Virial Equation of State Using Volume-Dependent Coefficients

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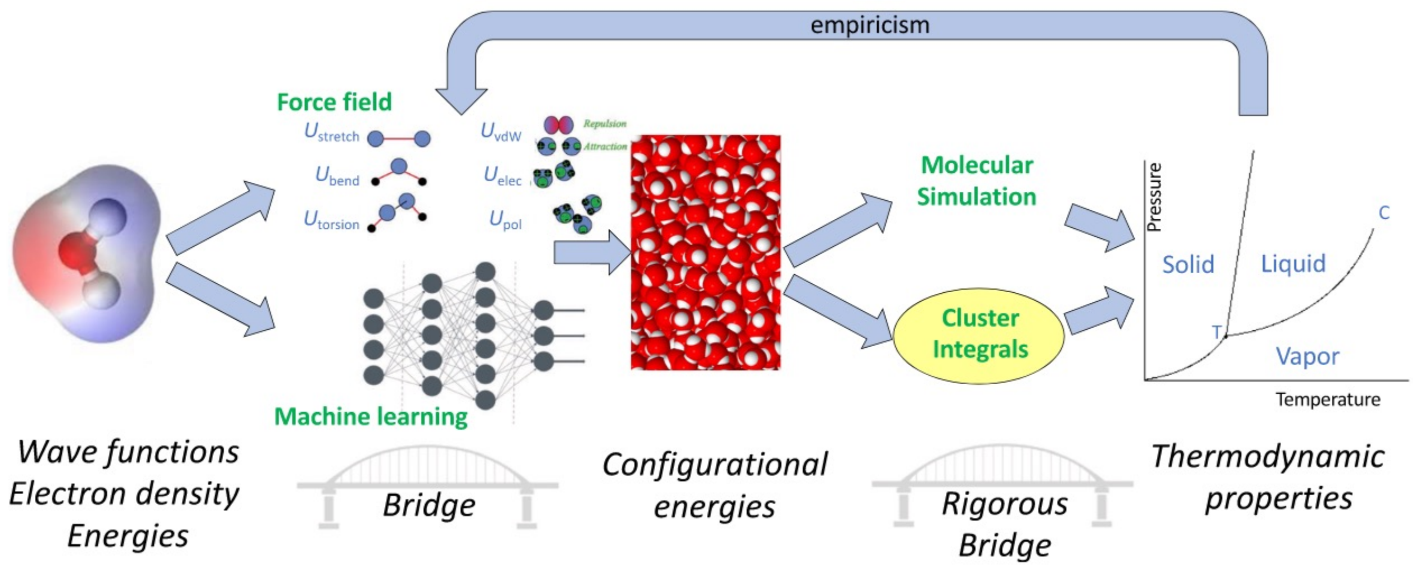

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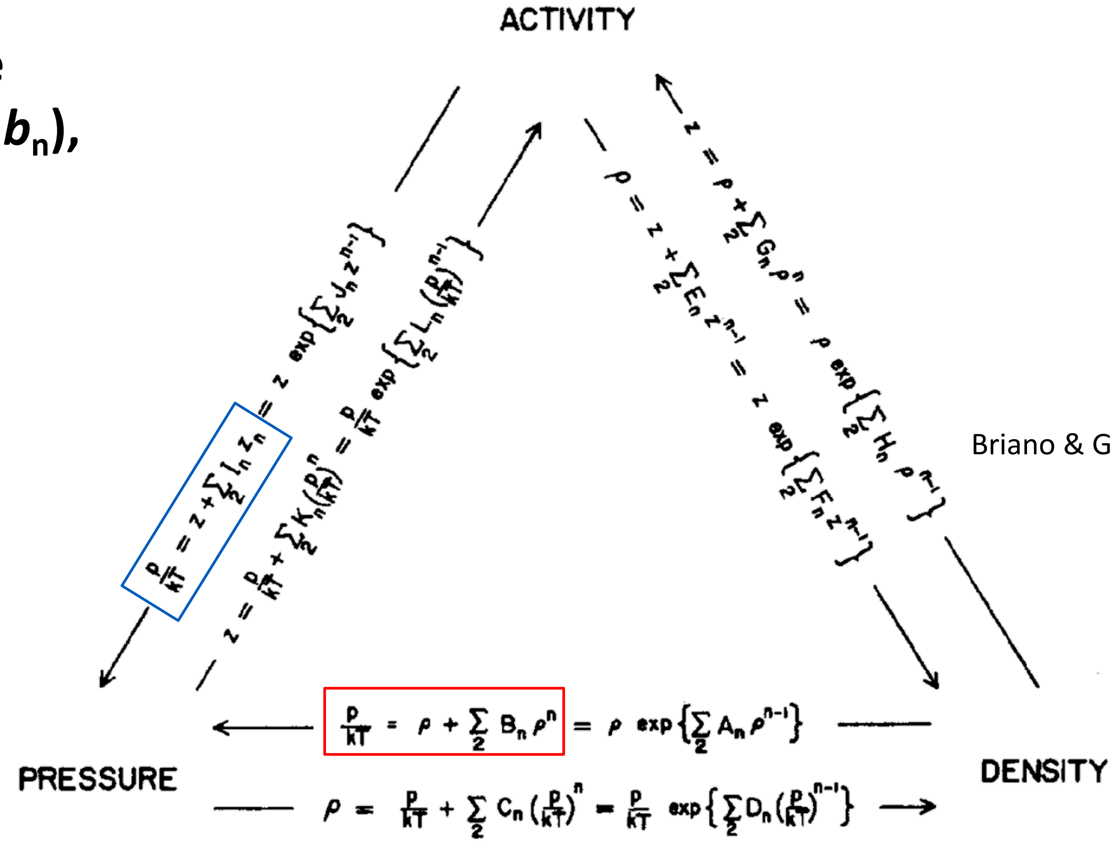
There are several ways to formulate a virial series, differing in choice of dependent and independent variables

Most common choices are the activity (z) series (coefficients b_n), and the density (ρ) series (B_n)

$$P(z) = kT \sum_{n=1}^{\infty} b_n z^n$$

$$P(\rho) = kT \sum_{n=1}^{\infty} B_n \rho^n$$

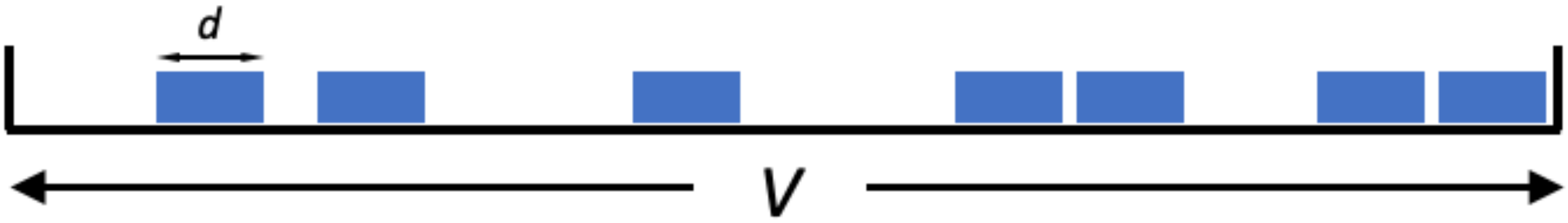
To simplify formulas, we will omit T dependence



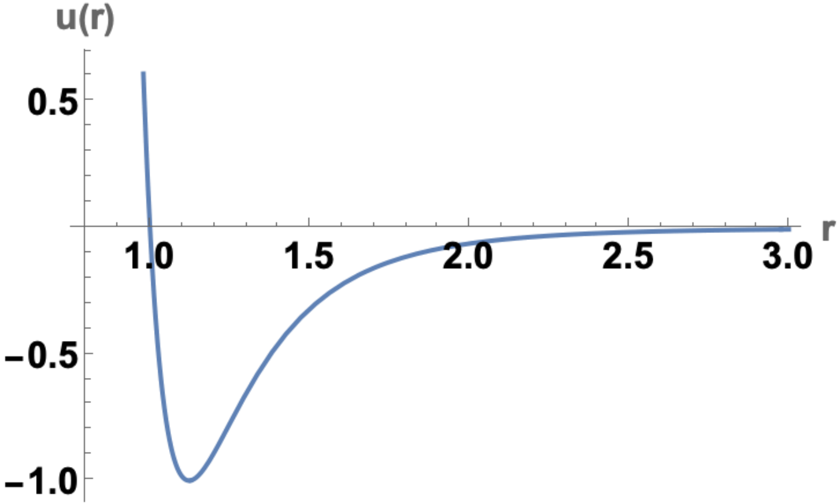
Briano & Glandt, 1980

We’ll consider two models in this presentation

Hard rods in 1D



Lennard-Jones in 3D



We'd like to understand the limits on the VEOS convergence

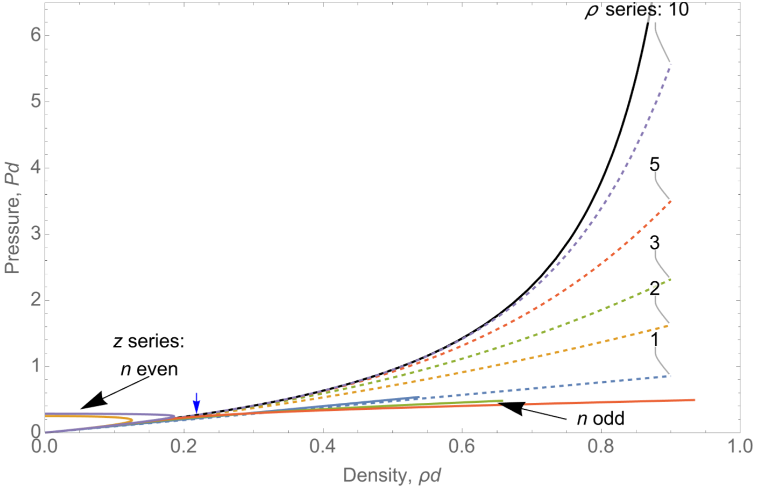
Density series strictly fails at and beyond spinodal/binodal

$$\sum_k kB_k\rho^{k-1} > 1$$

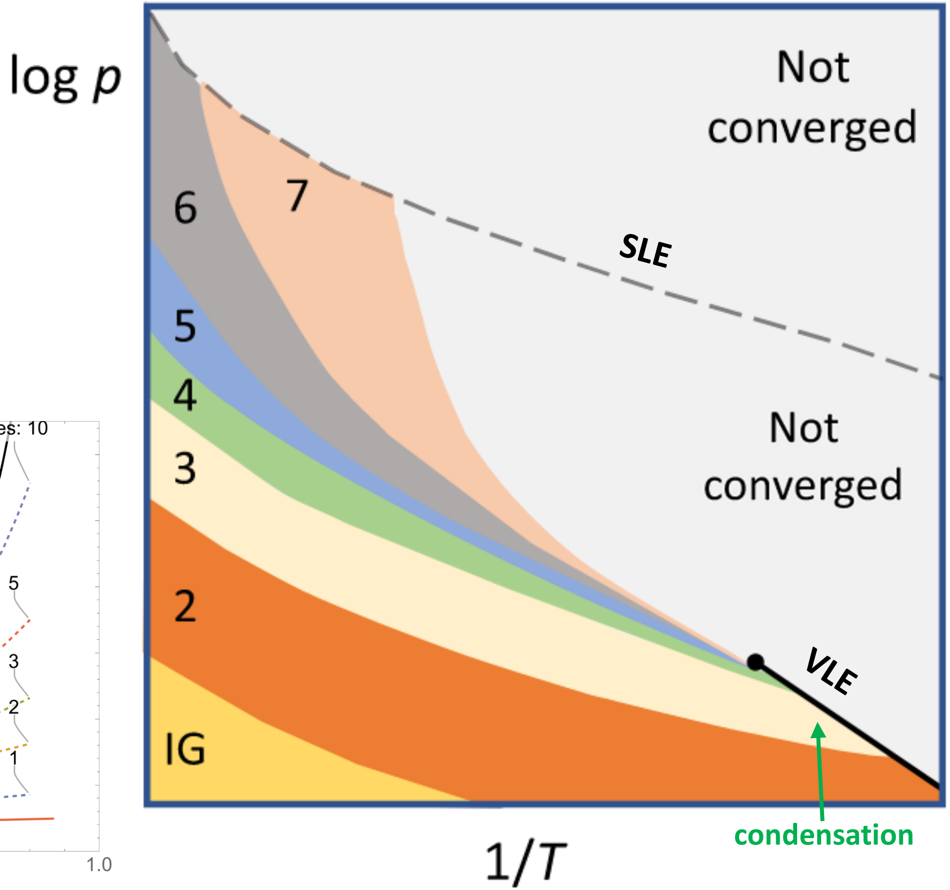
Difficulty converging beyond the Widom line

Activity series P(z) in general is worse

Hard-rod model

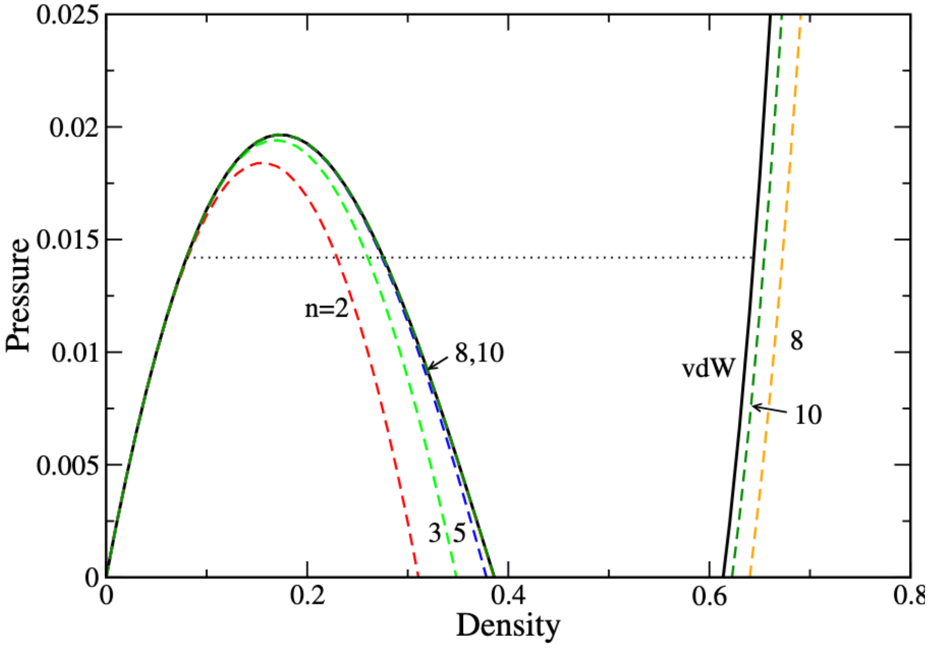


Density VEOS Convergence Map

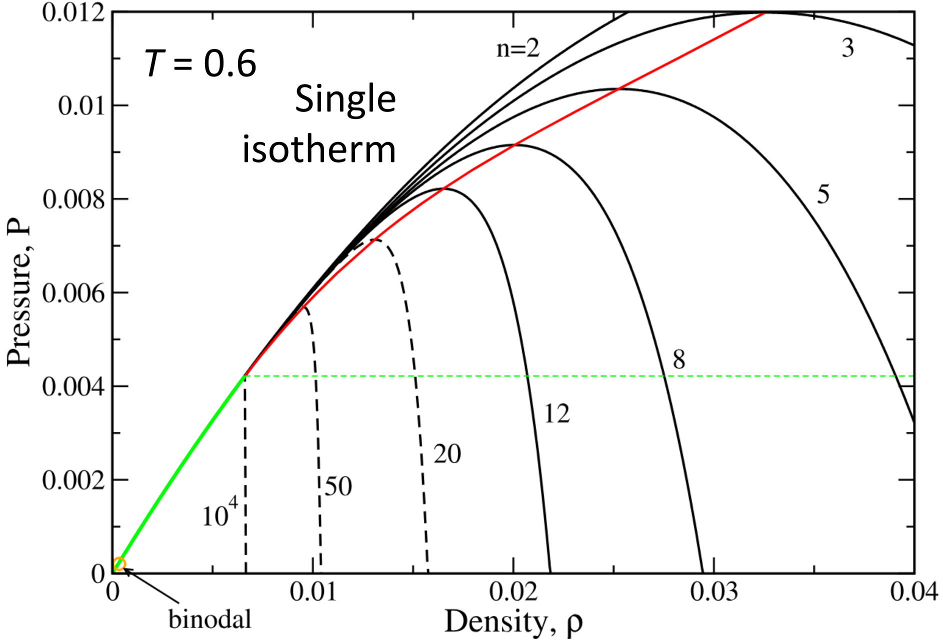


For molecular (rather than thermodynamic) models, the VEOS doesn't have a spinodal

vdW EOS



Lennard-Jones model



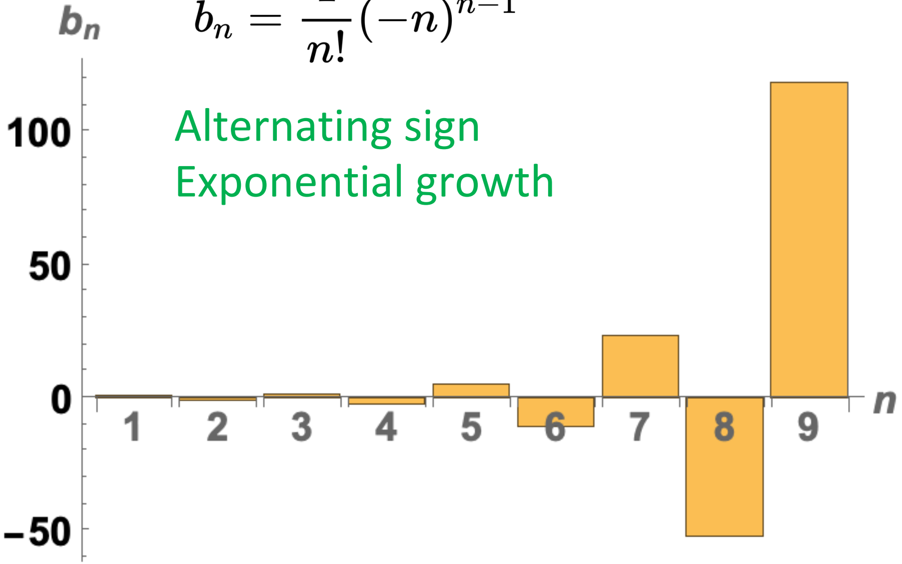
Activity-series and density-series coefficients are very different

1D Hard-rod model

Activity series

$$b_n = \frac{1}{n!}(-n)^{n-1}$$

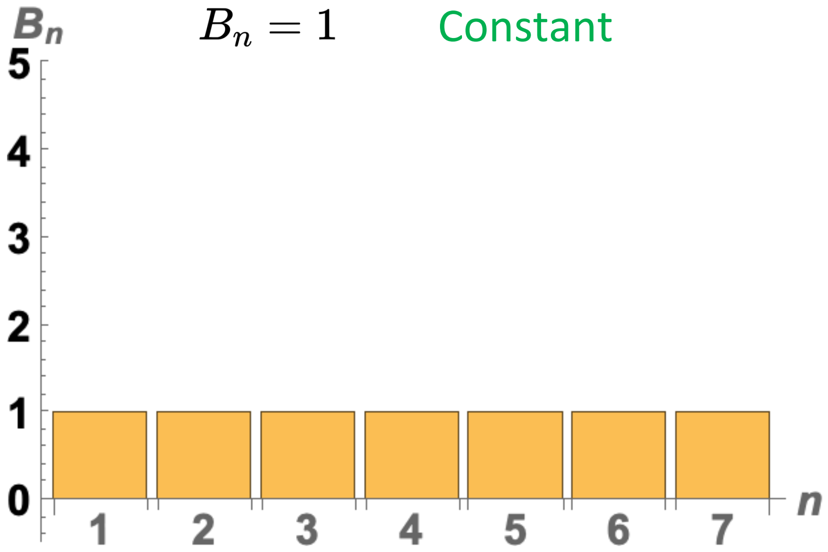
Alternating sign
Exponential growth



Density series

$$B_n = 1$$

Constant

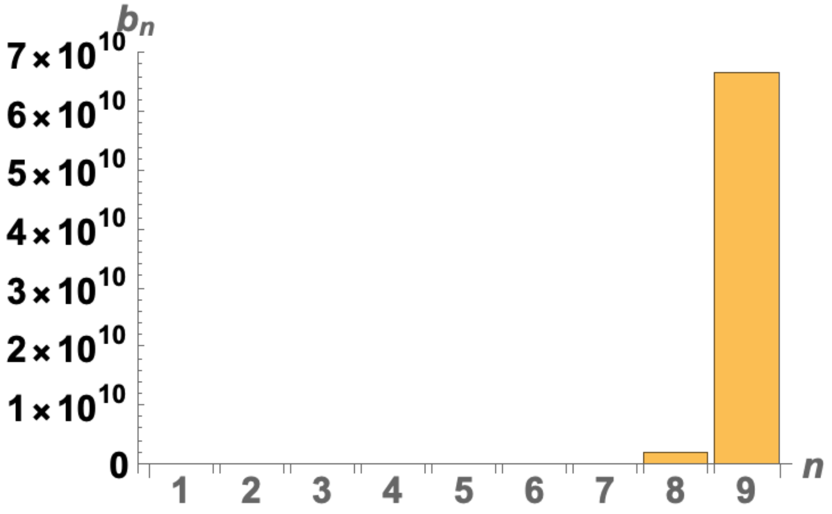


Activity-series and density-series coefficients are very different

3D Lennard-Jones, low temperature (T = 0.8)

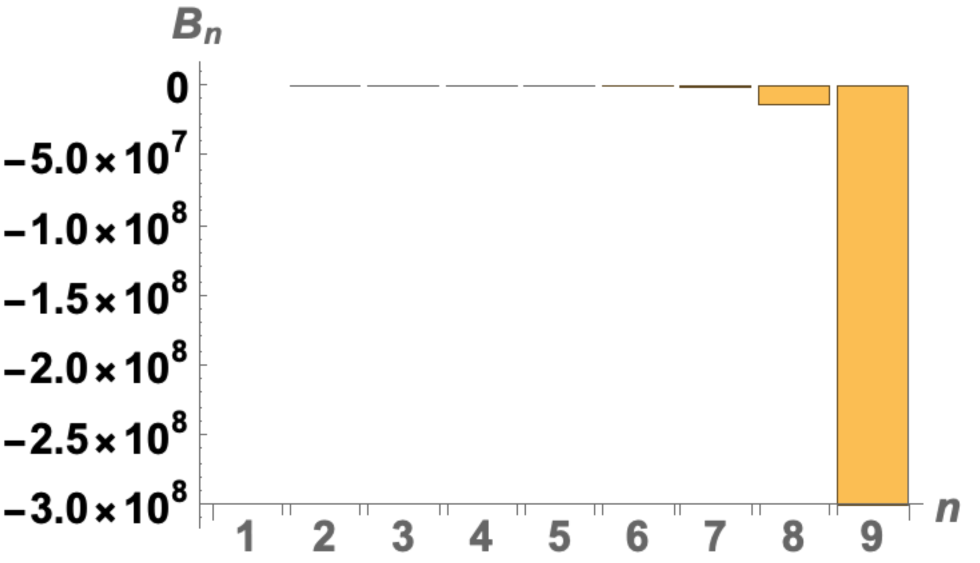
Activity series

All positive, growing exponentially



Density series

All negative, growing exponentially

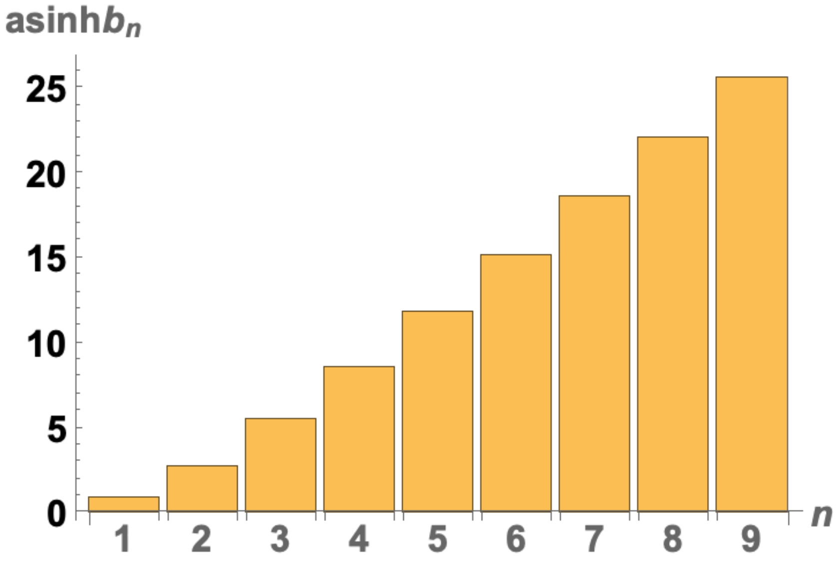


Activity-series and density-series coefficients are very different

3D Lennard-Jones, low temperature (*T* = 0.8)

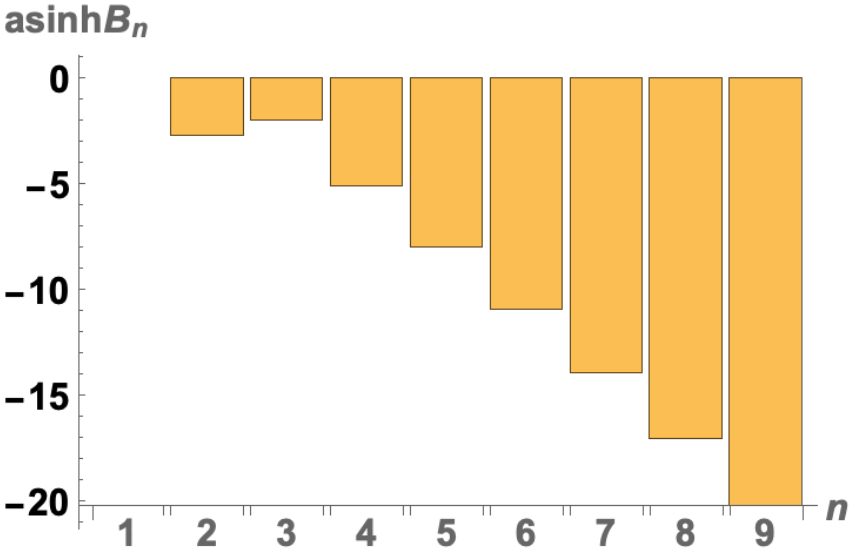
Activity series

All positive, growing exponentially



Density series

All negative, growing exponentially

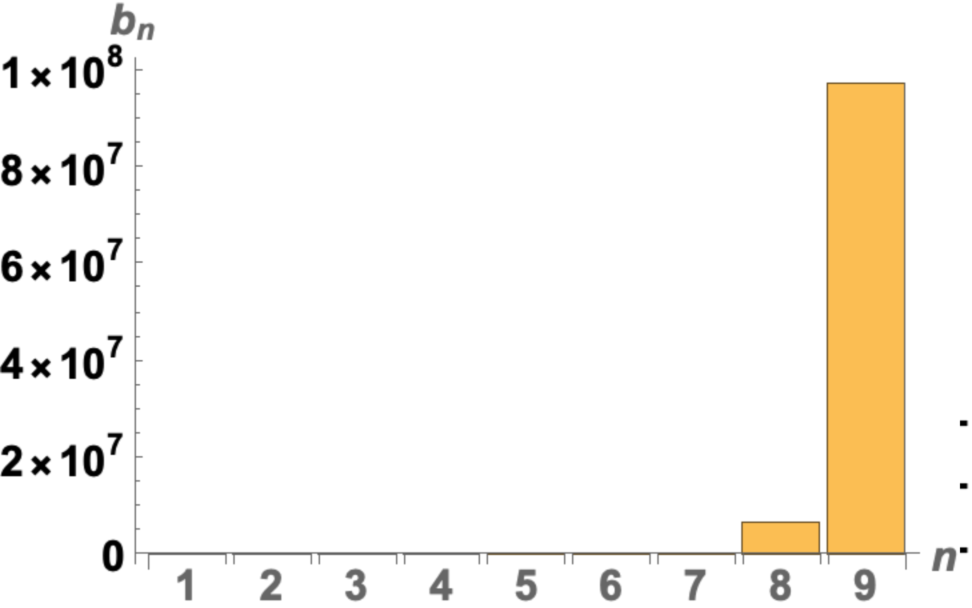


Activity-series and density-series coefficients are very different

3D Lennard-Jones, medium temperature (T = 1.2)

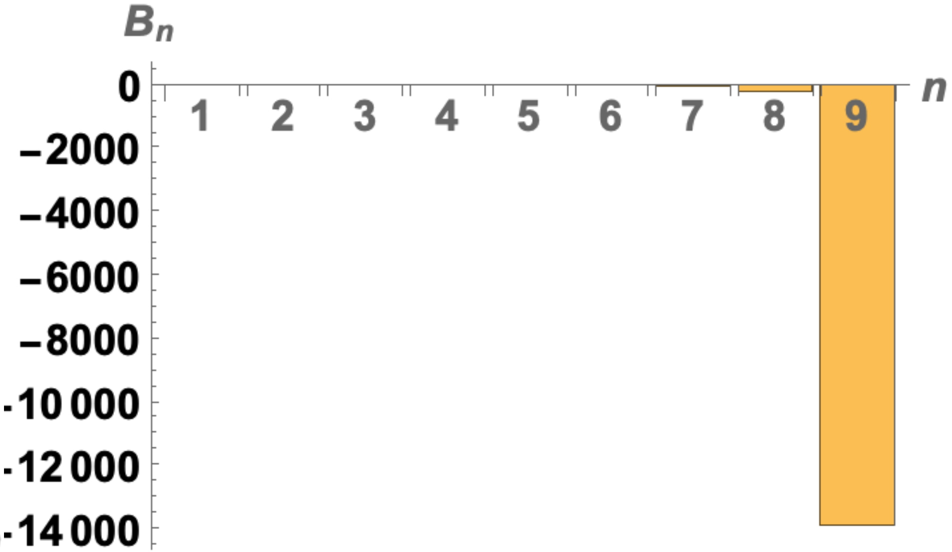
Activity series

All positive, growing exponentially



Density series

Mixed sign, growing exponentially

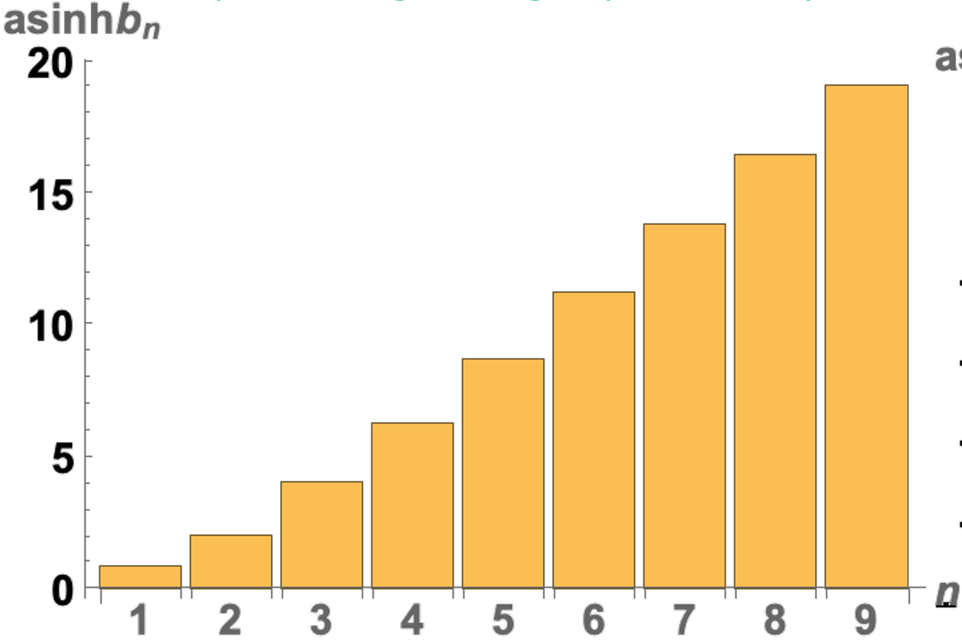


Activity-series and density-series coefficients are very different

3D Lennard-Jones, medium temperature (T = 1.2)

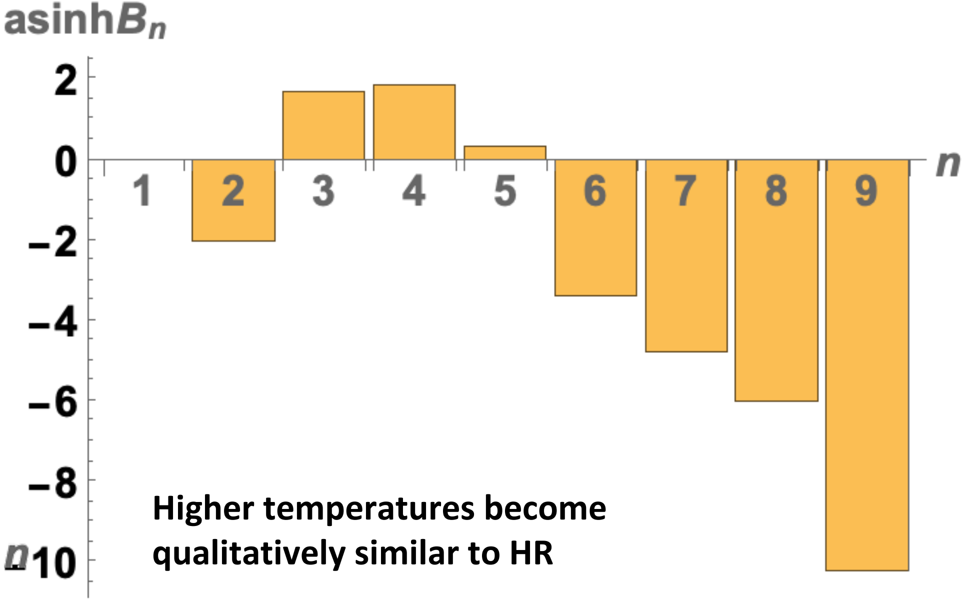
Activity series

All positive, growing exponentially



Density series

Mixed sign, growing exponentially

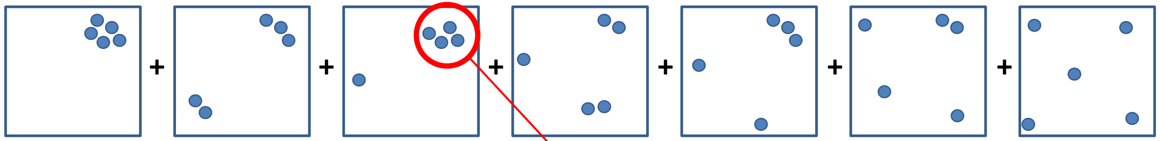


Higher temperatures become qualitatively similar to HR

There is a concise, exact* relation between the *N*-molecule canonical partition function and the b_n coefficients, $n \le N$

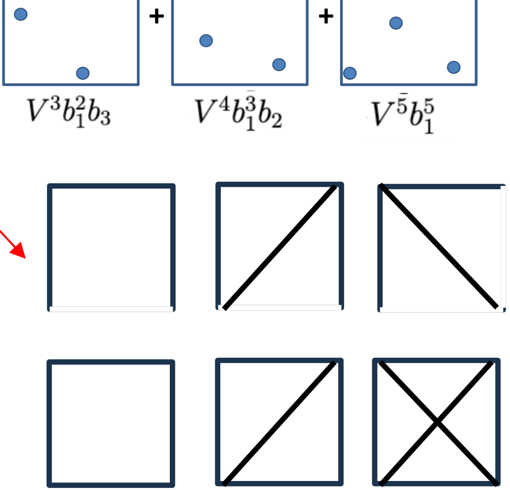
$$Z(N,V) = \sum_{\substack{\{m_j\} \\ \sum_{j=1}^{N} j m_j = N}} \prod_{j=1}^{N} \frac{(V b_j)^{m_j}}{m_j!}$$

Physical meaning



$$Z(5,V) = V b_5 + V^2 b_2 b_3 + V^2 b_1 b_4 + V^3 b_1 b_2^2 + V^3 b_1^2 b_3 + V^4 b_1^3 b_2 + V^5 b_1^5$$

b_j given by the reducible (singly-connected) integrals



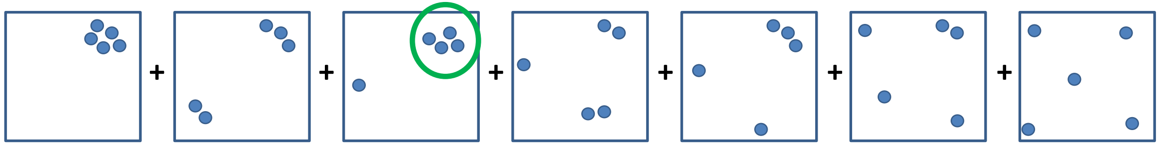
* $b_j = b_j(V)$

In principle, the b_n are volume dependent, and this is distinct from density dependent

$$Z(N,V) = \sum_{\substack{\{m_j\} \\ \sum_{j=1}^{N} j m_j = N}} \prod_{j=1}^{N} \frac{(Vb_j)^{m_j}}{m_j!}$$

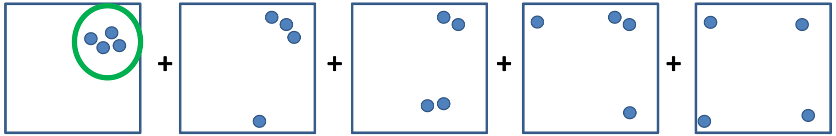
Physical meaning

$Z(5,V) =$



$$Vb_5 + V^2 b_2 b_3 + V^2 b_1 b_4 + V^3 b_1 b_2^2 + V^3 b_1^2 b_3 + V^4 b_1^3 b_2 + V^5 b_1^5$$

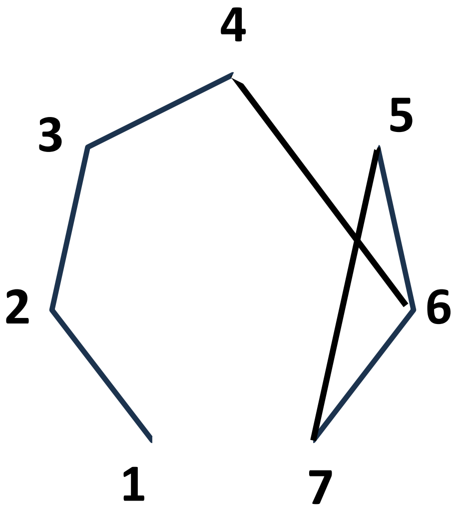
$Z(4,V) =$

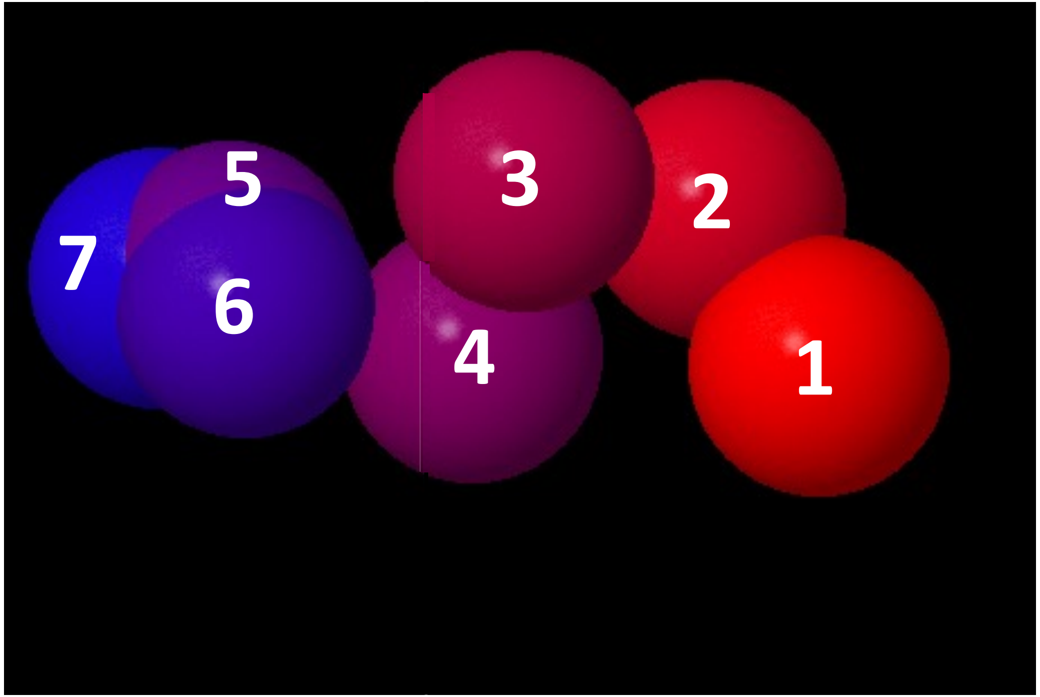


$$Vb_4 + V^2 b_1 b_3 + V^2 b_2^2 + V^3 b_1^2 b_2 + V^4 b_1^4$$

Volume-dependent virial coefficients

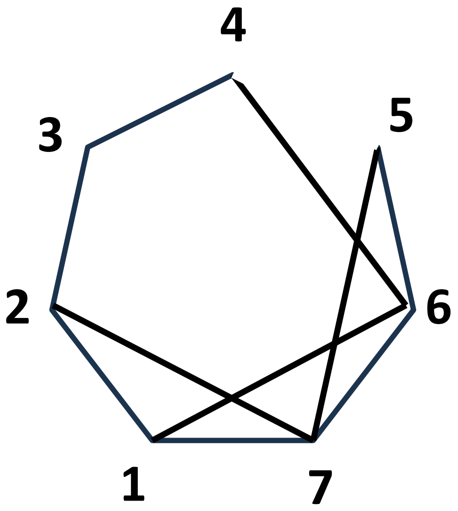
This configuration is not doubly connected. Contributes to b_7, but not to B_7

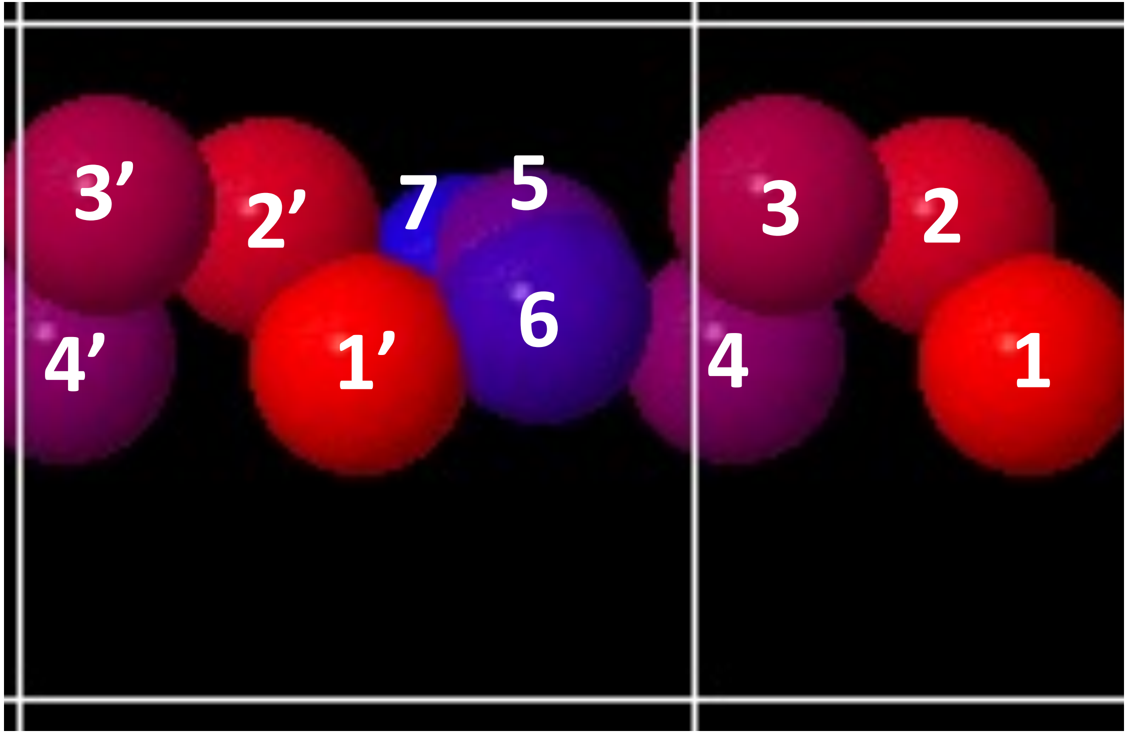




Volume-dependent virial coefficients

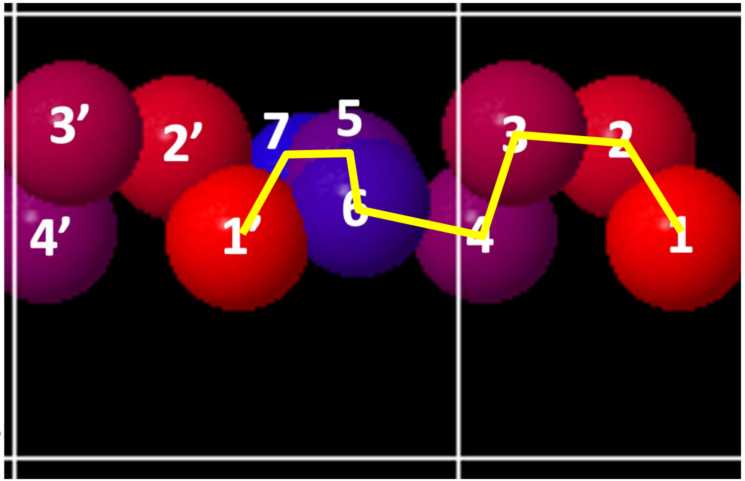
With PBC, the same configuration *is* doubly connected. It contributes to b_7 and B_7

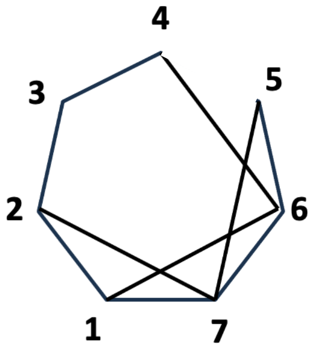




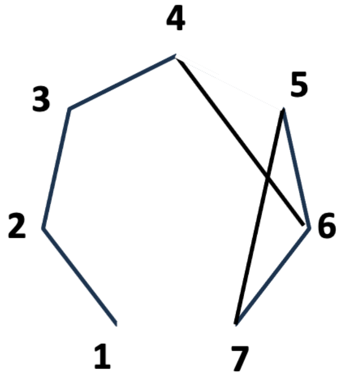
Some Features of PBC Volume-Dependent Virial Coefficients

- Volume dependence arises primarily for graphs that can connect an atom to one of its images.
- Can also arise at box lengths smaller than range of pair interaction
- For volumes larger than this, a graph will not be volume dependent
- Volume dependence arises only in doubly-connected graphs, or doubly-connected parts of singly-connected graphs

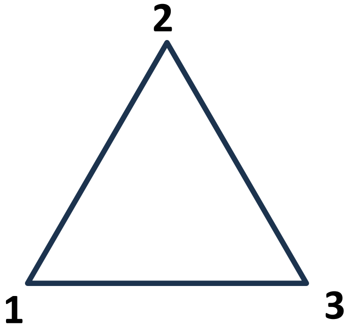




← This is volume dependent to larger volumes than this →



...which is about the same as this →



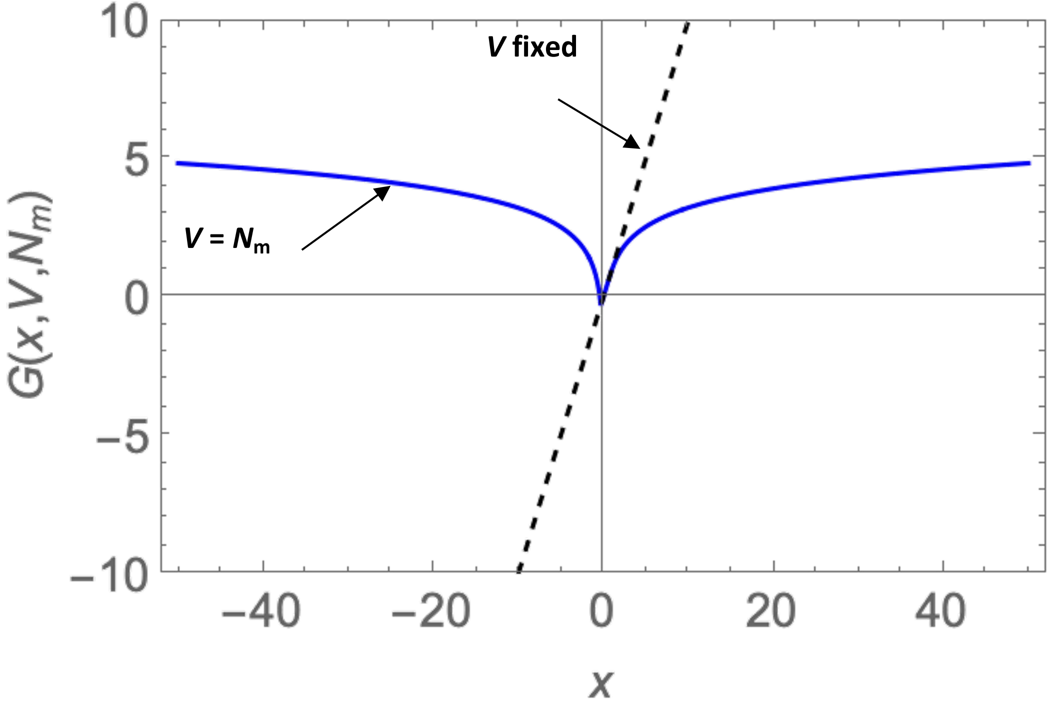
The *N*, *V* → ∞ limiting process underlying the VEOS is fraught, even without the issue of coefficient volume dependence

A term like this arises in the development of the activity series

$$G(x,V,N_\mathrm{m}) \equiv \frac{1}{V}\ln\sum_{n=0}^{N_\mathrm{m}}\frac{(Vx)^n}{n!}$$

$N_\mathrm{m} \rightarrow \infty$

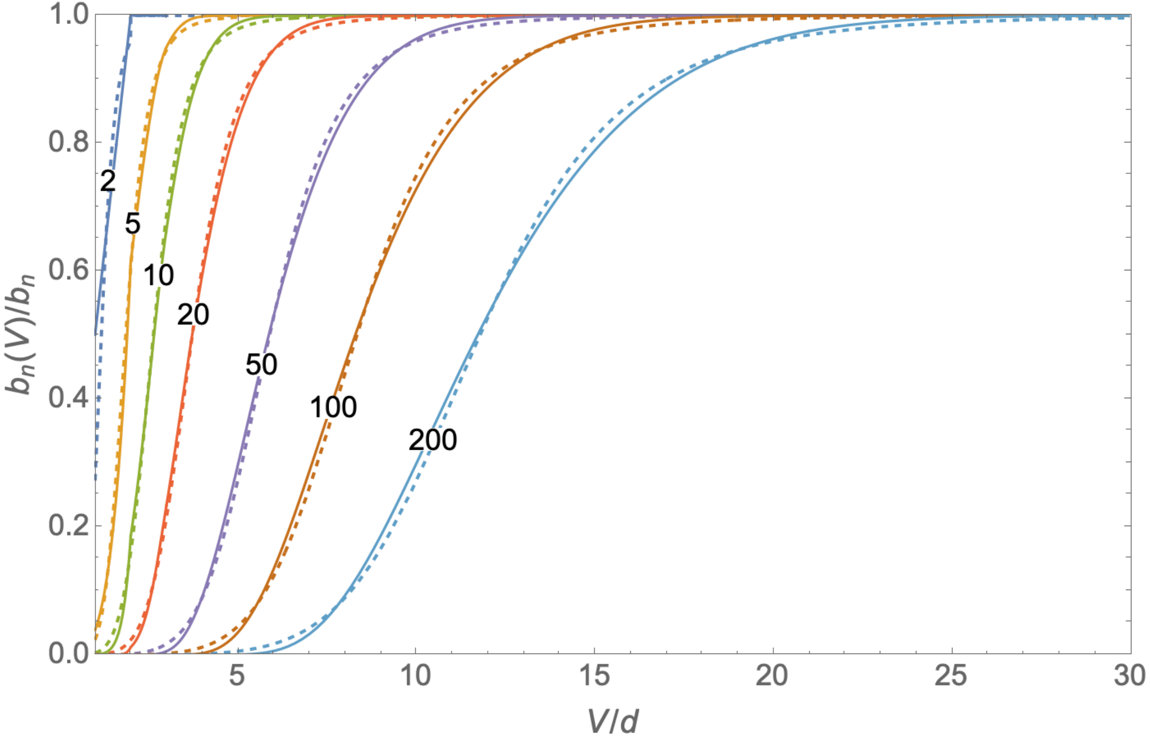
Its behavior differs markedly depending on how the simultaneous limit is performed



Activity-series b_n go to zero slowly with decreasing volume

1D hard-rod model (analytic results)

Exact (solid) and empirical fit (dashed)



$$Z(N,V) = \sum_{\substack{\{m_j\} \\ \sum_{j=1}^{N} j m_j = N}} \prod_{j=1}^{N} \frac{(V b_j)^{m_j}}{m_j!}$$

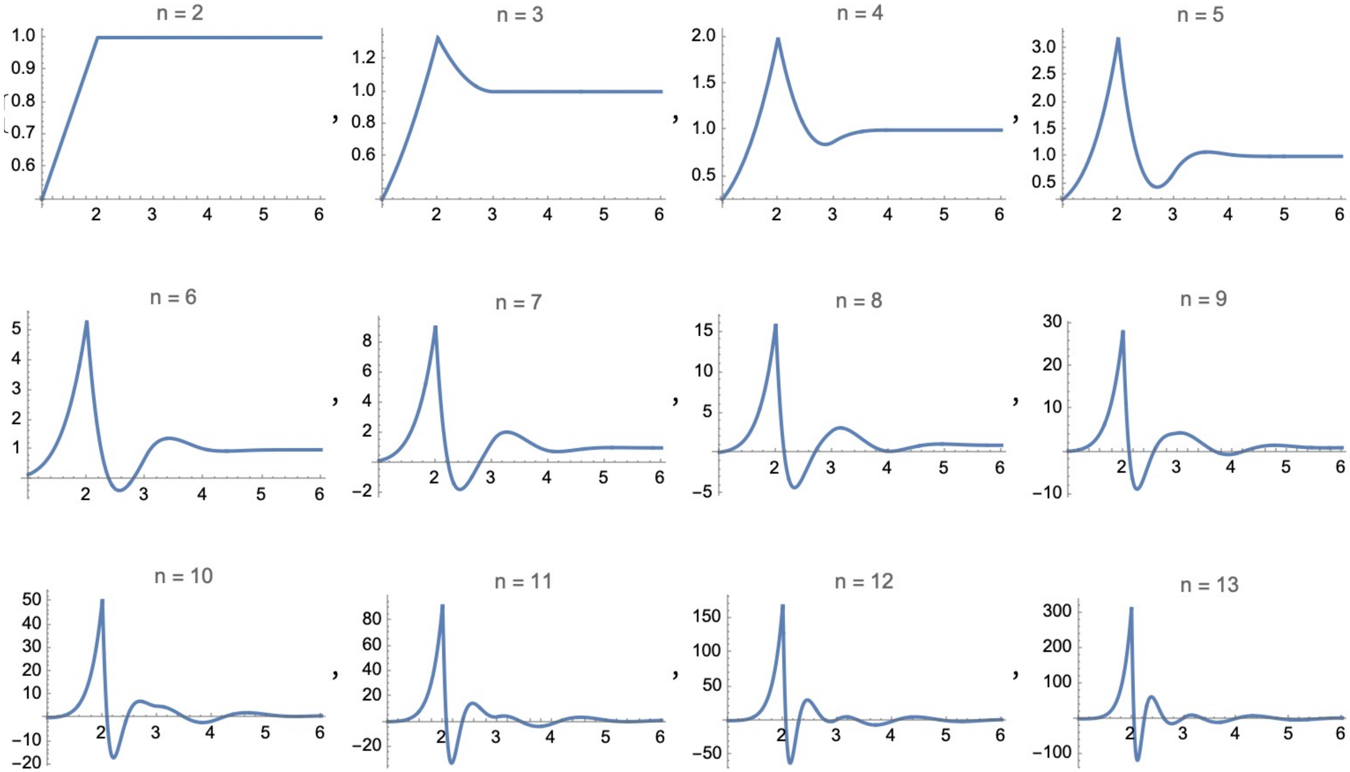
$= 0$ for small V

$$b_n^{\rm fit}(V) = \frac{3V^6}{3V^6 + n^3 d^6} b_n$$

$$V_{½} \sim \sqrt{n}$$

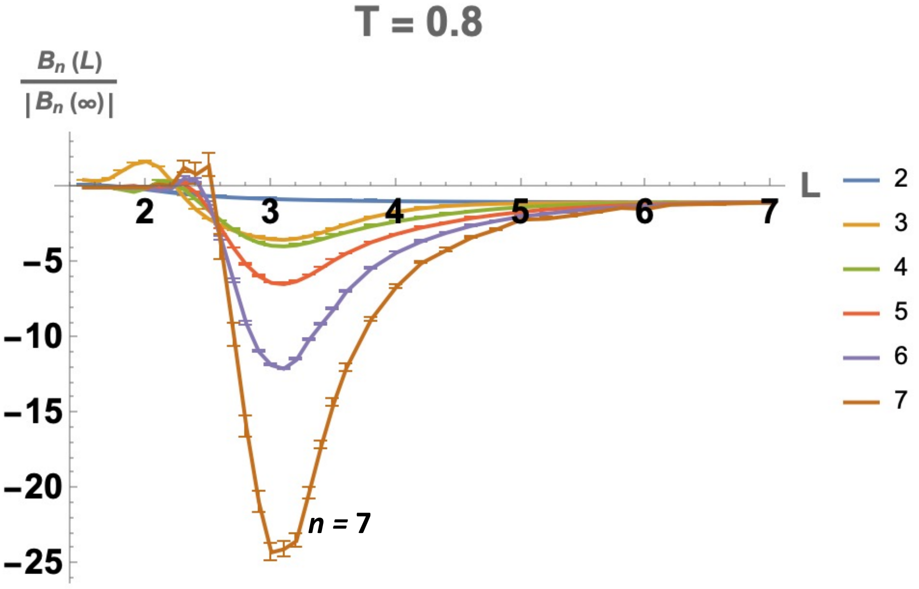
Density-series B_n have more complicated behavior

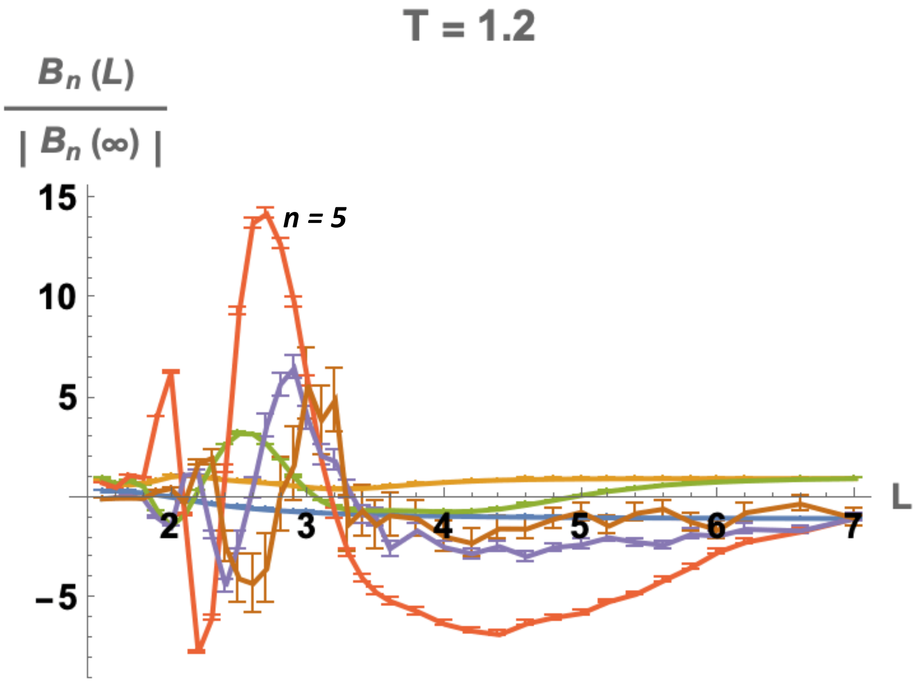
1D hard-rod model



Finite size makes B_n much more negative at lower T

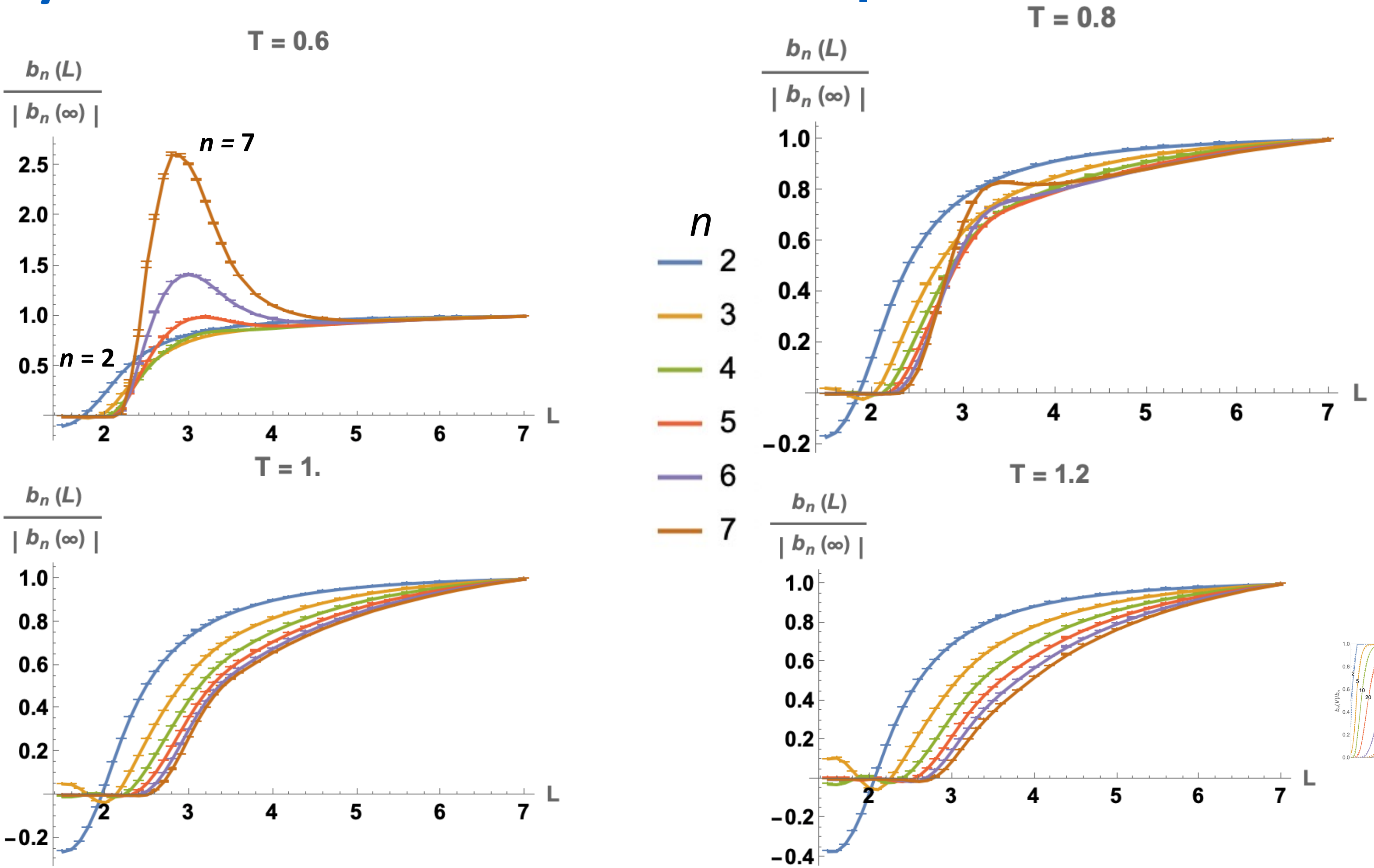
Lennard-Jones model



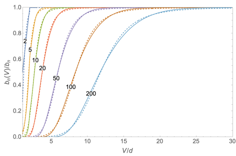


Activity-series coefficients are a bit simpler

Lennard-Jones model

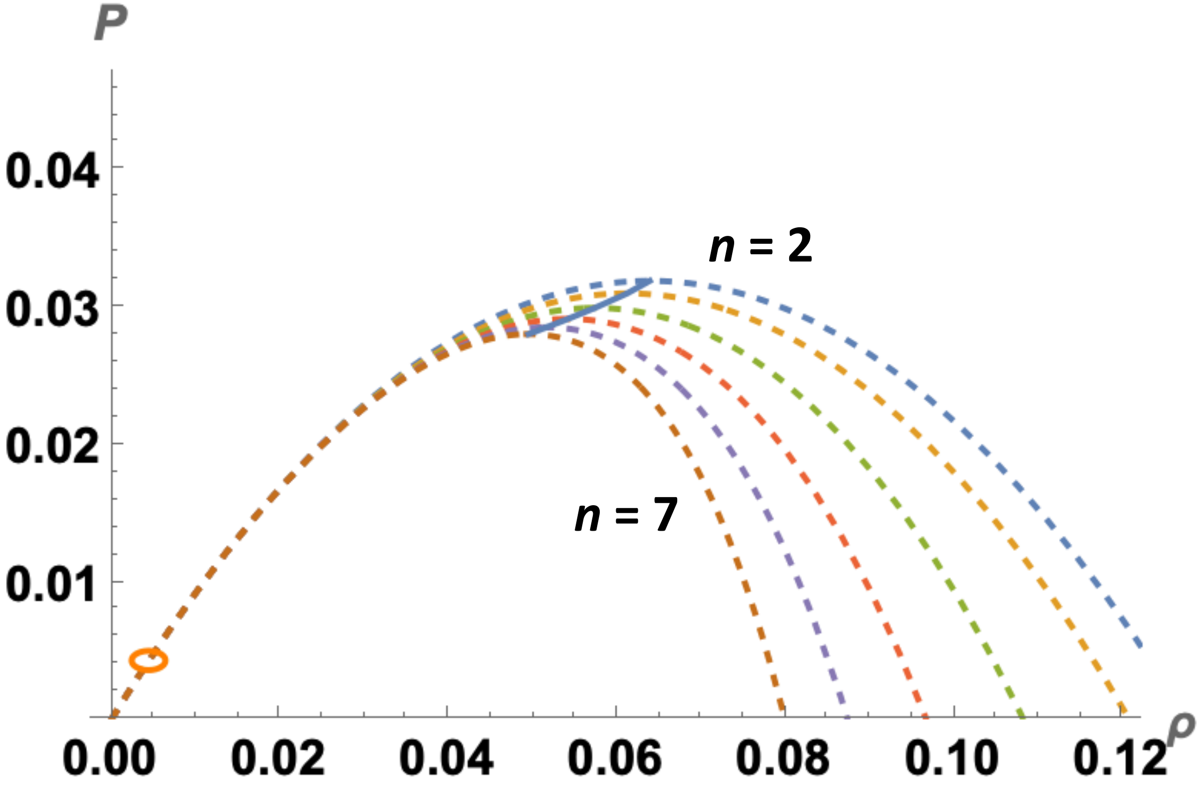


HR



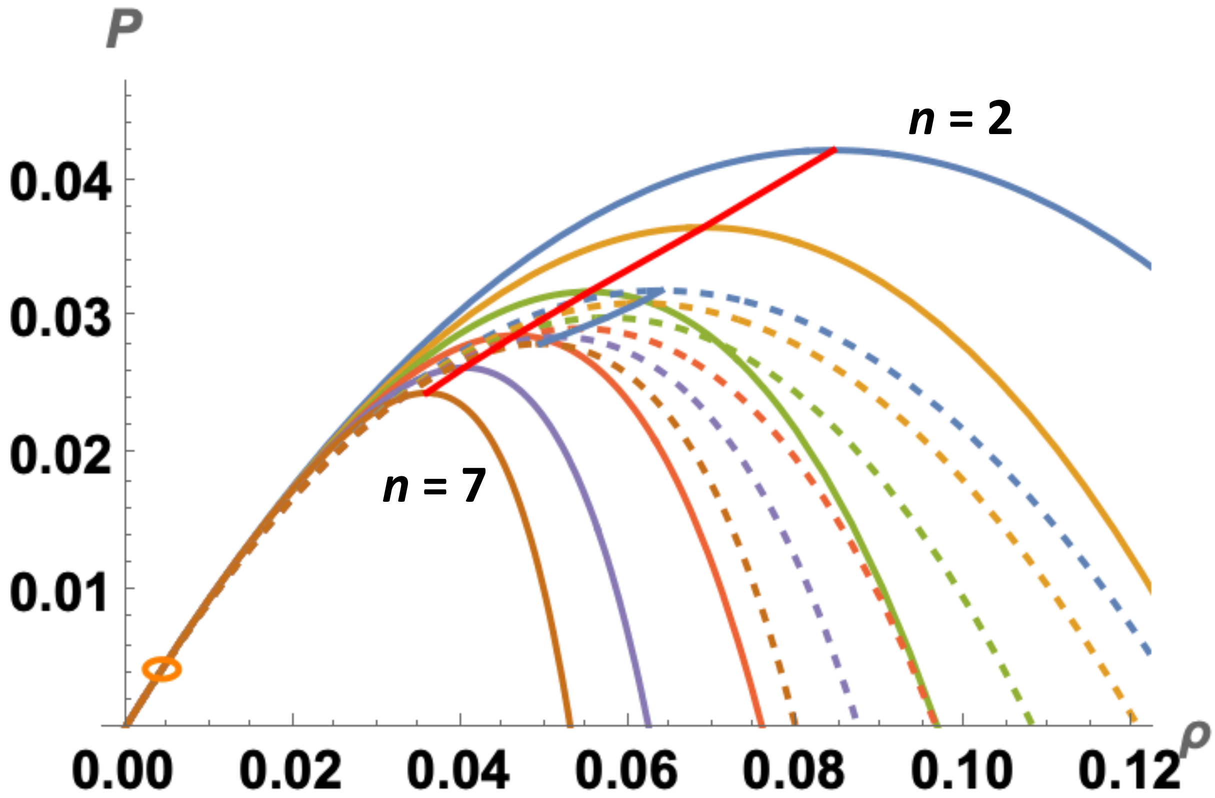
Volume dependence helps VEOS to detect condensation

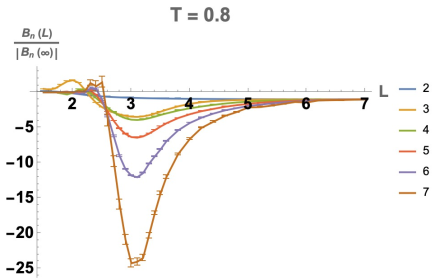
Volume-independent, *T* = 0.8



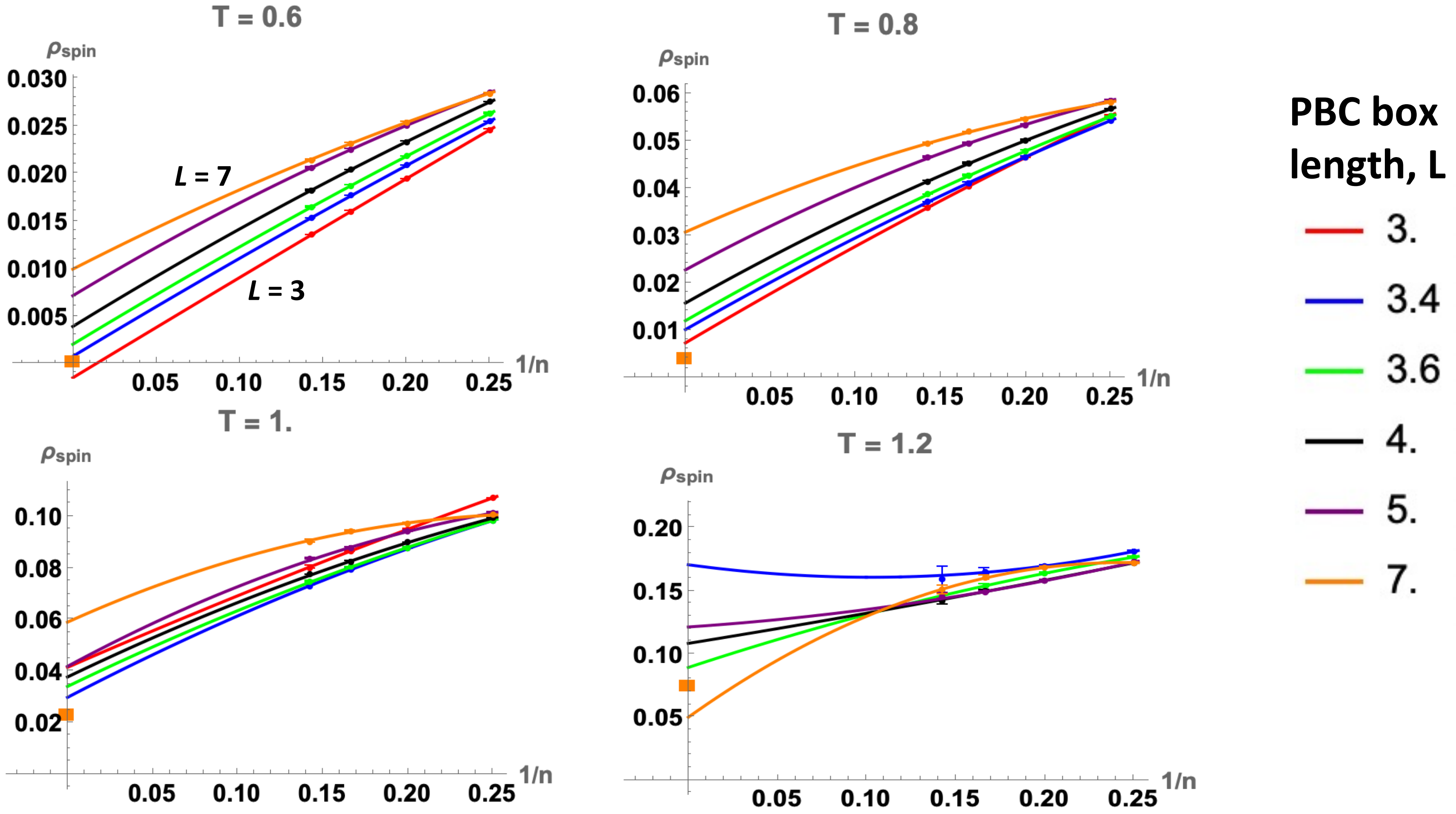
Volume dependence helps VEOS to detect condensation

Volume-dependent, *T* = 0.8, *L* = 3



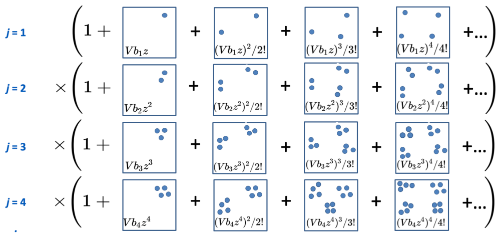


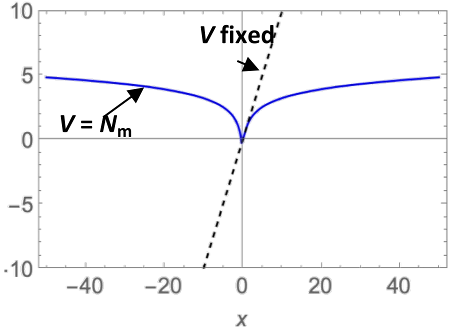
We can attempt extrapolation to infinite *n* to find condensation



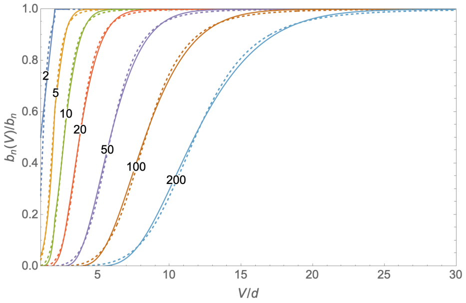
In summary, volume dependence of virial coefficients is an unexplored element of basic statistical mechanics

The thermodynamic limiting process for the formalism needs another look

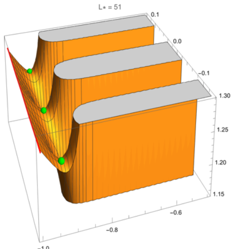




Some regularities are observed in the volume dependence of the coefficients, but too early to tell if it will be persistent or useful



In other work, we explored asymptotic methods to treat the framework, but find extreme difficulty with cancellation of large numbers



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Acknowledgments

Funding NSF

Buffalo: Andrew Schultz

Ukraine: Admiral Makarov National University of Shipbuilding Michael Ushcats

RIT: Steve Weinstein

Nate Barlow

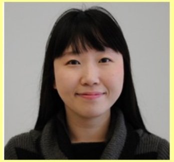
Arpit Bansal

Kate Shaul

PhD students: Navneeth Gokul

Shu Yang

Hye Min Kim



Jung Ho Yang

Jayant Singh

NIST: Allan Harvey, Mike Moldover

Nottingham: Richard Wheatley