 1(b), where \( Z(\rho) \) has been normalized by VEOS8. The region of convergence is larger for \( n = 6 \), as shown in Fig. 2. Still, for \( n = 6 \), the density at which VEOS7 deviates only 1% from VEOS8 is far below freezing, as shown in the magnification (Fig. 2(b)). This is in contrast to the \( n = 12 \) virial series, shown in Fig. 3, where convergence of the series is visible over a large density range and \( \bar{\rho}_f \) has a smaller magnitude, effectively making VEOS8 an accurate equation of state for the \( n = 12 \) soft-sphere fluid from low density to freezing. On the scale of Fig. 3(a), VEOS6, 7, and 8 are not distinguishable from the simulation data. As seen in the normalized Fig. 3(b) for \( n = 12 \), VEOS7 deviates (at most) 1% from the data and VEOS8 nearly matches the data to within its error bars.

We now continue to examine the convergence of the virial series for all \( n \) values given in Table I. To do this, we adopt the method used by Schultz and Kofke\(^13\) and compute the “remainder sum” \( r_m = \sum_{j=m+1}^{8} |\bar{B}_j| \bar{\rho}^j \) (note the absolute value)
FIG. 3. Compressibility factor $Z$ versus $\bar{\rho}$ for the $n = 12$ fluid, described by the truncated series VEOSJ ($J = 2 \ldots 8$). (a) Comparison with molecular simulation data\cite{8} (○), given up to the freezing density $\bar{\rho}_f$ (✽). (b) $Z$ normalized by VEOS8; uncertainty in the data is visible on this scale, shown by error bars.

as well as the full sum $s = \sum_{j=1}^{8} |\bar{B}_j|\bar{\rho}^j$ (where $\bar{B}_1 = 1$). We then measure the density, $\bar{\rho}_{1\%}$, at which the remainder is less than 1%, expressed as a fraction of the full sum. The absolute value of coefficients, we are not measuring deviation from the true virial series; rather, we are measuring the contribution of adding terms to an analogous series. The absolute value here permits us to bypass the issue of coefficients changing sign, and allows us to make a fair comparison of convergence across different $n$ values. The $\bar{\rho}_{1\%}$ values for $m = 4, 5,$ and 6 are plotted versus $1/n$ in Fig. 4(a), along with the freezing densities $\bar{\rho}_f$, taken from Agrawal and Kofke.\cite{14} Below, the $\bar{\rho}_f$ curve marks the fluid regime. In Fig. 4(a), notice that only the $n = 12$ case converges to within 1% over the full range of $\bar{\rho}$ in the fluid regime. For all other $n$ values (especially, $n < 9$), $\bar{\rho}_f$ is larger than $\bar{\rho}_{1\%}$. In Fig. 4(a), the region below the uppermost ($m = 6$) $\bar{\rho}_{1\%}$ curve is labeled as the VEOS regime. Within this regime, VEOS8 can be considered an accurate equation of state, within a tolerance. On the other hand, the asymptotic regime, also shown in Fig. 4(a), defines a density range (for each $n < 9$) at which VEOS8 provides an inaccurate description of the fluid behavior; this is explained in the remaining portion of the section.

For large $\rho$, VEOSJ (given by Eq. (1)) behaves like $Z \sim \rho^{J-1}$. Interestingly, several semi-empirical and theoretical models\cite{15–17} indicate that the correct large-$\rho$ behavior for soft-spheres is $Z \sim \rho^{n/3}$. In order to determine the severity of this discrepancy when examining the physically relevant density range, we measure deviation between the “true” $Z(\rho)$ values (from molecular simulation) and the $\rho^{n/3}$ asymptotic behavior. In Fig. 4(a), the asymptotic regime is defined above the curve $\bar{\rho}_{a80\%}$, which indicates densities where the molecular simulation data are within 80% of the asymptotic behavior. The values along this curve are determined in the following
behavior, more so for approximant, as classified by Chisholm. Here, we shall refer

\[ \frac{d \ln Z}{d \ln \rho} = \gamma / 3 \]

In Fig. 4(b), \( \frac{d \ln Z}{d \ln \rho} \) is plotted versus \( \rho \), and the asymptotic behavior for the \( n = 4, 6, \) and 12 fluids is given by the horizontal lines \( \frac{d \ln Z}{d \ln \rho} = 4/3, 6/3, \) and 12/3. Fits through the simulation data and VEOS8 for \( n = 4, 6, \) and 12 are also shown in Fig. 4(b). The freezing density, which is also the last point of the simulation data, is indicated by a \(*\). For \( n = 4 \) and \( n = 6 \), the data clearly approach the asymptotic behavior, more so for \( n = 4 \). The value \( \bar{\rho}_{80\%} \) is indicated in Fig. 4(b) for \( n = 4 \) and 6. For \( n = 12 \) (and greater, not shown), the data never come within 80\% of the asymptotic behavior. We shall now discuss the implications of this, with respect to the virial series.

In Fig. 4(a), it appears that, for \( n \geq 12 \), the VEOS regime encompasses most of the fluid regime, hence the virial series is expected to provide a reasonably accurate description of the correct thermodynamic behavior. As \( n \) becomes smaller (\( n \leq 8 \)), the asymptotic behavior is approached near the freezing density. For \( n \leq 6 \), the asymptotic regime encompasses most of the fluid regime, and the virial series is not expected to represent the correct behavior, especially at high densities. This is because the virial series is a truncated power series, with asymptotic behavior (at large \( \bar{\rho} \)) given by the order of its truncation. The deficiency of using the virial series for high density and low \( n \) is remedied in Sec. III, where we provide a method for enforcing the correct asymptotic behavior for any truncation of the virial series.

### III. ASYMPTOTICALLY CONSISTENT PADÉ APPROXIMANTS

As mentioned in Sec. I, the virial series can be approximately analytically continued beyond its radius of convergence by recasting the series as a judiciously chosen function that is analytic at \( \rho = 0 \). One of the most common types of analytic functions to use is the form of one polynomial in \( \rho \) divided by another polynomial in \( \rho \); these are called Padé approximants. When the order of the numerator and denominator are the same, they are called symmetric Padés, and the large-\( \rho \) behavior is finite. For the physical systems studied by Baker and Gammel, \( \rho \) the true asymptotic behavior was finite, which precluded the use of the known truncated power-series when the independent variable (in our case, \( \rho \)) became large. The correct behavior was obtained by recasting each power series as a symmetric Padé. Here, we use a similar approach to that of Baker and Gammel, except now to describe the soft-sphere system, we enforce a power-law asymptotic behavior.

#### A. Formulation

For the power series VEOSJ of order \( \rho^{J-1} \) given by Eq. (1), we construct \( [(M + k)/(M - 1 - k)]^{4/3} \) or \( [(M + k)/(M - k)]^{4/3} \) approximants of the form

\[
Z = \left[ \frac{\mathcal{A}_1 + \mathcal{A}_2 \rho + \mathcal{A}_3 \rho^2 + \cdots + \mathcal{A}_M \rho^{M+1} + \rho^{M+k}}{1 + D_2 \rho + D_3 \rho^2 + \cdots + D_{M-k} \rho^{M-1-k}} \right]^{\frac{4}{3}}, \quad J \text{ even}, \quad M = J/2, \tag{4a}
\]

or

\[
Z = \left[ \frac{\mathcal{A}_1 + \mathcal{A}_2 \rho + \mathcal{A}_3 \rho^2 + \cdots + \mathcal{A}_M \rho^{M+k}}{1 + D_2 \rho + D_3 \rho^2 + \cdots + D_{M-k} \rho^{M-k}} \right]^{\frac{4}{3}}, \quad J \text{ odd}, \quad M = (J - 1)/2, \tag{4b}
\]

respectively, where \( \mathcal{A}_1 = 1 \), such that the ideal-gas limit \( Z(0) = 1 \) is recovered. \( M \) is a positive integer specifying the order of the approximant and \( k \) is an integer \( \geq -M \) specifying the asymmetry between the numerator and denominator in Eq. (4). Note that symmetric Padés are not permissible with these definitions; a discussion is given later on the relevance of symmetric Padés to our problem. We choose \( \alpha = n/3 \) in Eq. (4) to match the asymptotic behavior for soft spheres, given by \( Z \sim \rho^{n/3} \) for large \( \rho \). The \( \mathcal{A} \) and \( D \) coefficients are calculated algebraically, such that the Taylor expansion of Eq. (4) matches the virial series up to order \( \rho^{J-1} \). Thus, Eq. (4) is an equation of state that matches both the \( \rho \rightarrow 0 \) and large-\( \rho \) behavior. In this sense, Eq. (4) is a type of multi-point Padé approximant, as classified by Chisholm. Here, we shall refer to Eq. (4) specifically as an asymptotically consistent approximant (ACA). The standard Padé form is recovered by choosing \( \alpha = 2k + 1 \) (\( J \) even) or \( \alpha = 2k \) (\( J \) odd) in the exponent of Eq. (4).

In Fig. 5, we show the various analytic continuations of the \( n = 4 \) virial series, using both standard and asymptotically consistent Padé approximants. For illustration, we choose to examine the \( n = 4 \) system because of its weakly converging virial series, shown in Sec. II (Fig. 1). It is clear from Fig. 5 that, as the order \( M \) increases, the ACAs coalesce into a curve that matches the simulation data. This is not the case for standard Padés, although they are significantly closer to the simulation data than VEOS8. The plot includes the asymmetric sequences of standard Padés, so that a direct comparison can be made with the ACAs. For example, when examining Fig. 5, one may track the Padé sequence \( \{[1/0],[2/1],[3/2],[4/3]\} \) or the asymptotically consistent sequence \( \{[1/0]^{4/3}, [2/1]^{4/3}, [3/2]^{4/3}, [4/3]^{4/3}\} \) or the sequence of virial series, etc. If convergence can be established for a given sequence in the density range of physical relevance, the approximant is useful; the more rapid the convergence, the more useful the approximant is for providing the limiting (true) behavior.
TABLE II. Compressibility factor $Z(\rho)$ for various soft-sphere fluids, evaluated using Eq. (4a) with $\alpha = 2k + 1$ (standard Padés, left) and $\alpha = 3/2$ (ACAs, right). * indicates a defective approximant. Note that the diagonal boldface entries (left) are virial series (VEOSJ), denoted by the $[(J - 1)/0]$ Padé. For comparison, molecular simulation data$^8,12$ are given, with uncertainty reported in the final digits.

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<th>$M$</th>
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<th>$Z$ (Molecular simulation)</th>
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<td>*</td>
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<td>Molecular simulation:8 17.456(8)</td>
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The convergence of the various approximants can perhaps be seen more clearly by choosing a specific density, fixing $k$ in Eq. (4), and examining $Z(\rho)$ for increasing approximant order, $M$. In Table II, we examine the convergence in this manner for $n = 4, 6,$ and 12 at $Z(\rho)$ close to freezing, where the virial series deviates the farthest from simulation data (see Fig. 4). For each $n$ value in Table II, two sub-tables are given, one for standard Padé’s (left) and the other for ACAs (right). Predictions from VEOS2, 4, 6, and 8 for the given density value are shown diagonally in boldface from top-left to bottom-right in the table of standard Padés. Approximant sequences of increasing order can be identified by increasing $M$, either vertically or diagonally in each sub-table, as indicated in the key at the top of Table II. Note, that reciprocal forms of the approximants (not shown in Table II) are unique for standard Padés (e.g., $[4/3] \neq [3/4]$), but not for ACAs (e.g., $[4/3]^{[4/3]} = [3/4]^{-[4/3]}$). When applied to the soft-sphere virial series, unique reciprocal Padé forms share the same poor convergence properties of the standard Padés shown in Table II. Padés and ACAs that have non-finite behavior in the physical domain (e.g., positive real poles) are considered defective, and are indicated by a * in the table.
When examining the $n = 4$ case in Table II, one can see a dramatic contrast between the convergence of ACA sequences and the lack of convergence in the standard Padé sequences. Here, the ACA sequences appear to converge to $\sim 108$, while the Padé sequences do not appear to converge at all. For comparison, Hoover et al.\textsuperscript{18} report a value of $Z(5.5) = 108.67$ (5\% uncertainty) from Monte Carlo molecular simulations of the $n = 4$ fluid. When examining the $n = 6$ case in Table II, it is clear that the virial series does not converge for $\bar{\rho} = 2.2$, which we also observed in Fig. 2 (Sec. II). Here, the Padé sequences in the first two columns appear to converge to $Z(2.2) \approx 40.6$, while the Padés in the last two columns have wildly different values. This inconsistency of Padés for the $n = 6$ system was observed by Tan et al.\textsuperscript{8} they suggested using the [5/2] and [4/3] Padés ($M = 4, k = 1$ and 0). The ACAs resolve this issue, as all approximants converge to similar values. For comparison, Tan et al.\textsuperscript{8} report a value of $Z(2.2) = 40.43$ (1\% uncertainty) from Monte Carlo molecular simulations of the $n = 6$ fluid.

For the $n = 12$ system (Table II), both the virial series and the ACAs converge to similar $Z$ values for $\bar{\rho} = 1.1$. This is also true for the standard Padés shown in the table. For comparison, Tan et al.\textsuperscript{8} report a value of $Z(1.1) = 17.456$ (0.8\% uncertainty) from Monte Carlo molecular simulations of the $n = 12$ fluid.

We now discuss the implications of using ACAs. The convergence properties of standard Padé sequences are such that the accuracy is expected to increase as $M \to \infty$, with $k$ held fixed.\textsuperscript{18} Like the partial sums of the virial series, a Padé sequence is a type of Cauchy sequence which, in this work, is required to limit to $Z$ for a fixed $\rho$ in order for the sequence to be useful. However, unlike the virial series, which may have a finite radius of convergence, Padé approximants to the virial series are expected to converge for the full range of $\rho$ in the fluid regime. Padés are especially useful if the Padé sequence approaches its limiting behavior much faster than the partial sum sequence of the virial series. To obtain optimal convergence acceleration, Baker and Gammel\textsuperscript{18} suggest constructing Padés that have the same asymptotic (in our case, large $\rho$) behavior as the physical system under study. For example, the symmetric Padé sequence is $[1/1], [2/2], [3/3]$, etc. Since symmetric Padés are guaranteed to have finite ($\rho^0$) asymptotic behavior, one would expect decent convergence acceleration as $M \to \infty$ for physical systems with finite asymptotic behavior. Following Baker and Gammel,\textsuperscript{18} this convergence acceleration is anticipated to hold for approximants defined by Eq. (4) for physical systems with power-law asymptotic behavior. It is clear from Table II that, when including more terms in the soft-sphere VEOS ($n = 4, 6$), the ACA sequences approach a limiting value, while the standard Padé sequences do not. Note, that if the asymptotic behavior is not approached within the fluid regime (e.g., $n = 12$, Fig. 4), any well-behaved approximant should suffice. In this case, however, the virial series will be accurate as well (Fig. 3, Table II), eliminating the need to compute approximants.

Table II indicates that, for a given order $M$, all variations in asymmetry $k$ of the ACA lead to the same behavior, within a reasonable tolerance; we verified this over the full range of $n$. ACAs are designed such that this tolerance becomes small as $\rho$ increases. Hence, $[7/0]^{n=21}$ ($k = 3$) appears to be as reasonable as any other ACA (i.e., any $k$) used to analytically continue VEOS8, where $M = 4$. The advantage of using $[7/0]^{n=21}$ is that the absence of a denominator precludes the existence of poles or negative-power branch points in the approximant. It should be mentioned that, for the soft-sphere cases studied here, complex and negative real poles or branch points are present in the ACAs that do have denominators. However, using $[7/0]^{n=21}$ allows us to demonstrate that the benefit of ACAs is not due to the allowance of poles or negative-power branch points in the function. In Table III, we make comparisons between the $[7/0]^{n=21}$ ACA, VEOS8, and simulation data for $n = 4$, 5, 6, 7, 8, 9, 24, 50, 80, and 200. As expected from Fig. 4 (Sec. II) and seen in Table III, the ACAs provide significant improvement over VEOS8 for $n < 9$ over the full range of densities. For $n \geq 9$, both the approximants and VEOS8 match the simulation data well. Before continuing, it should be noted that, even in the absence of $\bar{\rho}$ singularities that cause $Z(\rho) = \infty$, $[7/0]^{n=21}$ approximants do have branch point singularities if $n/21$ is not an integer. The significance of branch points is discussed in Sec. III D.

In order to make a clear connection between the soft-spheres and the hard-sphere ($n = \infty$) limiting case, we define $N_j = n/3 \sum_{J > 1} (J-1)/0$ in Eq. (4) and write the $[(J - 1)/0]^{n=21}$ approximant as

$$Z = \left\{ 1 + \frac{n}{1/3} \left[ N_2 \bar{\rho} + N_3 \bar{\rho}^2 + \cdots + N_J \bar{\rho}^{J-1} \right] \right\}^{(n/3)/(J-1)},$$

allowing us to take advantage of the identity $\lim_{m \to \infty} (1 + x/m)^m = e^x$. Letting $x = N_2 \bar{\rho} + N_3 \bar{\rho}^2 + \cdots + N_J \bar{\rho}^{J-1}$, $m = (n/3)(J - 1)$, and applying the exponential identity to Eq. (5) leads to an exponential approximant $[(J - 1)/0]^{n=21}$ for hard-spheres,

$$\lim_{n \to \infty} Z(\rho, n) = \exp(N_2 \bar{\rho} + N_3 \bar{\rho}^2 + \cdots + N_J \bar{\rho}^{J-1}).$$

The $N_j$ coefficients are found in the usual way, by equating like terms of the virial series with the Taylor expansion of Eq. (5) or Eq. (6). This leads to a linear system, which can be solved recursively; the solution is given in the Appendix for coefficients up to $N_{10}$. Note, that, unlike Eq. (5), the $N_j$ coefficients of Eq. (6) are independent of truncation (i.e., $[2/0]^{n=21} = [1/0]^{n=21} + N_1 \bar{\rho}^2$, $[3/0]^{n=21} = [2/0]^{n=21} + N_1 \bar{\rho}^3$, etc). This feature can be seen in the recurrence solution (Appendix), letting $n \to \infty$. Brianio and Glandt\textsuperscript{20} performed a comprehensive study of all virial-like series that could be written to relate the pressure, density, and activity, combined in pairs. They considered both standard power series, as well as series written as the argument of an exponential function, such as Eq. (6). They observed that the exponential form of the pressure-versus-density series (i.e., Eq. (6)) performs significantly better than the standard virial series when applied to hard spheres. Note that Eq. (6) is a DLog Padé approximant\textsuperscript{8} to the virial series, as it can be obtained by constructing the $[(J - 1)/0]$ Padé of $d(\ln Z)/d\bar{\rho}$. We examine Eq. (6) in further detail in Sec. III B.

The $N_j$ coefficients of the $[7/0]^{n=21}$ approximant are given in Table IV, and are computed using VEOS8 for soft-spheres.
The coefficients are shown to monotonically decrease with $n$, with the exception of $N_6$ for $n > 80$. This is in contrast with the virial coefficients given in Table I which, as Wheatley\textsuperscript{7} pointed out, oscillate with $n$ for low $n$. In Sec. III C, we take advantage of the monotonicity of the $N_j$ coefficients and develop a general equation of state for soft-spheres (for any $n$). But first, the properties of the hard-sphere exponential approximant given by Eq. (6) are examined.

### B. Exponential approximant hard-sphere equation of state

For hard-spheres, two additional virial coefficients are available\textsuperscript{9} beyond those shown in Table IV, $\bar{B}_9$ and $\bar{B}_{10}$, and so it is worth extending the order of our approximant. As mentioned in Sec. III A, the exponential approximant given by Eq. (6) has the unique feature that, as higher order

#### TABLE IV. Coefficients of $[7/0]\textsuperscript{[21]}$ for various soft-sphere fluids, computed using Eq. (5) and the known virial coefficients (Table I). Numbers in parenthesis give the error of the final digit, propagated from errors reported in Table I.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$N_2$</th>
<th>$N_3$</th>
<th>$N_4$</th>
<th>$N_5$</th>
<th>$N_6$</th>
<th>$N_7$</th>
<th>$N_8$</th>
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<tr>
<td>4</td>
<td>7.59346</td>
<td>131.5798</td>
<td>1283.141</td>
<td>7601.975(4)</td>
<td>27350.57(14)</td>
<td>55318(4)</td>
<td>51410(90)</td>
</tr>
<tr>
<td>5</td>
<td>6.46570</td>
<td>41.1613</td>
<td>214.013</td>
<td>706.9003(1)</td>
<td>1494.635(5)</td>
<td>1907.1(1)</td>
<td>1196(2)</td>
</tr>
<tr>
<td>6</td>
<td>3.71222</td>
<td>22.7777</td>
<td>84.941</td>
<td>208.52268(9)</td>
<td>341.325(1)</td>
<td>355.979(7)</td>
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<tr>
<td>7</td>
<td>3.00445</td>
<td>11.8848</td>
<td>30.0229</td>
<td>52.4377(1)</td>
<td>64.5983(9)</td>
<td>54.7066(6)</td>
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</tr>
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<td>8</td>
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<td>9.6378</td>
<td>21.2879</td>
<td>33.08562(7)</td>
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<tr>
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<td>2.5538</td>
<td>1.8187(1)</td>
<td>1.152(3)</td>
<td>0.58(2)</td>
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</tr>
<tr>
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<td>2.14275</td>
<td>1.17239</td>
<td>0.38028</td>
<td>0.1766(1)</td>
<td>0.138(3)</td>
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<td>12</td>
<td>2.11300</td>
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<td>0.09504</td>
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<td>0.04(2)</td>
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<td>$\infty$</td>
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<td>0.54831</td>
<td>0.04334</td>
<td>0.0575531(2)</td>
<td>0.07500(4)</td>
<td>0.01441(1)</td>
<td>0.0032(2)</td>
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The coefficients are shown to monotonically decrease with $n$, with the exception of $N_6$ for $n > 80$. This is in contrast with the virial coefficients given in Table I which, as Wheatley\textsuperscript{7} pointed out, oscillate with $n$ for low $n$. In Sec. III C, we take advantage of the monotonicity of the $N_j$ coefficients and develop a general equation of state for soft-spheres (for any $n$). But first, the properties of the hard-sphere exponential approximant given by Eq. (6) are examined.

#### TABLE IV. Coefficients of $[7/0]\textsuperscript{[21]}$ for various soft-sphere fluids, computed using Eq. (5) and the known virial coefficients (Table I). Numbers in parenthesis give the error of the final digit, propagated from errors reported in Table I.

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<td>$\infty$</td>
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<td>0.54831</td>
<td>0.04334</td>
<td>0.0575531(2)</td>
<td>0.07500(4)</td>
<td>0.01441(1)</td>
<td>0.0032(2)</td>
</tr>
</tbody>
</table>
truncations of the virial series are used to construct the approximant and additional $N_j$ coefficients arise, each lower-order $N_j$ coefficient retains its numerical value, which is in contrast with the approximant given by Eq. (5) for finite $n$. The first 7 coefficients of Eq. (6) are given in the bottom row of Table IV ($N_2$ through $N_6$); additionally, $N_0 = 0.0168(7)$ and $N_{10} = -0.0018(15)$. A comparison between the exponential approximant $[9/0]_\infty$, VEOS10, and molecular simulation data from Kolafa et al. is shown in Fig. 6, where the curves are normalized by a hard-sphere equation of state (KEOS) proposed by J. Kolafa, given in Boublík and Nezbeda. KEOS is one order more accurate than the Carnahan-Starling-like equation (KEOS) versus $\left(1/\bar{\rho}\right)$ Padé suggested by Clisby and McCoy and the WC2 equation of state given by Bannerman et al., these are also shown in Fig. 6. Although not shown in the figure, we have also compared with equations of state given by Sanchez and Lennard-Jones [21] and Tian et al. All aforementioned equations provide significant improvement over VEOS10, and are comparable in accuracy to the $[9/0]_\infty$ approximant defined by Eq. (6).

Lower order approximants are also shown in Fig. 6, in order to illustrate the convergence of approximant sequences. As seen in the figure, the sequence $[5/0]_\infty$, $[7/0]_\infty$, $[9/0]_\infty$ converges to the simulation data faster than the sequence VEOS6, VEOS8, VEOS10. Convergence cannot be established for the $[M + 1/M]_\infty$ Padé sequence containing $[5/4]$, as all lower order Padés in this sequence are defective (have positive real poles). Note that the $[5/4]_\infty$ Padé is the closest match to simulation data in Fig. 6. However, $[5/4]_\infty$ is better thought of as a fit to the data, as convergence of the $[M + 1/M]_\infty$ sequence does not allow one to deduce that $[5/4]_\infty$ is, in fact, the “best” Padé approximant for $J = 10$, without making a comparison with molecular simulation data.

A virial coefficient prediction matrix is given in Table V, which lists the coefficients of Taylor expansions of $[J − 1/0]_\infty$ approximants, given by Eq. (6). Coefficients beyond $B_2$ are the “predicted” virial coefficients; they are a direct result of the analytic continuation imposed by the approximant, and have not been calculated via the molecular interaction models that define the actual virial coefficients. If we Taylor expand the exponential approximant $[9/0]_\infty$ to, say, 16 terms, we could obtain predictions for $B_{11}$ through $B_{16}$ for hard spheres. We do not list these here, but one can easily compute them (for any order) from Eq. (6). It is interesting to note that although a variety of different hard-sphere equations of state are used, similar values for these extrapolated virial coefficients are found in the literature. The $[5/4]_\infty$ Padé, $[7/0]_\infty$ Padé, and $B_{12}$, shown here in Table V, also closely match the predictions of Guererro and Bassi. It has been conjectured that the coefficients of the hard-sphere virial series may become negative at sufficiently large $J$. To address this interest, we note that, while the predicted virial coefficients extracted from Eq. (6) monotonically decrease with increasing order $J$, they do not become negative (at least not up to $B_{16}$). This is also seen in the aforementioned virial coefficient prediction literature. Although negative coefficients may occur for higher-order extrapolations (e.g., Bannerman et al.), the margin of uncertainty here is large and such extrapolations are unsuitable for drawing conclusions on this issue.

![Figure 6](https://example.com/fig6.png)

**Figure 6.** Compressibility factor $Z$ (for hard spheres) normalized by Kolafa’s higher-order Carnahan-Starling-like equation (KEOS) versus $\bar{\rho}$. The truncated series VEOS1, asymptotically consistent (exponential) approximants $[J − 1/0]_\infty$, the $[5/4]_\infty$ Padé, and the WC2 equation of state [21] are compared against molecular simulation data [21] (c).

**Table V.** Demonstration of the potential for $[J − 1/0]_\infty$ approximants to predict hard sphere virial coefficients. For a given virial series of order $J$, including virial coefficients up to $B_j$ (shown in bold, from Clisby and McCoy), the “predicted” $B_{j+1}$ coefficients from the Taylor expansion of Eq. (6) are listed horizontally. For a truly predictive approximant, each predicted $B_j$ should limit to the actual virial coefficient as $J$ increases. Numbers in parenthesis give the error of the final digit, propagated from errors reported in Table I.

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\hat{B}_4$</th>
<th>$\hat{B}_5$</th>
<th>$\hat{B}_6$</th>
<th>$\hat{B}_7$</th>
<th>$\hat{B}_8$</th>
<th>$\hat{B}_9$</th>
<th>$\hat{B}_{10}$</th>
<th>$\hat{B}_{11}$</th>
<th>$\hat{B}_{12}$</th>
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<td>3</td>
<td>2.67955</td>
<td>2.15462</td>
<td>1.49022</td>
<td>0.91399</td>
<td>0.5069</td>
<td>0.2580</td>
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<td>0.0538</td>
<td>0.0224</td>
</tr>
<tr>
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<td>1.37141</td>
<td>0.79880</td>
<td>0.4155</td>
<td>0.2190</td>
<td>0.0847</td>
<td>0.0338</td>
<td>0.0126</td>
</tr>
<tr>
<td>5</td>
<td>2.12139</td>
<td>1.56990</td>
<td>1.11361(1)</td>
<td>0.7728(1)</td>
<td>0.5141(1)</td>
<td>0.3262(1)</td>
<td>0.1900(1)</td>
<td>0.1187(4)</td>
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<tr>
<td>6</td>
<td>1.09921(8)</td>
<td>1.0742(6)</td>
<td>0.5983(2)</td>
<td>0.2795(6)</td>
<td>0.1610(6)</td>
<td>0.0892(5)</td>
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<tr>
<td>7</td>
<td>0.7395(2)</td>
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<td>8</td>
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<td>0.313(1)</td>
<td>0.202(2)</td>
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As shown in each column of Table V, the predicted virial coefficients appear to limit to the actual virial coefficient (shown in bold) as \( J \) increases. Using VEOS6, the exponential approximant predicts \( B_7 \) through \( B_{10} \) within 2\% - 6\%. Recently, Ončák et al.\textsuperscript{26} constructed hard-sphere equations of state, using both lower order virial coefficients (in the same fashion as an approximant) and simulation data. Using VEOS6, the approximants of Ončák et al.\textsuperscript{26} predict \( B_7 \) through \( B_{10} \) within \( \leq 2\% \). Also, using the aforementioned approximants, one is able to predict high-order coefficients to a higher degree of accuracy and using fewer terms (e.g., proximants, one is able to predict high-order coefficients to generate higher-order approximants described in Sec. III A have coefficients defined by

\[ C_j = \frac{2}{j+1} \sum_{n=1}^{j+1} \frac{C_n}{n} \]

where \( C_1 \) through \( C_5 \) are given in Table VI and the \( N_j(\infty) \)'s are given in the bottom row of Table IV. We shall refer to this fitted general equation of state as asymptotically consistent approximant fit (ACAFIT), defined by Eq. (5), Eq. (7), and Table VI. By design, ACAFIT is exactly equal to Eq. (6) for \( n = \infty \).

To test ACAFIT for \( n \) values not used in the fit, a comparison is made against molecular simulation data (from Table III) for \( n = 7 \) and \( n = 50 \) in Figs. 7(a) and 7(b), respectively. One can see from Fig. 7(a) that ACAFIT provides substantial improvement over VEOS8 for \( n = 7 \). WFIT is given in Fig. 7(a) for reference only; as Wheatley\textsuperscript{7} points out, the fit is not constructed to do well for \( n < 10 \). For \( n = 50 \) (Fig. 7(b)), WFIT is a closer match to the simulation data than ACAFIT and VEOS8, although all equations of state do reasonably well.

Note that in our fit, we use VEOS8 to construct approximants for 5 different \( n \) values covering the range \( 4 \leq n < 10 \) and 5 values covering the range \( 10 < n \leq \infty \). In comparison, Wheatley\textsuperscript{7} used VEOS4 to construct effective hard-sphere equations for 19 different \( n \) values covering the range \( 10 \leq n \leq \infty \). While the asymptotic approximant method that we propose in Sec. III A stands on its own, the fit that we present in this section can always be improved by refining the set of hardness (\( n \)) values used and/or including higher order virial coefficients, as they become available through advances in computational methods and architecture.

In summary, if the virial coefficients and asymptotic behavior of \( Z(\rho) \) are known and \( n < 9 \), we suggest trying an asymptotic approximant in place of the virial series; one may use the formula given in the Appendix to build the approximant. If the virial coefficients are not known and \( 4 < n < 10 \), ACAFIT can be used as a reasonably accurate equation of state. If the virial coefficients are not known and \( 10 \leq n < \infty \), one may either use ACAFIT, or the effective hard-sphere fit given by Wheatley.\textsuperscript{7} For \( n \geq 12 \), one may also consider forming accurate equations of state by using the analytic forms of \( Z(\rho) \) given in Branka and Heyes.\textsuperscript{30}

### C. General soft-sphere equation of state

In Wheatley,\textsuperscript{7} an “effective hard-sphere” formulation was applied to the soft-sphere model, where an expansion in effective hard-sphere diameter was substituted into the soft-sphere virial series for each hardness \( n \). For \( n \geq 10 \), the effective hard-sphere diameter coefficients were observed to vary more smoothly with \( n \) than the virial coefficients, allowing Wheatley\textsuperscript{7} to generate fits for the hard-sphere diameter coefficients as a function of \( n \), leading to a general and accurate equation of state for \( n \geq 10 \); we refer to this here as WFIT. The \( \{70/162\} \)\textsuperscript{21} approximants described in Sec. III A have coefficients (Table IV) that similarly vary more smoothly with \( n \) than the virial coefficients (Table I), but now over the full range of \( n \). Using a least-squares method, we construct a general equation of state (for any \( \rho \) and \( n \)), given by Eq. (5) with coefficients defined by \( N_j = \dot{B}_j = (2\pi/3)^j(1 - 3/n) \) and

\[
N_j(n) = \exp[C_1(n + C_2/n^2 \ldots C_9/n^9)] - 1 + N_j(\infty),
\]

\[ j = 3 \ldots 8, \]

(7)

where \( C_1 \) through \( C_5 \) are given in Table VI and the \( N_j(\infty) \)'s are given in the bottom row of Table IV. We shall refer to this fitted general equation of state as asymptotically consistent approximant fit (ACAFIT), defined by Eq. (5), Eq. (7), and Table VI. By design, ACAFIT is exactly equal to Eq. (6) for \( n = \infty \).

### D. Branch points and radii of convergence of virial series

The radius of convergence of the virial series for \( Z(\rho) \) limits its range of utility, and is thus a critical characteristic of the series. As the density approaches this radius from below, additional terms are required to construct the series if one wishes to retain accuracy. Practically, the number of virial series terms is limited by our ability to calculate
that branch points, which are also singularities in the complex plane, could be the origin of a finite radius of convergence imposed on the virial series; this was suggested by Santos and de Haro\textsuperscript{29} for hard-spheres. For our soft-sphere approximant given by Eq. (5) (ACA), branch points arise when \( (n/3)(J − 1) \) is not an integer, and they are defined as \( \rho \) values, where the argument of the approximant is zero, thereby making derivatives of the approximant undefined (at some order). The virial series is, by definition, an expansion about \( \rho = 0 \); hence, the radius of convergence extracted from an ACA will be determined by the distance to the density closest to zero where a derivative of Eq. (5) is non-finite.

We first focus on very soft \( (n ≤ 8) \) soft-sphere fluids, which clearly access the asymptotic regime shown in Fig. 4(a), and thus where we are confident that the \( Z \sim \rho^{n/3} \) behavior is approached. The radii of convergence for expansions of the \( [(J − 1)/0]^{(n/3)(J − 1)} \) approximants are given in Table VII for \( n ≤ 8 \). For a fixed order, \( J \), the radii monotonically increase with \( n \), which is consistent with convergence behavior in the VEOS regime of Fig. 4(a) (for \( n ≤ 8 \)). For a fixed \( n \), the radii monotonically decrease with order \( J \). The values of the radii in Table VII are all of the appropriate order of magnitude, where one might expect the virial series to diverge. Certainly, for densities less than the values given in Table VII, the virial series converges well (c.f., Fig. 4(a)). Radii of convergence given by branch points of other ACAs (not shown), of the general form given by Eq. (4), are close to those given in Table VII. In contrast, the poles of various Padé\textsuperscript{30} (not shown), when applied to the soft-sphere virial series for small \( n \), impose radii of convergence that vary drastically at each order \( J \). This is expected, as convergent sequences of Padé’s cannot be constructed for small values of \( n \), as shown in Sec. III A, and their predictive behavior is erratic. In summary, the success of asymptotically consistent approximants over standard Padé approximants at forming convergent sequences of only 7-terms (see Sec. III A) suggests that, for small \( n \) \( (n ≤ 8) \), the radius of convergence imposed on the virial series for (very soft) soft spheres is more likely determined by branch point singularities rather than isolated singularities such as poles.

For large \( n \) \( (n ≥ 9) \), the asymptotic behavior is not approached in the fluid regime, and the virial series converges rather well (c.f., Fig. 4(a)). This suggests that the singularity

### Table VII. Radii of convergence of Taylor expansions of \( [(J − 1)/0]^{(n/3)(J − 1)} \) approximants, given by the branch point of smallest magnitude. If \( (n/3)(J − 1) \) is an integer, the approximant is a polynomial; these spaces are left blank. Numbers in parenthesis give the error of the final digit, propagated from errors reported in Table I.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( n = 4 )</th>
<th>( 5 )</th>
<th>( 6 )</th>
<th>( 7 )</th>
<th>( 8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1756</td>
<td>0.3588</td>
<td>0.7148</td>
<td>0.8876</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.1686</td>
<td>0.3079</td>
<td>0.5282</td>
<td>0.6242</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.1600</td>
<td>0.3017</td>
<td>0.4051</td>
<td>0.4968</td>
<td>0.5817</td>
</tr>
<tr>
<td>5</td>
<td>0.1475</td>
<td>0.2695</td>
<td>0.3716</td>
<td>0.4576</td>
<td>0.5341</td>
</tr>
<tr>
<td>6</td>
<td>0.1365</td>
<td>0.2598</td>
<td>0.3531</td>
<td>0.4314</td>
<td>0.5019</td>
</tr>
<tr>
<td>7</td>
<td>0.1319(3)</td>
<td>0.2498(2)</td>
<td>0.3399</td>
<td>0.4159(1)</td>
<td>0.4823(1)</td>
</tr>
<tr>
<td>8</td>
<td>0.1092(2)</td>
<td>0.2418(7)</td>
<td>0.3280(1)</td>
<td>0.4022(7)</td>
<td>0.4634(2)</td>
</tr>
</tbody>
</table>
closest to $\rho = 0$ lies in the range of densities in which the fluid solidifies, rendering the radius of convergence irrelevant, practically.

IV. DISCUSSION AND CONCLUDING REMARKS

Asymptotically consistent approximants (ACAs) are well-suited for the soft-sphere model because the “large” $\rho$ asymptotic behavior is, in fact, approached at relatively low densities, particularly for soft-sphere fluids with a low hardness ($n < 9$). When attempting to analytically continue the virial series for these fluids, standard Padé approximant sequences converge slowly, and no consistent limit (between sequences) is approached for the available 8-term series. This forces one to choose between different Padé’s, each describing drastically different thermodynamic behavior. Such a choice can be made only if molecular simulation data are available, in which case any chosen Padé is effectively a fit to the data. In the absence of simulation data, Padé approximants are thus rendered useless at predicting the behavior of soft-sphere fluids, particularly for $n < 9$. This is expected, since the integer power-law asymptotic behavior inherent to Padé’s is given by the difference in order between the numerator and denominator of the Padé. Since the asymptotic behavior is different for most Padé sequences that are constructed, it is impossible for all sequences to uniformly agree with the true large $\rho$ behavior of the fluid.

The analysis provided in this work validates the use of ACAs as accurate equations of state for soft-sphere fluids. The proposed approximant is a simple extension of a two-point Padé, satisfying the zero-density expansion (virial series) of compressibility, $Z(\rho)$, as well as the large $\rho$ asymptotic behavior; the method may be extended to other models, provided these behaviors are known. ACAs give one the freedom to explicitly prescribe an asymptotic behavior, and enable the construction of convergent sequences while holding the asymptotic behavior fixed. If convergence is achieved for all ACA sequences before exhausting all terms of a truncated power series (e.g., virial series), as is the case for soft-spheres, an approximant can be chosen from any sequence, and can be used as an accurate equation of state; this conclusion is validated through comparison with molecular simulation data.

Out of the possible ACA sequences, we suggest choosing the form with no denominator, so as to eliminate the possibility of non-finite $Z(\rho)$ behavior. Using this form, we take advantage of the monotonicity of the ACA coefficients with $n$, and construct a least-squares fit, which leads to an accurate soft-sphere equation of state for $Z(\rho, n)$, valid over the range $4 \leq n \leq \infty$ and for all densities in the fluid state. This general equation of state is validated against molecular simulation data, using values of $n$ not included in the fit. For hard spheres ($n = \infty$), the ACA limits to an exponential equation of state, which is closer to simulation data than the 10-term virial series for hard spheres, and is comparable in accuracy to other recent equations of state. Although it is impossible to tell without obtaining significantly more terms (i.e., virial coefficients), the success of ACAs over Padé’s in describing the soft-sphere fluid behavior indicates that branch points, rather than poles, are likely responsible for the divergence of the virial series, for small $n (n \leq 8)$.

The method provided here returns to the intentions of the seminal Padé paper by Baker and Gammel, in that we are simply choosing an approximant that matches the asymptotic behavior. We recognize that soft-spheres are a unique case where the large-$\rho$ behavior can be deduced as a simple power-law. However, perhaps the benefit of using ACAs to form accurate equations of state, shown here for soft-spheres, will motivate the development of techniques used to extract the asymptotic behavior of fluids described by more elaborate molecular potentials.

ACKNOWLEDGMENTS

This work is supported by the U.S. National Science Foundation (NSF) (Grant Nos. CHE-1027963 and CBET-0854340). N. S. Barlow is supported by the NSF award (Award No. CI-TraCS-1048579). Computational resources were provided by the University at Buffalo Center for Computational Research.

APPENDIX: RECURRENCE SOLUTION

Given VEOJ, the coefficients of $(J−1)/(J−1)^{(n/3)(J−1)}$ can be computed recursively. The first nine coefficients of Eq. (5) are given by

\[
N_2 = \tilde{B}_2, \quad N_3 = \tilde{B}_3 - C_1 N_2^2,
N_4 = \tilde{B}_4 - C_2 N_1^2 - 2C_1 N_3 N_2,
N_5 = \tilde{B}_5 - C_3 N_2^2 - 3C_2 N_1^2 N_3 - 2C_1 N_4 N_2 - C_1 N_3^2,
N_6 = \tilde{B}_6 - C_4 N_2^2 - 4C_3 N_1^2 N_3 - 3C_2 N_4 N_2^2 - 3C_2 N_2 N_3^2 - 2C_1 N_5 N_2 - 2C_1 N_4 N_3,
\]

\[
N_7 = \tilde{B}_7 - C_5 N_2^6 - 5C_4 N_1^2 N_3 - 4C_3 N_2^4 N_3 - 3C_2 N_4 N_2^3 - 3C_2 N_2 N_3^3 - C_1 N_2 N_3^2 N_4 - 6C_2 N_2 N_3 N_4 N_2 - C_2 N_3^2 N_4^2 - 2C_1 N_5 N_3 N_5 - C_1 N_4^2,
\]
\[ N_8 = \tilde{B}_8 - C_6 N_2^2 - 6 C_5 N_2^2 N_3 - 5 C_4 N_2^2 N_4 - 10 C_4 N_2^2 N_3^2 - 4 C_3 N_3 N_3^2 - 12 C_3 N_2^2 N_3 N_4 - 3 C_2 N_6 N_2^2 \]
\[ -4 C_3 N_2 N_3^2 - 6 C_2 N_2 N_3 N_5 - 3 C_2 N_2 N_4^2 - 2 C_1 N_7 N_2 - 3 C_2 N_2 N_4 N_4 - 2 C_1 N_6 N_3 - 2 C_1 N_5 N_4, \]
\[ N_9 = \tilde{B}_9 - C_7 N_2^3 - 7 C_6 N_2^2 N_3 - 6 C_5 N_2^2 N_4 - 15 C_5 N_2 N_3^2 - 5 C_4 N_2^2 N_5 - 20 C_4 N_2 N_3 N_4 - 4 C_3 N_3 N_3^2 \]
\[ -10 C_4 N_2 N_3 N_4 - 12 C_3 N_2^2 N_5 - 6 C_3 N_2^2 N_4^2 - 3 C_2 N_7 N_2^2 - 12 C_3 N_2 N_3 N_4 - 6 C_2 N_6 N_2 N_3 \]
\[ -6 C_2 N_2 N_3 N_5 - 2 C_1 N_6 N_2 - 3 C_2 N_2 N_5^2 - 3 C_2 N_2 N_4 N_3 - 2 C_1 N_7 N_3 - 2 C_1 N_6 N_4 - C_1 N_5^2, \]
\[ N_{10} = \tilde{B}_{10} - C_8 N_2^4 - 8 C_7 N_2^3 N_3 - 7 C_6 N_2^2 N_4 - 21 C_6 N_2 N_3^2 - 6 C_5 N_3 N_4^2 - 30 C_4 N_2 N_3 N_5 - 5 C_4 N_2 N_4 N_4 - 20 C_4 N_2 N_3^2 \]
\[ -20 C_4 N_2 N_3 N_4 - 10 C_4 N_2 N_3^2 N_3 - 4 C_3 N_7 N_2^2 - 30 C_4 N_2 N_3 N_4 - 12 C_3 N_2 N_3 N_4^2 - 6 C_2 N_7 N_2 N_3 - 6 C_2 N_6 N_2 N_4 - 3 C_2 N_2 N_4^2 - 2 C_1 N_6 N_2 \]
\[ -4 C_3 N_2 N_3 N_4 - 3 C_2 N_6 N_2^2 - 6 C_2 N_3 N_4 N_5 - 2 C_1 N_6 N_3 - C_2 N_4^3 - 2 C_1 N_7 N_4 - 2 C_1 N_6 N_5, \]

where

\[ C_q = \prod_{q=1}^{Q} \frac{1 - q^j}{q + 1}. \]


