

# Vapor-phase metastability and condensation via the virial equation of state with extrapolated coefficients

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## Abstract

Recently reported virial coefficients for the Lennard-Jones model are extrapolated to very high order, and the results are used to study the behavior of virial equation of state (VEOS). Convergence of the VEOS is examined in the context of gas-phase metastability and condensation. Comparison to molecular simulation data shows that the VEOS can accurately describe the equation of state over much of the metastable region, and the stability limits of very low-order isotherms correspond well with simulation-based estimates of the spinodal densities. However, as higher-order terms are added to the density series, the VEOS becomes less capable of characterizing metastable states, and instead appears to be moving toward a description of condensation. The fully-summed VEOS based on virial coefficients extrapolated to infinite order abruptly ends in the metastable region with a branch-point singularity. This form represents the culmination of a sequence of curves in which the pressure reaches a maximum before turning downward, both more sharply and at lower density with increasing series order; the corresponding sequence of maxima converge to the point where the fully-summed VEOS diverges. Thus, the extrapolation-based fully-summed VEOS exhibits the qualitative features of condensation, but it fails to provide quantitative agreement with condensation densities established by molecular simulation. The shortcomings point to a need to better understand the behavior of the virial coefficients with increasing order, perhaps with consideration of the volume dependence of the cluster integrals on which the VEOS is based.

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## 1. Introduction

The virial equation of state (VEOS) [1, 2, 3] holds a unique position in the statistical thermodynamics of fluids. On the one hand, it is an engineering equation of state, providing the pressure as a simple function of the density and temperature (and mole fraction, for mixtures). On the other hand, it is a molecular-based model, which provides a rigorous characterization of a fluid explicitly in terms of its molecular interactions. In this respect, it is capable of accommodating a wide variety of molecular-scale complexities, including density inhomogeneities [4, 5, 6], non-pairwise interactions [7, 8, 9, 10], electrostatics [11], molecular flexibility [12], nuclear quantum effects [10, 13, 14], and more.

While the molecular-level sophistication of the VEOS continues to be demonstrated in various ways, its thermodynamic-level sophistication is only beginning to become appreciated. Indeed, the simple power-series formulation of the VEOS belies a physical richness that is not captured in any other thermodynamic model. First, it should be noted that the VEOS describes behavior in the thermodynamic limit [15, 16]. The VEOS to second order, for example, is not subject to finite-size effects similar to those that would afflict a molecular simulation of two molecules, even though the  $n$ th virial coefficient  $B_n$  involves an integral of only  $n$  molecules. Second, because it represents behavior in the thermodynamic limit, the VEOS can capture the physics responsible for thermodynamic singularities. This is particularly so when applied in alternative but closely-related formulations [16, 17]. Finally, when expressed in terms of a molecular model, with coefficients computed via cluster integrals, the VEOS in principle captures all features related to fluctuations. Indeed, its fundamentally non-classical character appears to make it amenable to resummation using approximants formulated to express known critical behavior [18, 19].

At subcritical temperatures, the behavior of the VEOS is still open to investigation, and it is interesting to consider what might be expected from a fully-summed series, if such could be obtained. Before considering this question, it must be noted that there is a volume dependence in the true equation of state that is not captured by the VEOS when using coefficients as conventionally formulated via infinite-volume cluster integrals [20]. This behavior is

sometimes described as involving volume-dependent virial coefficients. Properly generalized, the virial framework should be able to accommodate these effects, which may provide a means for it to describe high-density and even condensed phases reliably. This generalization and its capabilities are almost completely unexplored. For now, we consider the VEOS in its prescribed form, in which cluster integrals at all orders are defined using an infinite volume.

There has long been speculation that the VEOS will diverge at the binodal density, precluding any characterization of metastability. However, Ushcats [16] has pointed out that without a confining volume, the VEOS cannot recognize a liquid phase. If this is the case, then the binodal is not likely to be a point of significance to the series. Instead, the VEOS may continue smoothly beyond it, thereby characterizing a metastable phase, until it reaches a point of local instability — the spinodal. Mayer and Mayer proved [20], rigorously, that the summed VEOS is invalid beyond the pressure maximum associated with a spinodal, so it cannot exhibit a van der Waals loop. This restriction can be understood also in terms of fluctuations, which cannot allow the VEOS to support an unstable phase (*i.e.*, one having negative compressibility).

In this work, we will consider these points in more detail. We will make use of recent calculations [21] for virial coefficients of the Lennard-Jones model, which at low temperature provide values up to sixteenth order in density. In the next section, we present an extrapolation of these new results to infinite order. Then, in Sec. 3, we study the behavior of the VEOS when used with these extrapolated coefficients, contrasting with the behavior of a simple mean-field equation of state. The study is performed in the context of condensation, metastability, and approach of the spinodal instability. Finally, we provide concluding remarks in Sec. 4.

## 2. Theory and Model

The Lennard-Jones (LJ) model is defined by the spherically-symmetric intermolecular potential:

$$u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

which gives the pair energy  $u$  as a function of separation  $r$ ; henceforth all quantities related to the LJ model will be expressed in “LJ units,” defined such that the size and energy parameters  $\sigma$  and  $\epsilon/k_B$  are unity (where  $k_B$

is Boltzmann’s constant). We will briefly discuss what is now known about the virial coefficients for the LJ model, and consider extrapolations to high order.

Calculation of virial coefficients  $B_n(T)$  for any realistic molecular model is a computationally intensive task. The CPU-time required to evaluate a coefficient to a given fractional precision increases exponentially with coefficient order  $n$  [22]. Recent advances in technique [23, 24, 25, 26] allow calculation to considerably higher order than was previously possible, but still there is a practical limit of about  $n \approx 10$  for which coefficients can be obtained. The difficulty is less at lower temperature, and this feature has recently permitted us to complete calculations [21] up to  $n = 16$  at  $T = 0.6$ . At this low temperature, all high-order coefficients are negative, and their magnitude increases exponentially with coefficient order  $n$ . The behavior in fact appears to be quite regular, and amenable to extrapolation. However, one should be aware that the results can depend delicately on the extrapolation method. In the end, we will be summing products of exponentially-growing extrapolated terms ( $B_n$ ), each multiplying an exponentially diminishing quantity ( $\rho^n$ , where  $\rho < 1$  is the number density).

We attempted an extrapolation using the ideas presented by Marikanto et al. [27], who showed that the virial coefficients could be related to physical clusters. The clusters are treated as being in mutual equilibrium, with equilibrium constants  $K_n$  evaluated such that the system of non-interacting clusters is consistent with the VEOS [28]. The  $K_n$  are related to the work of formation for the clusters, which when properly reduced grows with the surface area, or  $n^{2/3}$ . This relation was confirmed by simulation [27], and can be used to guide an extrapolation of the  $K_n$ , which in turn can be used to compute the  $B_n$  for large  $n$ . Unfortunately, our attempt at implementing this extrapolation yielded  $B_n$  values that alternated in sign, which is unlikely based on the behavior observed at lower  $n$  (a test involving prediction of known coefficients from lower-order terms was qualitatively incorrect in this manner as well). It is possible that the extrapolation is invalid because we have not yet reached a sufficiently large value of  $n$  to allow application of this framework. Consequently, we did not pursue this avenue further.

Rather than focus on the coefficients themselves, we find that more can be discerned by examination of their incremental ratio. Accordingly, in Fig. 1 we plot this quantity using the available coefficients at three low temperatures ( $T = 0.6, 0.7$ , and  $0.8$ , respectively). We observe an approximate linear

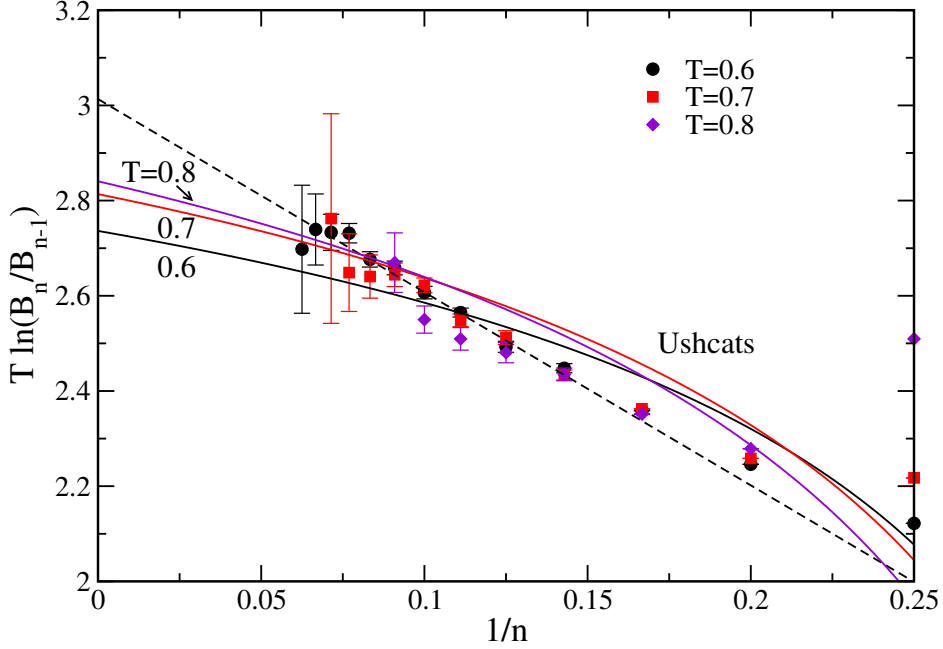


Figure 1: Lennard-Jones virial coefficients in a form suitable for extrapolation;  $x$ -axis is reciprocal of the order of the virial series. Points are data from Ref. [21], at the indicated temperatures, and shown with 68% confidence limits. Dashed line is the fit given by Eq. (1), and solid lines are based on the fit from Ushcats, given by Eq. (2). All quantities are given in LJ units.

relationship of the form:

$$T \ln \frac{B_n(T)}{B_{n-1}(T)} = -\frac{a}{n} + b, \quad (1)$$

which over this range of temperature is approximately independent of  $T$  for larger  $n$ ; a weighted least-squares fit gives  $a = 4.06$  and  $b = 3.01$ . Ushcats [29] proposed a form for  $B_n(T)$  for the LJ model:

$$B_n(T) = -\frac{0.01}{(n-1)(n-2)} \left(\frac{2.2}{T}\right)^{3.51(n-1)}. \quad (2)$$

This relation was developed using the coefficients available at the time, which extended only up to  $n = 8$ , and for a limited set of temperatures. The incremental ratio derived from this form is included in Fig. 1.

The recursion relation defined by Eq. (1) corresponds to the following expression for  $B_n(T)$ :

$$B_n^e(T) \propto \exp\left(\frac{-a\psi(n+1) - \gamma a + bn}{T}\right) \approx C(T)n^{-a/T}e^{bn/T}, \quad (3)$$

where  $\gamma$  is Euler's constant,  $\psi$  is the digamma function, and the “e” superscript on  $B_n$  indicates that it is the extrapolated form for the coefficient. The approximation in Eq. (3) is based on  $\psi(n+1) \sim \ln n + O(1/n)$ , and thus is valid for  $n \rightarrow \infty$ ; the proportionality constant  $C(T)$  must be determined to match one of the  $B_n(T)$ , which we will take to be  $B_{10}(T)$ . This expression is what we will use henceforth for our extrapolation of  $B_n(T)$ .

At low temperature, each  $f$ -bond added to a graph [1, 2, 3] in the sum for  $B_n$  introduces a multiplicative factor of approximately  $\exp(1/T)$  to the value of the graph, assuming that the particles joined by the bond are able to access high-weight configurations. Such access may not be possible geometrically if the particle has many such bonds, so there is a limit to how many  $\exp(1/T)$  factors can be introduced with each increment in  $n$ . With the leading-order temperature dependence in Eq. (3) (or equivalently, Eq. (1)) showing that  $B_{n+1} \sim e^{b/T}B_n$ , we can interpret  $b$  as the effective number of bonds added with the addition of each new point, in the limit  $n \rightarrow \infty$ .

As has been demonstrated several times before [30, 29, 31], with an extrapolated form for the high-order virial coefficients, it is often possible to generate a closed-form equation of state through analytic summation of the virial series. Such an equation is of course only as good as the extrapolation on which it is based. We can perform such a summation here, using the extrapolation for  $B_n$  given in Eq. (3), which sums over powers of the density  $\rho$  using:

$$\sum_{n=1}^{\infty} n^{-a/T} e^{bn/T} \rho^n = \text{Li}_{\frac{a}{T}}(e^{b/T} \rho), \quad (4)$$

where  $\text{Li}_x(z)$  is the polylogarithm function. The extrapolated form for  $B_n(T)$  given by Eq. (3) does not provide a good estimate of the lower-order coefficients, so we write our resummed equation of state with the extrapolated coefficients replaced by the accurate values known from MSMC calculation

[21], thus:

$$\beta P^e(\rho, T) = \left[ \sum_{n=1}^{n_{\max}(T)} (B_n(T) - B_n^e(T)) \rho^n \right] + C(T) \text{Li}_{\frac{a}{T}}(e^{b/T} \rho), \quad (5)$$

where we take  $B_1(T) \equiv 1$ , and  $n_{\max}(T)$  is the largest value of  $n$  for which a reliable  $B_n$  is known at the given temperature; also,  $\beta \equiv 1/k_{\text{B}}T$ . The “e” superscript on the pressure  $P$  indicates its origin in the extrapolation of the virial coefficients; likewise, we will refer to the equation of state given by Eq. (5) as the “*e*VEOS”.

### 3. Results and Discussion

#### 3.1. Convergence of the virial series for the van der Waals equation of state

For context, let us first consider the behavior of a mean-field model of a fluid. In Fig. 2, we present a subcritical isotherm for the van der Waals (vdW) equation of state:

$$P = \frac{T\rho}{1 - \rho} - \rho^2, \quad (6)$$

in which the usual size and energy parameters are taken to be unity. The familiar van der Waals loop is evident, representing the behavior that a fluid displays when the effects of fluctuations are suppressed. This is the equation of state exhibited by a fluid that is constrained to remain homogeneous in density. In this framework, fluctuations needed to generate two phases of different density must be introduced explicitly. Thus, condensation is understood through comparison of the free energy of the single homogeneous phase to that of a composite system of the same overall density but formed from two fluid phases, each homogeneous but having different densities. Full consideration of all possible cases finds two globally stable coexisting densities that can be identified via the Maxwell construction, and indicated by the tie line in the figure. The maximum in pressure at  $\rho = 0.173$  for this temperature is the spinodal, and marks the density  $\rho_{\text{spin}}$  at which the system becomes locally unstable: for  $\rho > \rho_{\text{spin}}$ , infinitesimal fluctuations in density can yield two regions of slightly higher and lower density, respectively, and together these are more stable than the homogeneous phase. Without a special construction, however, the vdW equation of state will not recognize

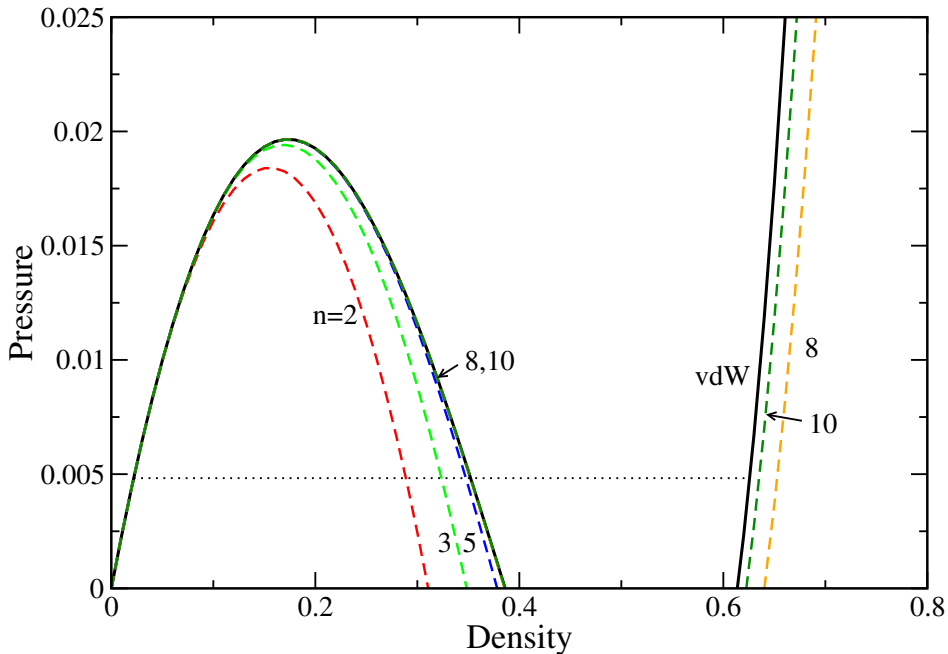


Figure 2: Subcritical isotherm ( $T = 0.8T_c$ ) of the van der Waals (vdW) equation of state (solid black line), and approximation to it via the VEOS given to several orders in density (dashed lines, with order indicated by the value of  $n$ ). Horizontal dotted line connects the coexisting vapor and liquid densities. All quantities are in units that make the vdW parameters unity.

this, because it is a mean-field model and is therefore constrained to describe strictly homogeneous systems.

Virial coefficients are easily derived for the vdW equation:  $B_2 = 1 - 1/T$ ;  $B_n = 1, n > 2$ . Figure 2 also presents the VEOS based on these coefficients. The vdW equation possesses no singularity for  $\rho < 1$ , so unsurprisingly, the virial series converges uniformly to the vdW equation of state. The fully-converged VEOS exhibits a well-defined spinodal that is distinct from the binodal, because the fluid model it is based upon does. The VEOS to sufficiently high order even captures the full van der Waals loop, and shows no recognition of the effects of condensation, or the region of constant pressure indicated by the tie line. Again, it cannot show such features because they are not present in the model it is based upon; they must be added through external considerations.



### 3.2. Convergence of the virial series for the LJ model

We will contrast the behavior of the vdW model with that exhibited by a non-classical model, specifically one defined according to the LJ intermolecular potential. We first examine the behavior of the VEOS when applied to a subcritical isotherm of the LJ model. Figure 3 presents a low-temperature ( $T = 0.6$ ) isotherm according to the VEOS at increasing order in density. The nature of the convergence of the series clearly differs from that illustrated for a mean-field model in Fig. 2. The curves, and in particular their maxima, do not converge quickly to a clear spinodal. Instead, they appear to march steadily toward the binodal (condensation) density. As they do so, their shape becomes increasingly sharp, such that at the highest order VEOS plotted, the isotherm reaches its maximum and then drops off almost discontinuously to large negative values. This progression ends, however, well short of reaching the binodal density, which is indicated on the figure.

Figure 3 also shows the  $e$ VEOS (green line), the equation of state based on extrapolation of the virial coefficients, as given in Eq. (5). The polylogarithm  $\text{Li}_x(z)$  has a branch-point singularity at  $z = 1$ , and accordingly,

$$\rho^*(T) \equiv e^{-b/T} \quad (7)$$

represents an upper bound to the radius of convergence of the extrapolated virial series (this could also be concluded through a standard ratio test of convergence). This density is indicated in the figure by termination of the  $P^e$  isotherm at approximately  $\rho = 0.0066$ . It is clear that the VEOS fails to converge for densities greater than this value. Notably, the progression of spinodal densities (red line) with increasing virial order converges to this point, indicating that at its density of divergence, the  $e$ VEOS is attempting to describe a pressure maximum. This outcome is consistent with the analysis of Mayer and Mayer [20], who showed that the VEOS diverges where  $dP/d\rho = 0$ . We comment more on this point in the next section.

If we were to assert that the singularity in the  $e$ VEOS indicates the condensation density, then we would have  $\rho_{\text{cond}}(T) = \rho^*(T)$ . In this scenario, the condensation density is expressed in terms of the limiting value of  $B_n/B_{n-1}$  as  $n \rightarrow \infty$ . Interestingly, the Mayers [20] reached the same conclusion regarding the connection between the saturated-vapor density and this limiting behavior of  $B_n$ . Their reasoning applies at low temperature, and considers  $B_n$  for large  $n$  to be similar to the partition function of a crystal, which they connect via thermodynamics to the density of a vapor in equilibrium with it.

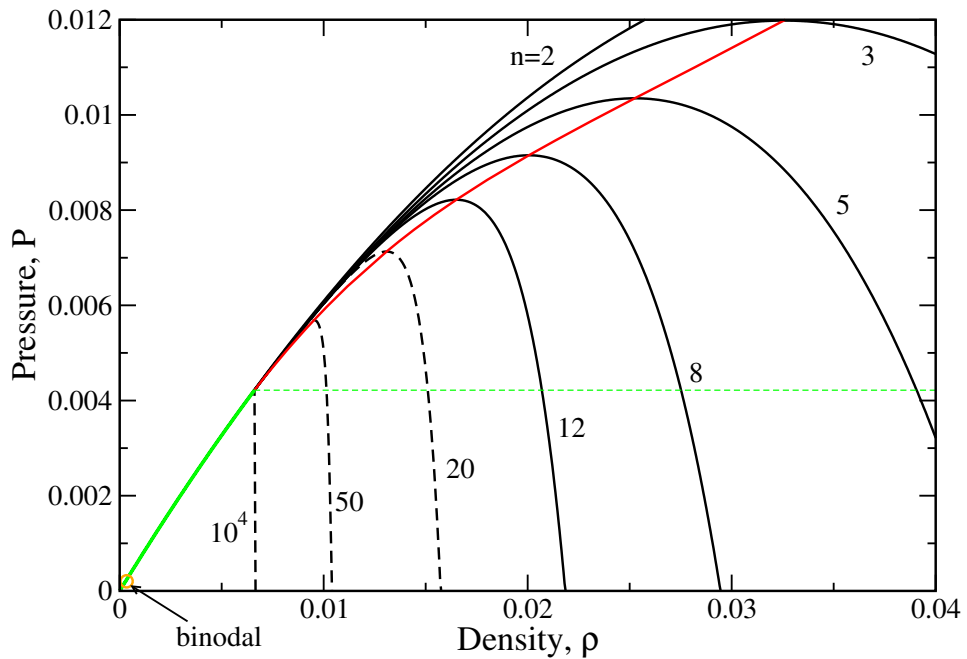


Figure 3: Virial equation of state for the LJ model at  $T = 0.6$ . Each black curve shows the VEOS to the indicated order  $n$  in density (shown by the number next to each line); dashed lines indicate virial series that make use of extrapolated coefficients, as given by Eq. (3). The red line is the locus of maxima (spinodals) for the set of curves. The green line is the  $e$ VEOS, the closed-form equation of state given by Eq. (5), and the horizontal dashed green line shows its constant-pressure extension dictated by the UEOS. Circles are results from molecular simulations performed as part of this work (confidence limits on these points are much smaller than the symbol size); the (orange) binodal circle is indicated, and the other (blue) circles show metastable conditions..

In Fig. 4 we examine this formulation quantitatively by comparison with the condensation density determined from molecular simulation [32]. Using  $b = 3.01$ , as given by the fit described in Eq. (1), we see that  $\rho^*(T)$  from Eq. (7) significantly overestimates the condensation density. The extrapolation proposed by Ushcats (Eq. (2)) leads to  $\rho^*(T) = (T/2.2)^{3.51}$ , and is seen on the figure to be even further removed from the condensation line. The parameter  $b$  that defines  $\rho^*(T)$  can be adjusted to bring the estimated binodal into better agreement with simulation data, and our attempt at this is shown in the figure. We find that increasing  $b$  to about 4.3 would bring Eq. (7) into the same density range as the correct behavior, although the temperature dependence would remain unsatisfactory. To improve this aspect as well, at large  $n$  the temperature dependence must depart from the universal form suggested by Fig. 1, such that the  $1/n \rightarrow 0$  intercept increases with decreasing temperature.

The value  $b = 4.3$  is well outside the range of any reasonable linear extrapolation of the data given in Fig. 1. This result, along with the poor description of the temperature dependence of the binodal, indicates that new effects enter into the behavior when the virial coefficients are applied at higher order. Conceivably, the coefficients themselves simply do not extrapolate in a linear fashion (when expressed as  $\ln(B_n/B_{n-1})$  versus  $1/n$ ), and that significant curvature develops as  $1/n \rightarrow 0$ . Behavior such as this is needed if there is to be a connection between the conventional VEOS and true condensation. Alternatively, or in addition, it may be that new volume dependencies enter into the framework when coefficients at high order are introduced. The VEOS is developed under the assumption that the system volume is much larger than the spatial extent of the relevant clusters. It has been acknowledged from the beginning [33] that this assumption will fail when cluster-integral methods are applied in the context of condensed phases. This is a possible, if not likely, explanation for why the singularity of the  $e$ VEOS does not coincide with the known condensation density.

To summarize, we are left with two plausible explanations for why the  $e$ VEOS fails to recognize the true binodal density: (1) the extrapolation given by Eq. (1) is invalid, and should curve sharply upward as  $1/n \rightarrow 0$ ; and/or (2) new volume dependence emerges for large clusters, such that the conventional VEOS is invalid when summed to high order.

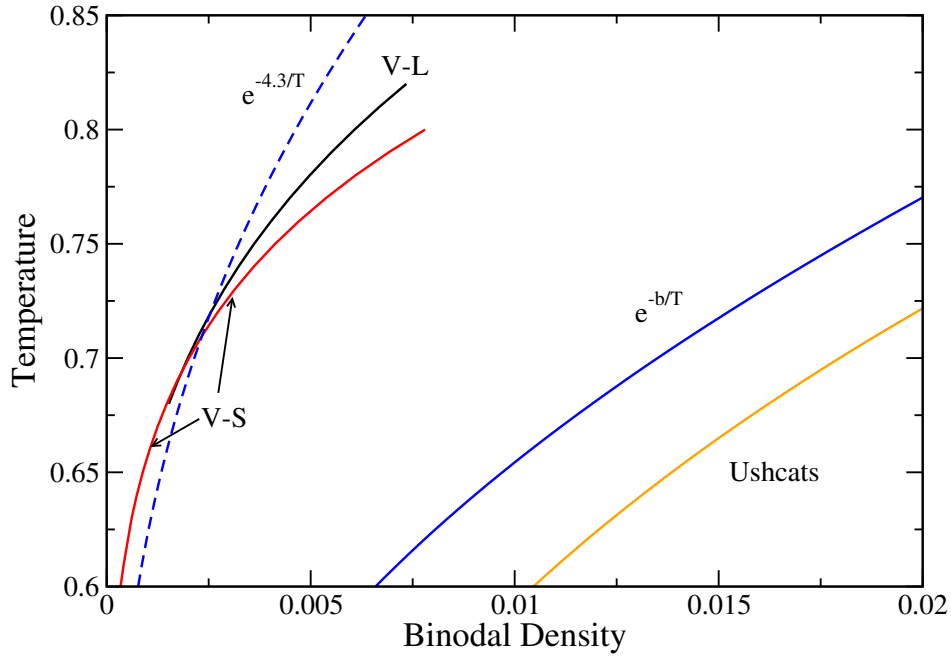


Figure 4: Vapor saturation line. Lines labeled “V-L” (black) and “V-S” (red) are the saturated vapor as determined by molecular simulation [32] for coexistence with the liquid and solid phases, respectively. Blue solid line shows  $\rho^*(T)$  according to Eq. (7), using  $b$  as determined from the fit in Eq. (1); blue dashed line is the same, but with  $b = 4.3$  as adjusted to yield better agreement with saturation densities from simulation. Orange line is the singularity density as predicted from Ushcats’ extrapolation. All quantities are given in LJ units.

### 3.3. Metastable region and spinodal

Apart from the issue of condensation, it is worthwhile to consider what physical behavior can be inferred from the conventionally formulated VEOS (i.e., with no added volume dependence) as it extends into the metastable region. One might ask how the VEOS can represent metastable states: the virial coefficients are defined in terms of configuration integrals, and therefore capture all effects of fluctuations, so how could a more stable condition “hide” from the VEOS? It would require that states that are in fact metastable appear to the VEOS to be globally stable conditions. This will happen if the VEOS is missing key elements needed to characterize the liquid and thereby recognize it as a competitor to the metastable vapor. Truncation of the VEOS can of course cause this, assuming that high-order coefficients are needed to describe liquid-like densities correctly. But even in a fully-summed form (e.g., the  $e$ VEOS), such an outcome could result if, as discussed above, the conventional VEOS does not have the full volume dependence needed to characterize the liquid. So we have a basis for expecting that the conventional VEOS has relevance to the metastable condition, and in particular can perhaps be summed at densities exceeding the binodal. Further, none of the considerations allowing this will preclude characterization of local instabilities, so we can also consider the VEOS in the context of locating the spinodal.

To investigate, let us first ascertain the accuracy of the VEOS in the metastable region. We normally gauge the accuracy of the VEOS at a given density either by examining the sequence of pressures it gives with increasing series order (thereby assessing whether the series is converged), or by comparing to independent data known to be accurate (e.g., from simulation). Both approaches are problematic in the metastable region: the extrapolated VEOS is not converged for  $\rho > \rho^*$ , and its validity for  $\rho < \rho^*$ , where it is converged, hinges on the accuracy of the extrapolation of the coefficients, which is uncertain; studies via simulation rely on the system not surmounting the free-energy barrier that separates it from the liquid state, and one cannot expect such behavior as the spinodal is approached too closely. However, sufficiently far from the spinodal density, simulation of metastable conditions can be performed reliably and reproducibly (provided that the simulated system size and/or amount of sampling is not too large).

Accordingly, we performed grand-canonical Monte Carlo (MC) simulations of several subcritical isotherms of the LJ model, for densities in the expected metastable vapor region. At each density, the volume was selected

to yield average numbers of particles of order  $10^5$ . Ten runs were performed at each density. Systems were equilibrated at a chemical potential corresponding to the binodal, and then “quenched” to the target chemical potential to begin the run, which sampled  $5 \times 10^8$  MC trials. The configurational energy provides a leading indicator of cluster formation and condensation, so we monitored this property to identify whether a system starts to form a liquid. Any simulation exhibiting such behavior was not included in results for the metastable systems.

In Fig. 5, results from the simulations are compared to the VEOS for three subcritical temperatures:  $T = 0.6, 0.8,$  and  $1.0$ . For each temperature, we plot pressures in excess of the value given by the second-order VEOS at that temperature (VEOS2), allowing the data to be presented on a scale where differences are easier to discern. We plot the third- to ninth-order VEOS in this manner, and terminate each line where the total pressure (i.e., not subtracting VEOS2) goes through a maximum — its spinodal density. A filled triangle marks the binodal density for each temperature, so we can see that much of the plotted region is metastable. The VEOS, particularly at metastable densities where the ninth-order series *appears* to have converged for the displayed scale, agrees very well with our simulation data (which themselves are quite precisely determined). However, based on the behavior displayed in Fig. 3, we expect that with additional terms, eventually the higher-order VEOS will peel away from the “converged” ninth-order series. This behavior will be observed for any density greater than  $\rho^*(T)$ , which (based on Eq. (7)) is indicated for each temperature by an open triangle in the figure. Linhart et al. [34] performed MD simulations of the LJ vapor in the NVT ensemble, and their results for  $T = 0.8$  and  $1.0$  are presented on the figure as well. Their data are noisier than ours, but they extend to higher density. In fact, the scatter in their data at each temperature is about as large as the range of variation of the third- to ninth-order VEOS. There is nevertheless a clear difference between the data for the two temperatures, and each data set is consistent with its respective VEOS. From the comparisons with our simulation data and that of Linhart et al, we conclude that the VEOS provides a meaningful description of the equation of state in the metastable region, as long as is not extended to too-high order.

Let us now turn to consideration of the limit of local stability, and see what connection the VEOS may have to the spinodal. The spinodal density is an elusive quantity, one which has long proved difficult to pin down with much certainty, even using molecular simulation. Phenomenological

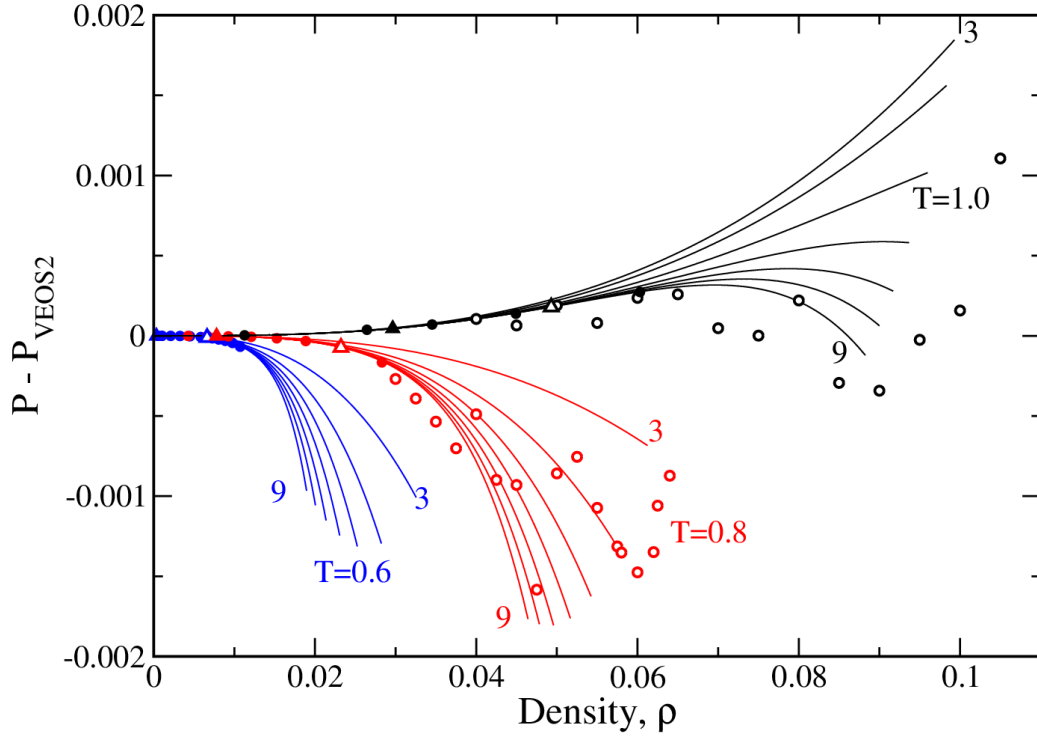


Figure 5: LJ equation of state in the metastable region, showing data for three subcritical temperatures, as indicated. Lines are based on pressures given by VEOS, smoothly varying as the series order is increased from  $n = 3$  to  $n = 9$ , as indicated by the labels. See text for further description. Open circles are MD simulation data from Linhart et al. [34] (which were not reported with confidence limits). Filled circles are data taken as part of the present work, with 68% confidence limits smaller than the symbol size. The densities where the  $\epsilon$ VEOS (Eq. (5)) diverges at each temperature are shown by the open triangles, and the filled triangles indicate the binodal density (based on our own unpublished calculations for  $T = 0.6$  and  $0.8$ , and from Lotfi [35] for  $T = 1.0$ ).

simulation-based approaches attempt to identify the spinodal as the point at which the simulated system first shows no ability to maintain a vapor-like density, for even a short period [34]. This density however is strongly system-size dependent. More formal approaches have attempted to construct free-energy surfaces, and examine conditions at which barriers to nucleation vanish [36, 37, 38, 39]. Results from these approaches depend on the choice of order parameters used to define the free-energy surface [37], and they too can be system-size dependent [36]. Consequently, definitive values of the spinodal density have not been established. Such an outcome is probably inevitable. The notion of a spinodal is inherently a mean-field concept, in which fluctuations play no role. A statistical mechanical treatment of metastability will necessarily include effects of fluctuations, but these must be restricted via constraints that remove the condensed phase from consideration [40]. As the nominal spinodal is approached, it becomes increasingly difficult to fence off the condensed-phase configurations from those that are essential to defining the metastable behavior.

The study by Linhart et al. [34] described above identifies the spinodal density as that where the system exhibits no “induction period,” during which certain clustering measures are observed to remain constant at vapor-like values. The spinodal estimates reported in that work are consistent with observations of metastable regions derived from our own (more limited) simulations, so we will use the Linhart et al. data as the basis for comparison of spinodals derived from the VEOS. Such a comparison is presented in Fig. 6. We note first that the point of divergence of the  $e$ VEOS,  $\rho^*(T)$ , is well below the Linhart et al. spinodal values, and indeed lies closer to the binodal than to the spinodal. This result suggests that the point of divergence of the conventional VEOS is unrelated to the limit of local stability. We also show in the figure the spinodals that would be indicated by the VEOS when truncated at a low order. Interestingly, these points have a good correspondence to the Linhart et al. spinodal densities. Considering that the spinodal represents the condition at which the barrier to nucleation vanishes for even the smallest clusters, it is reasonable that the spinodal could be estimated by the low-order VEOS. Its ability to do so may be hampered by inaccuracies associated with early truncation of the series, but based on the variation of the VEOS with order as demonstrated in Fig. 5, such inaccuracies will be at most a few percent at the conditions of interest. The higher-order VEOS should capture the small-cluster instability as well, but its increasing ability to describe larger clusters instead pulls its spinodal toward a description of the binodal.



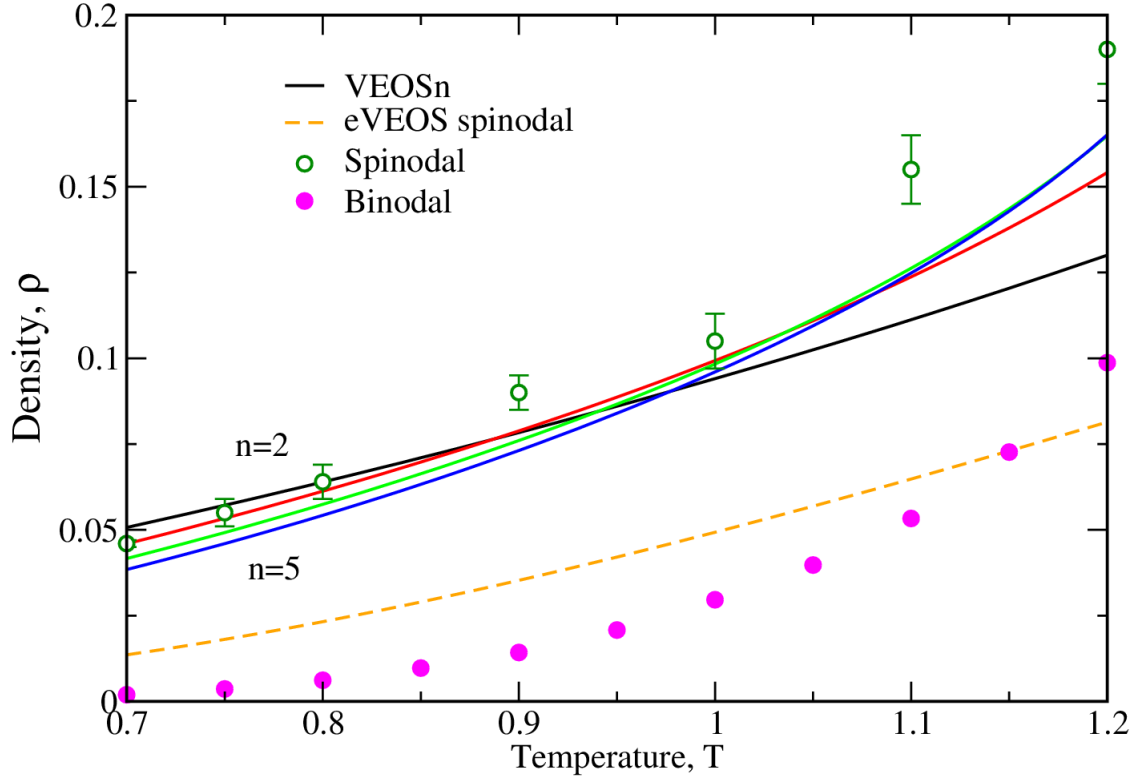


Figure 6: Spinodal line for the LJ model. Open circles are simulation-based spinodal data of Linhart et al. [34]. Solid lines are spinodals according to the VEOS, proceeding from 2nd to 5th order as labeled and as additionally indicated by colors:  $n = 2$  (black); 3 (red); 4 (green); 5 (blue). Dashed line is the spinodal according to the  $e$ VEOS ( $\rho^*(T)$  from Eq. (7) using  $b = 3.01$ ); filled circles are binodal points according to Lotfi et al. [35]. All quantities are given in LJ units.

### 3.4. Vapor-liquid coexistence

Finally, let us consider the manner in which a virial-like, cluster-based treatment could describe the full range of vapor-liquid behavior if the issues regarding high-order coefficients can be resolved. As mentioned above, it has been known since the work of Mayer [20], and emphasized now by Ushcats [16, 29, 41, 42], that the VEOS cannot converge for any density  $\rho > \rho_{\text{spin}}$ . To circumvent this limitation, Ushcats [16] turned to a formulation of the VEOS that is based in the canonical ensemble [17], thereby avoiding manipulation of infinite series and their convergence issues. The starting point is the configurational integral  $Z_N(V)$  for  $N$  molecules in a volume  $V$ , which for a pairwise-additive potential  $u_{ij}$  can be expressed:

$$Z_N = \frac{1}{N! \Lambda^{3N}} \int_V \prod_{i < j} (1 + f_{ij}) d\mathbf{r}^N, \quad (8)$$

where  $f_{ij} \equiv e^{-\beta u_{ij}} - 1$  is the Mayer function and  $\Lambda$  is the de Broglie wavelength. Expansion of the product leads to a sum of terms involving integrals of products of the  $f_{ij}$ . The various terms can be consolidated to yield  $Z_N$  as an  $N$ th-order polynomial in  $V$ , with coefficients given in terms of the same irreducible cluster integrals that appear in expressions for the  $B_n$ . As usual, it is assumed that the volume is large enough to not affect the cluster integration, so the  $V$ -polynomial coefficients are themselves independent of  $V$ . Then, differentiation of  $\ln Z_N$  with respect to  $V$  yields the pressure as a ratio of finite-length polynomials in  $V$ . As it involves no infinite series, this expression for the pressure is not subject to the convergence limitations that hinder the application of the VEOS as usually formulated. In particular, it is not limited to  $\rho < \rho_{\text{spin}}$ .

Ushcats [16] developed a computationally tractable  $N$ -dependent version of this equation of state, which we will refer to as the Ushcats equation of state (UEOS). He proved and demonstrated [16, 42] that in the limit  $N \rightarrow \infty$ , the UEOS simplifies in two ways: (1) for  $\rho < \rho_{\text{spin}}$ , the UEOS is identical to the VEOS; and (2) for  $\rho \geq \rho_{\text{spin}}$ , the UEOS is flat, and independent of density (this remarkable feature has been known for some time [17], but perhaps is not widely appreciated). A plot examining convergence of the UEOS would find that the curves are the same as in Fig. 3, except that the pressure is continued as a flat line past the point where it reaches a maximum. We show one such line extending from the  $n \rightarrow \infty$  isotherm.

It is clear from this figure that the UEOS has, at least qualitatively, the features needed to capture the phenomenon of condensation. The pressure maximum grows increasingly sharp for  $n \rightarrow \infty$ , essentially becoming discontinuous in the limit. The pressure turns completely flat beyond the apparent point of condensation, in accord with the behavior of a real fluid past its condensation density. Even so, the UEOS prescribes no end-point to this constant-pressure behavior, so the approach as yet cannot describe coexistence with the liquid.

#### 4. Conclusions

Through comparison with simulation data, we show that the partially summed VEOS has relevance to the metastable region, and in particular the very low-order series appears to have some ability to locate the spinodal density. However, as additional terms are introduced, and the VEOS becomes more true to the actual physics governing the fluid behavior, it becomes less capable of capturing the metastable system. Instead, summing to increasingly high order causes the apparent spinodal to march toward lower and lower density, with a concomitant narrowing of the range of applicability of the VEOS in the metastable region. Using extrapolated virial coefficients, the process converges to a point that has the appearance of a binodal — the fully-summed VEOS isotherm ends sharply with what is effectively a non-zero slope — but this point of convergence lies well above the true binodal density.

Despite its long history, there remains some disagreement in the literature regarding how phase transitions should be rationalized [43]. There is the more conventional “two-phase” view, which approaches phase transitions from a standpoint of coexistence — this leads to the familiar conditions of equality of temperature, pressure, and chemical potential between or among coexisting phases. Contrasted with this is the “one-phase” view, which approaches a phase transition strictly as a phenomenon involving loss of stability of a phase. In this framework, the nature or properties of the other phase are irrelevant.

Superficially, a treatment of condensation using the VEOS (or more precisely, the UEOS) appears to adhere to the one-phase ansatz: the apparent convergence of the spinodals to a binodal-like point as increasingly higher order  $B_n$  are added suggests that the condensation point can be fully characterized by the vapor properties alone. However, for this to work quanti-

tively, we have shown that the extrapolated virial-coefficient ratio must curve sharply upward as  $1/n \rightarrow 0$  to reach the intercept needed for the conventional VEOS (i.e., without added volume dependence) to show condensation at the density established by simulation. Such a qualitative change is possible, but it would be indicative of the emergence of new features affecting the value of the virial-coefficient cluster integrals, presumably features that in some way are associated with condensation.

The failure of the one-phase approach as realized in the VEOS to capture condensation quantitatively has led us to speculate that the treatment ultimately requires accommodation of the volume dependence of high-order coefficients. Such considerations may introduce the new features required to bring about the needed curvature in the extrapolation of the virial coefficients. Ushcats has pointed out [42] that these same considerations are necessary to address the clear flaw in the UEOS, *viz.* the lack of any way to terminate the constant-pressure branch of the equation of state at high density (and thereby locate the saturated liquid). It appears likely then that the UEOS approach to condensation is indeed a two-phase treatment, inasmuch as the same effects that determine the liquid-phase properties are also needed to locate the condensation density accurately.

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