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Communication: Analytic continuation of the virial series through the critical point using parametric approximants

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The mathematical structure imposed by the thermodynamic critical point motivates an approximant that synthesizes two theoretically sound equations of state: the parametric and the virial. The former is constructed to describe the critical region, incorporating all scaling laws; the latter is an expansion about zero density, developed from molecular considerations. The approximant is shown to yield an equation of state capable of accurately describing properties over a large portion of the thermodynamic parameter space, far greater than that covered by each treatment alone. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4929392]

A longstanding aim of statistical physics is the formulation of equations of state that accurately describe the thermodynamic surface of a fluid both at, near, and away from its critical point. The idea is to bridge the singular behavior of the pressure-density-temperature relationship at the critical point with the regular behavior exhibited away from it. This transition in structure, which agrees with experimental observation,[1] can be modeled using a "crossover" function that patches together two equations of state; a review of these methods can be found in Ref. 2. In this communication, we use an alternative approach to accomplish the same goal, by analytically continuing the known zero-density expansion into the critical region. In this manner, we fuse the two approaches without invoking an explicit crossover function.

The virial equation of state describes the dependence of pressure on density of a fluid in the single-phase regime via a series expansion about the ideal-gas limit,[3]

$$P = k_B T \sum_{j=1}^{J} B_j(T)\rho^j, \quad B_1 = 1, \tag{1}$$

where P is the pressure, ρ is the number density, k_B is the Boltzmann constant, and T is the temperature. From here on, we refer to the J-term virial series as VJ. Note that the virial coefficients B_j are functions only of T, and the jth coefficient is given in terms of integrals over positions of j molecules.[4] The number of integrals appearing for each coefficient increases rapidly and nonlinearly with the order of the coefficient. The Mayer sampling Monte Carlo approach is an effective way to compute these integrals, using importance sampling.[5] Here, we look at the square-well (SW) model fluid; however, the method we present may be applied to any fluid if virial coefficients and certain critical properties are known.

The spherically symmetric SW model describes hard core particles of diameter σ, such that the pair energy $u(r) = \infty$ for separations $r < \sigma$, surrounded by an attractive well such that $u(r) = -\epsilon$ for $r < \lambda\sigma$; otherwise, $u(r) = 0$. We use the model with $\lambda = 1.5$, for which the first six virial coefficients have been computed in such a way that the explicit T dependence of each coefficient is known.[6] In the following, all quantities are given in units such that σ and ϵ/k_B are unity.

Wherever a singularity (physically motivated or not) exists in a function, a series representation such as Eq. (1) will have its radius of convergence bounded by the singularity, and an increasing number of terms will be required to preserve accuracy as the singularity is approached. This behavior is especially problematic if only a few terms in the series are readily available, as is the case for the virial series. The problem can be overcome by using a so-called approximant — that is, a well-defined function that shares (or at least mimics) the same singularity, while formulated such that its Taylor expansion matches the series up to a desired order. By incorporating the location and/or type of singularity that causes the series to diverge, approximants analytically continue a divergent series.[7] A common approximant of this type is the Padé (i.e., a rational-function approximant),[8] exemplified by the Carnahan-Starling equation of state for hard-sphere fluids.[9] Even if the radius of convergence of a series is infinite, it may be possible to accelerate its convergence via a well-formed approximant, such as one that matches known asymptotic behavior.[10,11]

Approximants are a natural choice to analytically continue the virial series of molecular model fluids with critical points, inasmuch as the asymptotic behavior on approach of the critical point is known. Widom's hypothesis prescribes the appropriate scaling laws for all thermodynamic quantities.[12] For nonclassical fluids, there is a branch-point singularity at the critical point, $(\rho, P, T) = (\rho_c, P_c, T_c)$, with an order that

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depends on the thermodynamic quantity and the path of approach in ρ-P-T space. When taking the perspective of "simple scaling," these branch points are characterized as follows:

$$\left(\frac{P}{P_c}-1\right) \sim \pm D\left|\frac{\rho}{\rho_c}-1\right|^{\delta},\ T=T_c,\ \rho\to\rho_c, \tag{2a}$$

$$\frac{\partial P}{\partial\rho} \sim \frac{P_c}{\rho_c\Gamma^+}\left(\frac{T}{T_c}-1\right)^{\gamma},\ \rho=\rho_c,\ T\to T_c^+, \tag{2b}$$

$$\frac{C_v}{T} \sim \frac{P_c A^+}{\rho_c T_c^2\alpha}\left(\frac{T}{T_c}-1\right)^{-\alpha},\ \rho=\rho_c,\ T\to T_c^+, \tag{2c}$$

$$\left(\frac{\rho}{\rho_c}-1\right) \sim \pm B_0\left|\frac{T}{T_c}-1\right|^{\beta},\ \text{at coexistence},\ T\to T_c^-, \tag{2d}$$

where C_v is the isochoric heat capacity; δ, γ, α, and β are (for nonclassical fluids) non-integer universal critical exponents; and D, Γ^+, A^+, and B_0 are fluid-specific critical amplitudes.[2] The critical exponents are related through the formulas $\gamma = \beta(\delta-1)$ and $\alpha = 2-\beta(\delta+1)$.[13] Thus, one may characterize the order of the branch point along all paths in the thermodynamic space with knowledge of only two exponent values.

While more sophisticated models of criticality, e.g., mixed-field scaling,[2] can be introduced to the framework, the basic formulation indicated in Eq. (2) is suitable for the purposes of forming an approximant that is both effective and straightforward in its application.

Approximants have been used to examine a *single* path of approach for lattice models (viz., along the critical isochore)[7,14–16] and for molecular model fluids (along the critical isotherm).[17] Here, we are interested in an analytic continuation of the virial series that incorporates the first three scaling paths given in Eq. (2), so that we may obtain an equation of state valid at low density, the critical region, and intermediate regions. Care is required to ensure that singularities enforced at the critical point do not introduce anomalies away from the critical region. To enforce all scaling laws given in Eq. (2) at (and *only* at) the critical point, Schofield[18] proposed a parametric (r,θ) coordinate system, defined via

$$(T/T_c-1) = r(1-b^2\theta^2); \qquad (\rho/\rho_c-1) = r^{\beta}k\theta, \tag{3}$$

where $b>1$ is a universal parameter and θ has been normalized such that the coexistence curve corresponds to $\theta=\pm1$. More generally, $(\rho/\rho_c-1) = r^{\beta}M(\theta)$, where $M(\theta)$ can be any odd analytic function of θ. For several fluids, $M(\theta)$ has been observed to be nearly linear in θ, prompting the widespread use of the so-called "linear model" $M(\theta)=k\theta$ (see Ref. 19 and references therein). It follows from Eq. (3) and the critical scaling law along the coexistence curve (Eq. (2d)) that $k = B_0(b^2-1)^{\beta}$. Thus, although the focus of this work is to improve the region where the virial series is applicable (i.e., $T\geq T_c$ and subcritical gas phase), the fluid-specific amplitude B_0 (defined for $T\to T_c^-$ along coexistence) is needed to transform between (r,θ) space and (ρ,T) space in Eq. (3).

Our approximant is formed by taking Schofield's model and adding an asymptotically subdominant (for $T\to T_c$, $\rho\to\rho_c$) auxiliary function that enables the matching of virial coefficients, while not affecting the critical scaling (Eq. (2)) or amplitude relations (Eq. (5)). Specifically, the approximant is given, together with Eq. (3), as

$$\begin{aligned} P_{\mathrm{A}J} = \underbrace{P_1(T)}_{\text{“background” term}} + r^{\beta\delta}\Big[&\underbrace{\tilde a\theta(1-\theta^2) + \tilde a k\left(p_0+p_2\theta^2+p_4\theta^4\right)r^{\beta}}_{\text{Schofield's scaling function}} \\ &+ \underbrace{f(\theta)\sum_{j=1}^{J} d_j(T)r^{(j+1)\beta}}_{\text{auxiliary function}}\Big], \end{aligned} \tag{4}$$

where $\tilde a \equiv P_c a$, with a a fluid-specific but temperature-independent model parameter, and $P_c \equiv P_1(T_c)$, as determined by the approximant. The coefficients p_0, p_2, p_4, and b are functions of the critical exponents,[2] provided in the supplementary material.[20] The subscript AJ indicates that the J-term virial series (VJ) is used to construct the "AJ" approximant. Since k appears in coordinate transformation equation (3) and a does not, we enforce the former and predict the latter in the approximant. Once a is known, critical amplitudes of Eq. (2) may be calculated from Schofield's equation as follows:[2]

$$\begin{gathered} D = a(b^2-1)b^{\delta-3}/k^{\delta},\quad \Gamma^+ = k/a, \\ A^+ = ak(2-\alpha)(1-\alpha)\alpha p_0. \end{gathered} \tag{5}$$

The only singularity explicitly enforced by the approximant occurs at the critical point, $r=0$, which is a branch point of $P_{\mathrm{A}J}(r,\theta)$. In general, $f(\theta)$ in the auxiliary function is free to choose. Although several choices lead to a convergent description of the SW fluid, we use $f(\theta)=\theta$ in what follows, as this leads to a desirable scaling property (discussed below). The choice of the r-dependence in the auxiliary function given in Eq. (4) allows the approximant to reduce to a critical isotherm approximant when $T=T_c$, similar to the one given in Ref. 17, such that $P = P_c - A(\rho)(1-\rho/\rho_c)^{\delta}$. The approximant given by Eq. (4) at $T=T_c$ differs from the one in Ref. 17 in that it relies on knowledge of B_0, and is not restricted to $\rho<\rho_c$.

For convenience, Table I summarizes the universally known quantities, fluid-specific known quantities, and unknowns to be determined by matching virial coefficients. We take the critical amplitude that determines k and the critical properties ρ_c and T_c to be known, since these properties specify the transformation between (ρ,T) coordinates and parametric (r,θ) coordinates in Eq. (3).

The unknowns of approximant equation (4) ($\tilde a$, $P_1(T)$, and $d_j(T)$'s) are obtained in the following way. First, the critical amplitude parameter $\tilde a$ is obtained by evaluating Eq. (4) along

TABLE I. Quantities appearing in approximant equation (4). External inputs are boldface; other inputs listed below are functions of these. Critical values δ and β are taken from Ref. 21, T_c and ρ_c are taken from Ref. 22, and B_0 is taken from Ref. 23. Virial coefficients are taken from Ref. 6 (duplicated in Ref. 20). Values in parentheses are the 68% confidence limits of the last digit of the tabulated quantity.

Inputs (universal)	Inputs (SW, $\lambda = 1.5$)	Unknowns
$\delta = \mathbf{4.789(2)}$	$T_c = \mathbf{1.2179(3)}$	$\tilde a$
$\beta = \mathbf{0.3265(3)}$	$\rho_c = \mathbf{0.3067(4)}$	$P_1(T)$
$b = 1.1665$	$B_0 = \mathbf{1.926}$	$d_1(T), d_2(T), \ldots$
$p_0 = 0.5282$	$k = 1.3806$	
$p_2 = -0.9974$	$B_1, B_2, \ldots, B_J$	
$p_4 = 0.5783$		

TABLE II. Properties obtained from Eqs. (4) and (5) for the SW fluid ($\lambda = 1.5$), for each approximant of order J. Values in parentheses are the 68% confidence limits of the last digit of the tabulated quantity, propagated from uncertainty in the virial coefficients.

J	P_c	$\tilde{a}$	D	Γ^+	A^+
2	0.097 996	2.4535	0.024 380	0.5627	0.365 10
3	0.096 093	2.2252	0.021 682	0.6204	0.331 12
4	0.095 39(1)	2.056(3)	0.019 89(3)	0.671(1)	0.305 9(4)
5	0.095 21(4)	1.97(1)	0.019 1(2)	0.700(5)	0.294(2)
6	0.095 3(1)	2.03(6)	0.019 6(6)	0.68(2)	0.30(1)

the critical isotherm ($\theta = -1/b$ from Eq. (3) for $\rho < \rho_c$). For this purpose, we set $d_J(T_c) = 0$ in Eq. (4) and determine the unknowns $\tilde{a}$, $P_1(T_c)$, and $d_1(T_c) \ldots d_{J-1}(T_c)$ such that the Jth-order expansion of Eq. (4) about $\rho = 0$ is equal to the Jth-order virial series Eq. (1). Equating powers in ρ, this yields a system of $J + 1$ equations and $J + 1$ unknowns that can be solved analytically. Values of $\tilde{a}$ are recorded in Table II along with $P_c = P_1(T_c)$ for the SW fluid, using up to the six virial coefficients currently available.[6] Critical amplitudes are also given in Table II, using the relations in Eq. (5). Substituting $\tilde{a}$, $P_1(T_c)$, and $d_j(T_c)$'s back into Eq. (4) leads to description of $P(r,\theta)$ along the critical isotherm, which is converted to $P(\rho,T)$ through Eq. (3).

The critical isotherm is shown in Fig. 1(a). The approximant retains the low-density behavior of the virial series, but whereas the virial series diverges upon approach to critical point, the approximant follows δ-scaling imposed by Eq. (2a) (indicated in Fig. 1(a) inset) and continues beyond ρ_c, following simulation data.

For off-critical isotherms (i.e., $T \neq T_c$), the parameter $\tilde{a}$ now becomes an input to approximant equation (4). The unknown functions $P_1(T)$ and $d_1(T) \ldots d_J(T)$ are chosen such that the Jth-order expansion of Eq. (4) about $\rho = 0$ is equal to the Jth-order virial series for every desired T value. One again obtains a system of $J + 1$ equations and $J + 1$ unknowns for each T. Steps for constructing this system are described in the supplementary material,[20] along with virial coefficients for the SW fluid, and computer codes that implement the parametric model (for any fluid) including calculation of derived properties, such as the free energy, etc.

Supercritical isotherms described by the virial series are shown in Fig. 1(b). Although there are no physically motivated singularities for $T > T_c$, the virial series converges poorly for densities beyond ρ_c, and particularly so as T descends toward T_c; this behavior is consistent with observations for the Lennard-Jones model[25] and model alkanes[26] over the same range of T/T_c. Figure 1(c) shows that careful treatment of the critical singularity using approximant equation (4) remedies this behavior and greatly accelerates the convergence. Each sequence of approximants appears to converge uniformly toward a limiting isotherm for all $T \geq T_c$, and all densities examined (which extend up to $2\rho_c$). Subcritical isotherms in the vapor region are not shown, since the virial series already performs well there, leaving little room for the approximant to provide improvement.

An application of Schofield's original model (scaling + background term in Eq. (4)) towards the SW fluid is also shown in Figs. 1(a) and 1(b). Here, the approximant determines the parameters P_1 and a. This (traditional) parametric model aligns with simulation data upon approach to the critical point. However, without the additional degrees of freedom provided by the auxiliary function in (4), the model is incapable of matching the correct low-density behavior as described by the virial series; performance also degrades with increasing $T > T_c$.

The temperature dependence of the approximant may be observed along vertical lines through the isotherms of Fig. 1; these isochores are shown in Fig. 2(a). For $\rho < \rho_c$, the virial series and approximant are indistinguishable on the scale of the figure and are both aligned with simulation data. For $\rho \geq \rho_c$, the virial series diverges (only V6 shown) as $T \to T_c$, while the approximant converges smoothly and remains aligned with the data.

The piece labeled "Schofield's scaling function" in Eq. (4) imposes γ-scaling, as prescribed by Eq. (2b), along the critical isochore for *all* T, not just $T \to T_c$. Choosing $f(\theta) = \theta$ in the auxiliary function of Eq. (4) allows that the asymptotic behavior due to γ-scaling is experienced only on approach

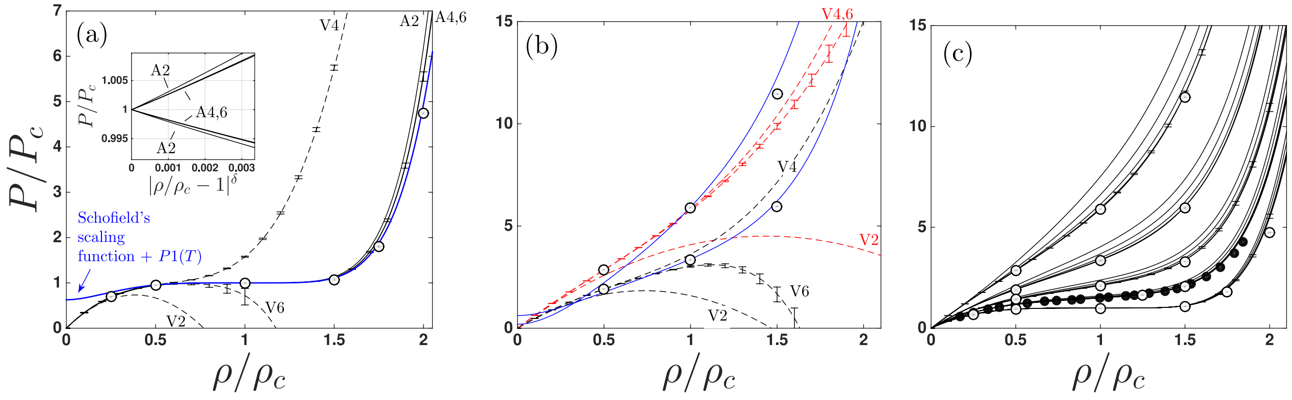

FIG. 1. Isotherms of the SW fluid ($\lambda = 1.5$) as described by the virial equation of state (Eq. (1)) and approximant equation (4) with $f(\theta) = \theta$. (a) $T = 1.2179$ (T_c). Inset highlights that P follows $|\rho/\rho_c - 1|^\delta$. (b) Virial series (dashed curve) and Schofield's scaling function + $P_1(T)$ (solid lines) for $T > T_c$: $T = 2$ (top) and $T = 1.6$ (bottom). (c) Approximant for $T \geq T_c$ (bands of curves, top to bottom) $T = 2, 1.6, 1.4, 1.3, T_c$. Each band shows A2 through A6 (top to bottom). Curves are compared with MD values (○) for a system of 2000 atoms and MC data[24] (●). Uncertainty on the data points is smaller than the symbol sizes. Errorbars on the curves specify the 68% uncertainty propagated from uncertainty in the virial coefficients.

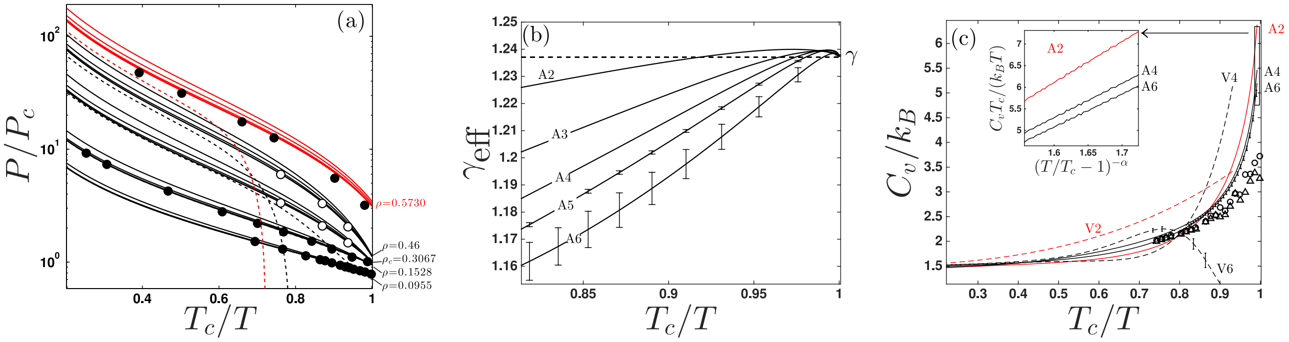

FIG. 2. Isochores of the SW fluid ($\lambda = 1.5$) as described by the virial equation of state (Eq. (1)) and approximant equation (4) with $f(\theta) = \theta$. (a) Each band of curves shows A2 through A6 (top to bottom) and V6 (dashed curve, indistinguishable from A6 for bottom two curves) compared with MC data[27] (●, 2048 atoms) and MD values computed by the authors for a system of 2000 atoms (○). (b) Approach to γ-scaling along critical isochore, given by Eq. (6). (c) Specific heat along the critical isochore as described by approximant and by virial series, compared with MC data[27] (△, N = 500; ○, N = 2048) for $\rho = 0.3056$ (we take $\rho_c = 0.3067$). Inset highlights that C_v/T follows $(T/T_c - 1)^{-\alpha}$. Error bars specify the 68% uncertainty propagated from uncertainty in the virial coefficients. Uncertainty on the data points is smaller than the symbol sizes.

to the critical point, which is the correct behavior for the SW fluid.[22] This can be observed by plotting the effective γ exponent

$$\gamma_{\text{eff}} = [\partial \ln(\partial P/\partial \rho)/\partial \ln(T - T_c)]_{\rho_c} \tag{6}$$

versus T_c/T, as shown in Fig. 2(b) for various orders of the approximant along the critical isochore.

As stated in Ref. 22, the combination of a weak C_v/T singularity ($\Delta T^{-0.1099}$) and a persistently strong background term (here, $P_1(T)$) makes the detection of α-scaling difficult. If one looks sufficiently near the critical point (within 1% of T_c), this singular behavior becomes dominant, as shown in the inset of Fig. 2(c). In this figure, the specific heat from the approximant is compared with that of the virial series and simulation data. Here is an example where the approximant is converging to the correct (divergent) singular behavior which, due to finite-size effects, cannot be captured by simulation without more sophisticated processing.[22] As mentioned in Ref. 19, the ability to describe both P and C_v correctly is a stringent test on the validity of the equation of state.

To summarize, the virial equation of state and the universal critical scaling laws are two cornerstones of the statistical mechanics of fluids. They both have strong theoretical foundations, and in their respective domains they represent fluid properties more accurately than any other theoretical or computational method. In combining them, we have formed an equation of state that simultaneously describes scaling behavior as the critical point is approached along all paths, possesses the correct low-density expansion as given by the virial series, and is analytic in the thermodynamic parameter space except at the critical point itself. The use of series continuation to bridge these two distinct regions accomplishes the transition from singular to regular behavior without the need for an explicit crossover function. Moreover, the treatment retains all the features that make the virial equation appealing: (1) it connects to molecular behaviors, such that most of its key parameters can be determined rigorously for a given intermolecular potential and (2) it can be improved systematically, such that its accuracy at a given state can be gauged by examination of the convergence of a sequence of approximants.

This study suggests that critical anomalies affect the convergence of the virial series for temperatures extending well into the supercritical. Consequently, the approximant's explicit treatment of the critical singularity accelerates the convergence of the virial series not only in the vicinity of the critical region but also over much of the entire space of non-condensed fluid states.

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[20] See supplementary material at http://dx.doi.org/10.1063/1.4929392 for virial coefficients, parametric coefficients, algorithms, and computer programs.

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