Sandia National Laboratories

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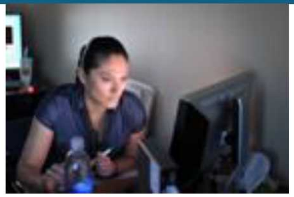
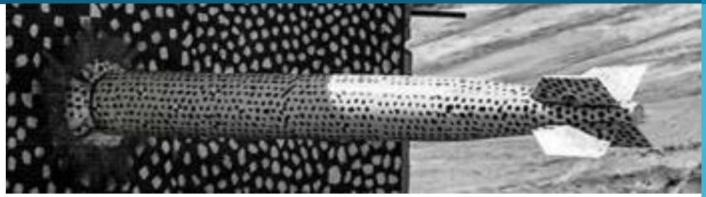
Improved hard sphere radial distribution function in the CRIS equation of state model





Authors:

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Background

- Accurate equation of state (EOS) models for various materials are needed as input into high-level shock physics codes
- The EOS is typically defined in terms of the Helmholtz free energy, which is often split into 3 terms:

$$A(\rho,T) = A_0(\rho) + A_i(\rho,T) + A_e(\rho,T)$$

Cold Curve ($A_0(\rho)$)

Thermal Ionic ($A_i(\rho,T)$)

Thermal Electronic ($A_e(\rho,T)$)

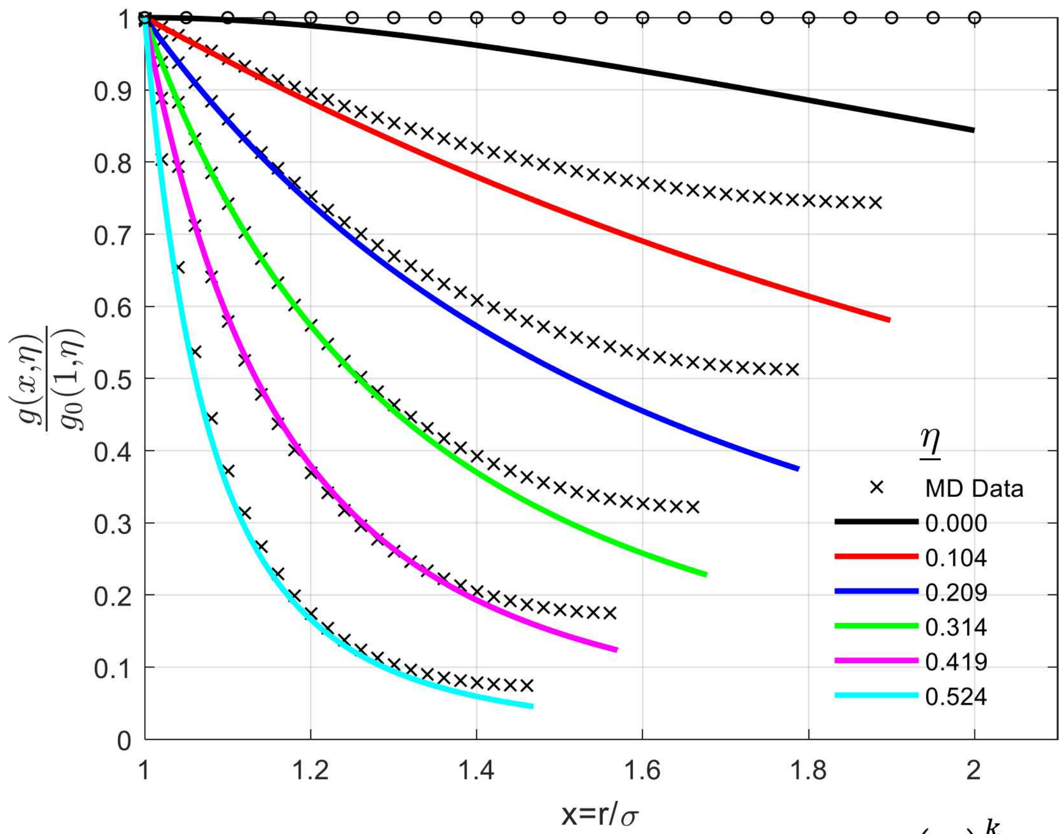
- The cold curve is used as an input into the CRIS model, which can be obtained from theory, experiment, or both
- The output of the CRIS model includes the first two terms of the Helmholtz free energy equation: $A_0(\rho) + A_i(\rho,T)$, which can then be added to the thermal electronic term for a full EOS
- The CRIS model has previously been used to develop the equation of state for metals (Au, Mo, Al, Ta, Pb, Ti, Cu, W), gases (H, D_2, N, O, C, CO, CH_4, Xe, Ar), and other materials (Basalt, Ice, $CaCO_3$, SiO_2)

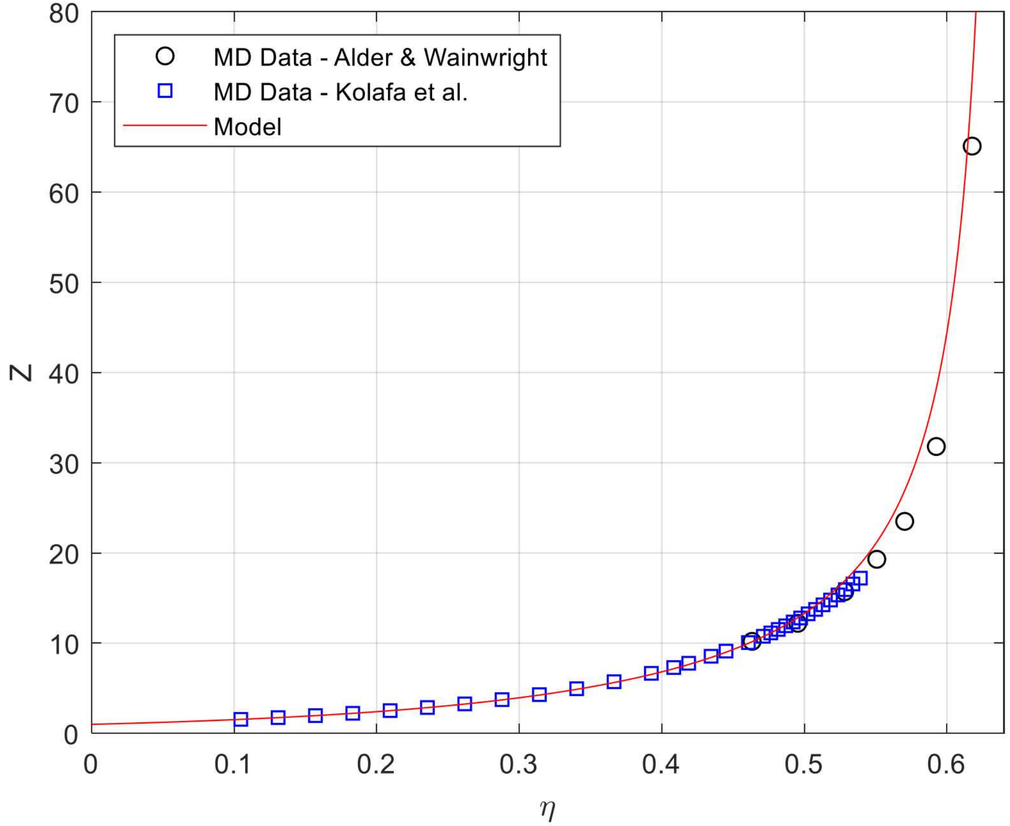
The CRIS Model

- Calculates thermodynamic properties by expanding about a hard sphere reference system
- First we start with the free energy of the hard sphere reference fluid A_0
- Then we add the first order term: $\langle\phi\rangle_0 = \frac{\sqrt{2}\pi}{3}\int_{\sigma_0}^{r_M}\phi(r,\eta)g(r,\eta)r^{-1}dr$
  - $\phi(r,\eta)$ = scaled cold curve, used as the interaction potential
  - $g(r,\eta)$ = radial distribution function (RDF)
  - η = packing fraction, σ_0 = hard sphere diameter
  - r_M = cutoff radius determined by solving the normalization condition: $1 = \frac{\sqrt{2}\pi}{3}\int_0^{r_M} g(r,\eta)r^{-1}dr$
- Up to first order, we have: $\bar{A} = A_0 + N\langle\phi\rangle_0$
- We can then calculate the hard sphere diameter by minimizing: $\left(\frac{\partial\bar{A}}{\partial\eta}\right)_{V,T,N} = 0$
- The 2nd order corrections are defined as:
  - Fluctuation correction:
    - $\Delta A_1 = -NkT\frac{\sqrt{2}\pi}{3\eta}\int_{\sigma_0}^{r_M}\frac{dr}{r}\int_{\eta}^{\eta^*}\left(\frac{\bar{\eta}}{\eta}\right)g(r,\bar{\eta})f(\bar{\eta})d\bar{\eta}$
      - $f(\bar{\eta}) = \frac{d(\bar{\eta}z)}{d\bar{\eta}}$
  - Soft sphere correction:
    - $\Delta A_2 = -NkT2\pi\rho\int_0^{\sigma_0}\left(\frac{\eta^*}{\eta}\right)^2 g(r,\eta^*)r^2dr$
- The Helmholtz free energy of the system is defined as: $A = A_0 + N\langle\phi\rangle_0 + \Delta A_1 + \Delta A_2$

KERLEY, G. I. (1980). PERTURBATION THEORY AND THE THERMODYNAMIC PROPERTIES OF FLUIDS. II. THE CRIS MODEL. *THE JOURNAL OF CHEMICAL PHYSICS*, *73*(1), 478-486.

Challenges with the CRIS model





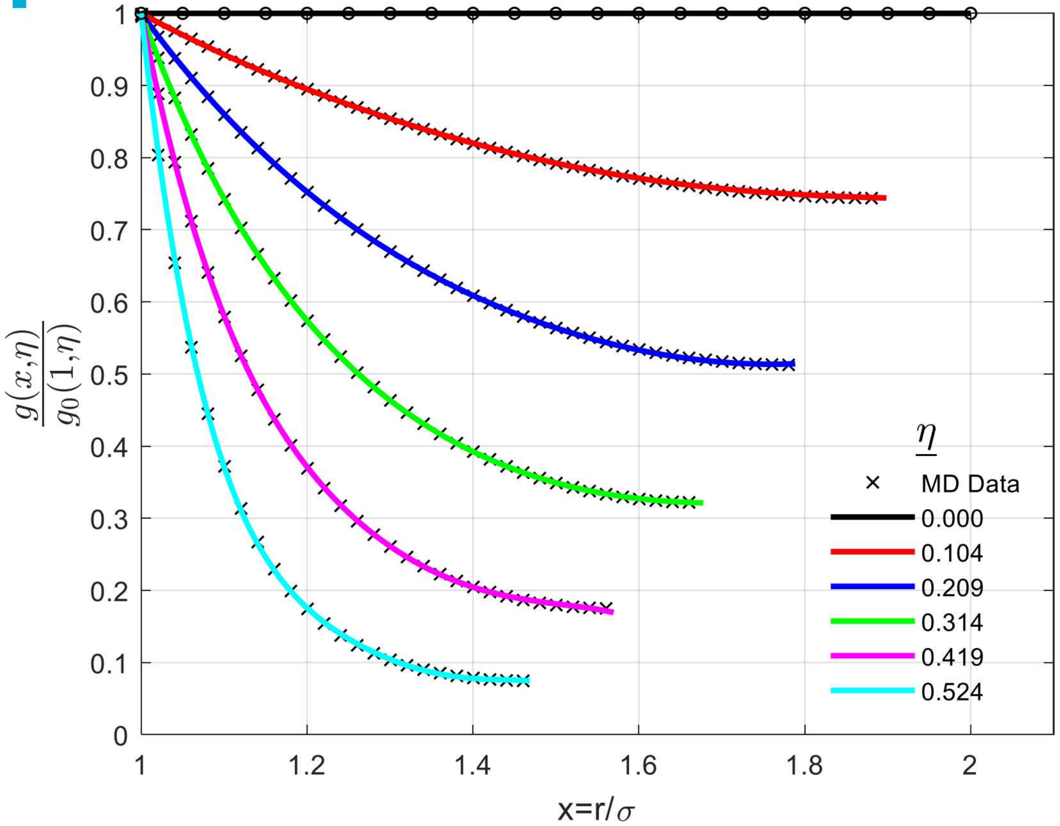
$$g(x,\eta) = \frac{x g_0(1,\eta)}{[1 + C(\eta)(x-1)]^3} \qquad C(\eta) = \frac{1 + \sum_{k=1}^{3} B_k \left(\frac{\eta}{\eta_c}\right)^k}{3\left(1 - \frac{\eta}{\eta_c}\right)}$$

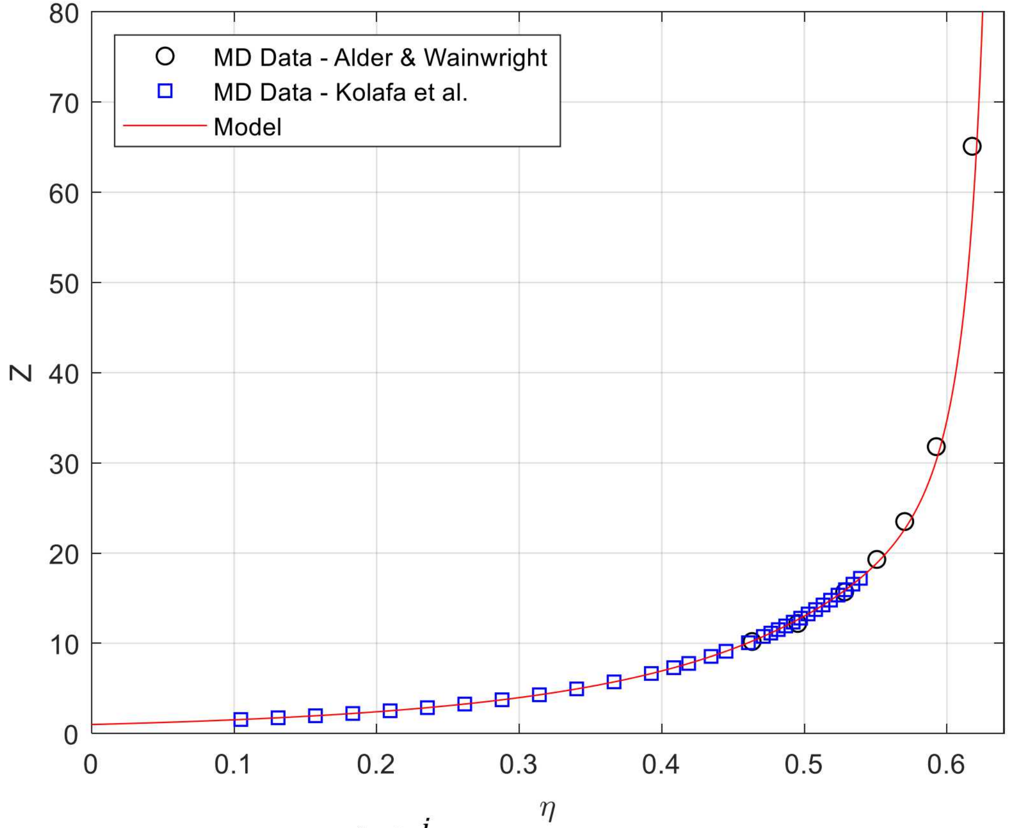
$$Z = \frac{PV}{NkT} = 4\eta g_0(1,\eta) + 1 = 1 + \frac{3\eta}{(\eta_c - \eta)} + \sum_{k=1}^{4} k A_k \left(\frac{\eta}{\eta_c}\right)^k$$

- $g(x,\eta)$ does not represent the hard sphere RDF well over the range of integration
- ΔA_2 integrates x<1, and there is a pole in $g(x,\eta)$ in this regime
- The fit to Z is good for $\eta < 0.5$, but is slightly inaccurate for $\eta > 0.5$

ALDER, B. J., & WAINWRIGHT, T. E. (1960). STUDIES IN MOLECULAR DYNAMICS. II. BEHAVIOR OF A SMALL NUMBER OF ELASTIC SPHERES. *THE JOURNAL OF CHEMICAL PHYSICS*, *33*(5), 1439-1451.
KOLAFA, J., LABÍK, S., & MALIJEVSKÝ, A. (2004). ACCURATE EQUATION OF STATE OF THE HARD SPHERE FLUID IN STABLE AND METASTABLE REGIONS. *PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, *6*(9), 2335-2340.

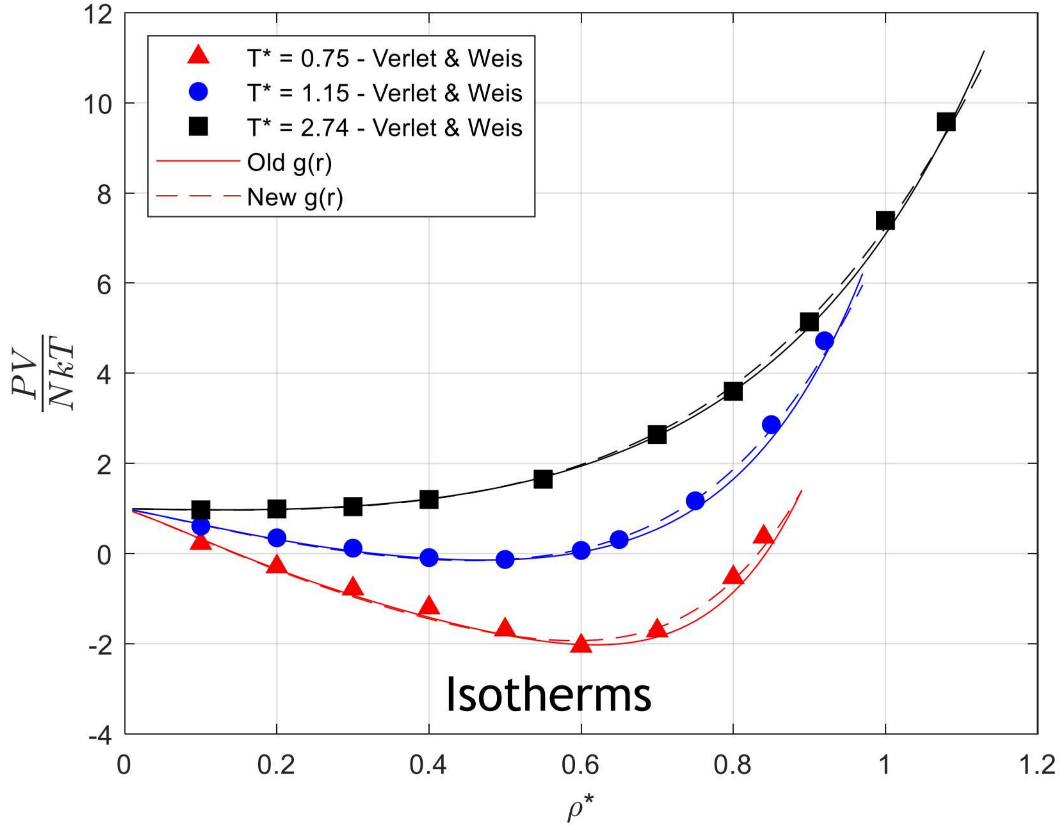
Improving the RDF

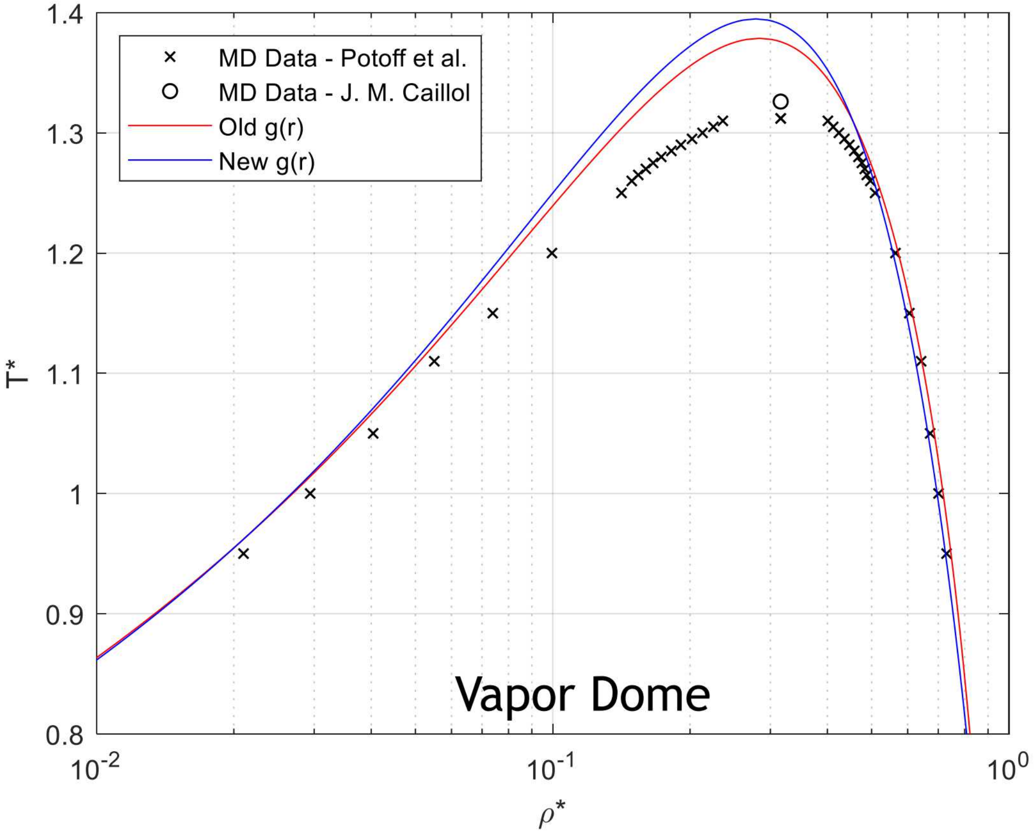




- $g(x,\eta)$ is fit to a 5th order polynomial for x ∊ [1:x_M]: $g(x,\eta) = g_0(1,\eta)\sum_{i,j=0}^{i,j=5} C_{ij}(x-1)^i \left(\frac{\eta}{\eta_c}\right)^j$
- Coefficients are fixed due to asymptotic limits:
  - $C_{00} = 1$ and $C_{i0} = 0$ for $i > 0$ since $\frac{g(x,\eta)}{g_0(1,\eta)} = 1$ when $\eta = 0$ and $C_{0j} = 0$ for $j > 0$ since $\frac{g(x,\eta)}{g_0(1,\eta)} = 1$ when $x = 1$
  - $C_{11} = -\frac{9}{2}\eta_c$, $C_{21} = \frac{3}{2}\eta_c$, $C_{31} = \frac{1}{2}\eta_c$, $C_{41} = C_{51} = 0$ from the density expansion as $\eta \to 0$
  - 20 unconstrained parameters remain
- Z is refit (first 3 coefficients are the same) so that it is consistent with the $g(x,\eta)$ approximation: $g_0(1,\eta) = \frac{1}{4\eta}\left(\frac{3\eta}{(\eta_c-\eta)} + \sum_{k=1}^{1-4,10,14} kA_k \left(\frac{\eta}{\eta_c}\right)^k\right)$

Effects of Changing the RDF





- We used the Lennard-Jones (LJ) potential as a test case, since we know the exact potential
- At lower densities, the relative effect of the RDF is not as important since the ideal gas term is dominant
- The new RDF improves the pressure, and is more accurate in the liquid regime than the old RDF
- The new RDF makes the estimate of the critical point worse

VERLET, L., & WEIS, J. J. (1972). EQUILIBRIUM THEORY OF SIMPLE LIQUIDS. *PHYSICAL REVIEW A*, *5*(2), 939.
POTOFF, J. J., & PANAGIOTOPOULOS, A. Z. (2000). SURFACE TENSION OF THE THREE-DIMENSIONAL LENNARD-JONES FLUID FROM HISTOGRAM-REWEIGHTING MONTE CARLO SIMULATIONS. *THE JOURNAL OF CHEMICAL PHYSICS*, *112*(14), 6411-6415.
CAILLOL, J. M. (1998). CRITICAL-POINT OF THE LENNARD-JONES FLUID: A FINITE-SIZE SCALING STUDY. *THE JOURNAL OF CHEMICAL PHYSICS*, *109*(12), 4885-4893.

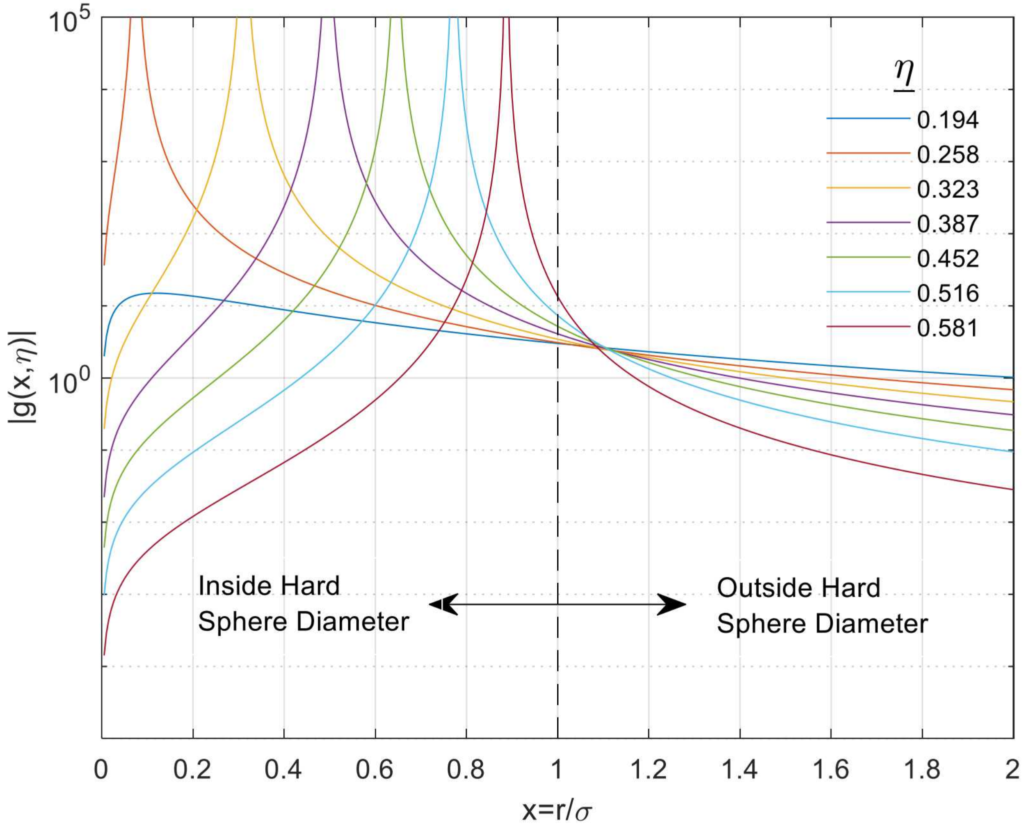
Summary & Conclusions

- The CRIS model has been used for decades at institutions around the world for developing equations of state for various materials
- However, the CRIS model inaccurately models the RDF for the hard spheres
- We improved the RDF using a 5th order polynomial function and added higher order terms to $\frac{PV}{NkT}$ to make it consistent
- The improved RDF more accurately models the isotherms of the LJ fluid, compared to molecular dynamics
- Unfortunately, the critical point of the LJ fluid is more over-estimated with the new RDF
- Since the critical point is extremely sensitive to small changes in the free energy, future work may involve fitting the RDF to have the EOS better match the vapor dome, while maintaining accurate isotherms

Any Questions?

Backup Slides

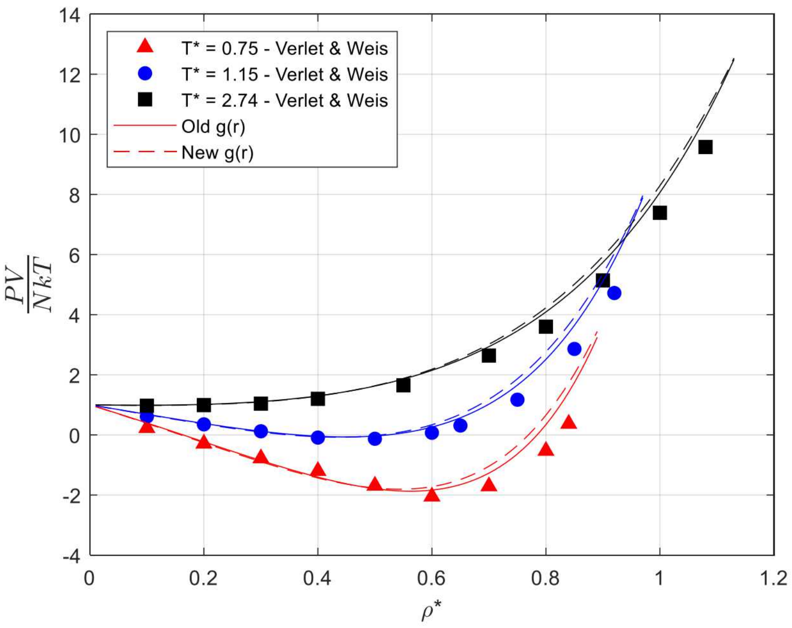
CRIS ΔA_2 Integration



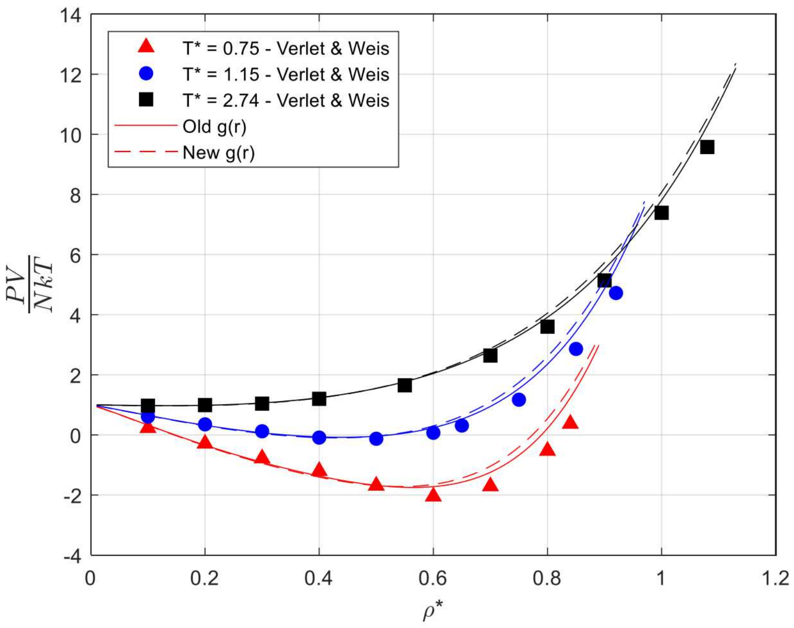
- $\Delta A_2 = -NkT2\pi\rho \int_0^{\sigma_0} \left(\frac{\eta^*}{\eta}\right)^2 g(r,\eta^*) r^2 dr$

Isotherms of the LJ Fluid

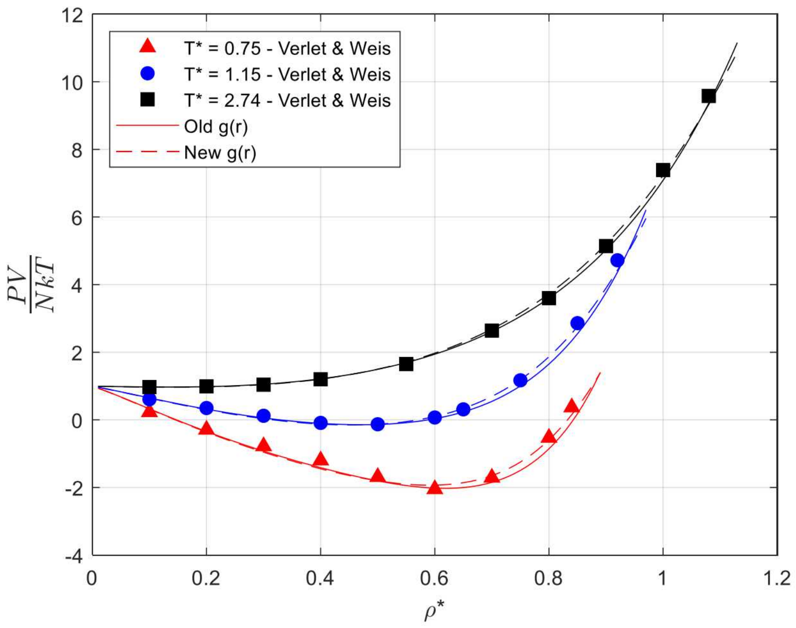
$$A = A_0 + N\langle\phi\rangle_0$$



$$A = A_0 + N\langle\phi\rangle_0 + \Delta A_1$$



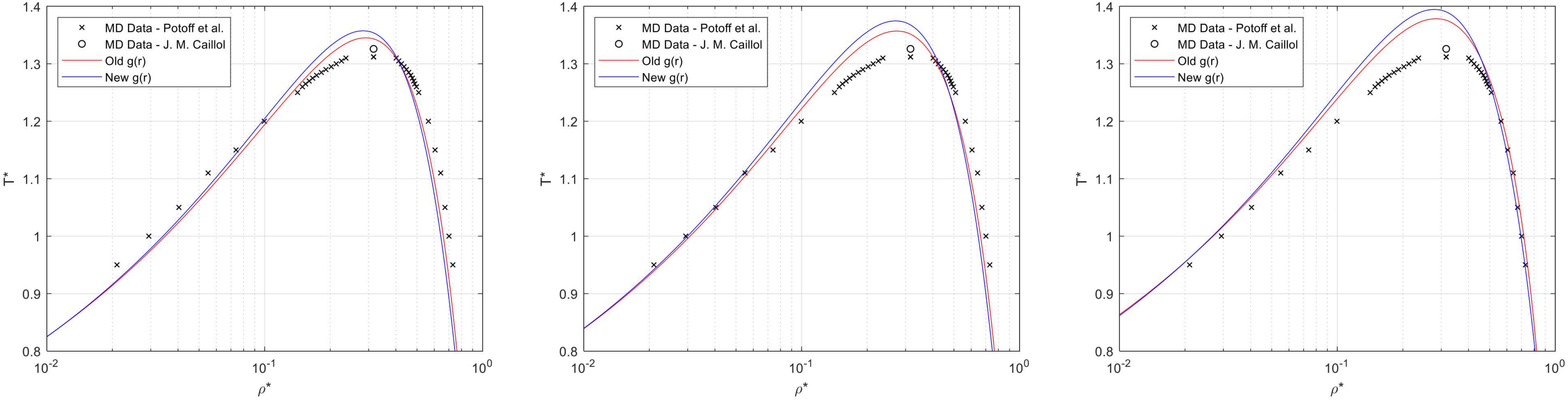
$$A = A_0 + N\langle\phi\rangle_0 + \Delta A_1 + \Delta A_2$$



VERLET, L., & WEIS, J. J. (1972). EQUILIBRIUM THEORY OF SIMPLE LIQUIDS. *PHYSICAL REVIEW A*, *5*(2), 939.

Vapor Dome of the LJ Fluid

$$A = A_0 + N\langle\phi\rangle_0 \qquad A = A_0 + N\langle\phi\rangle_0 + \Delta A_1 \qquad A = A_0 + N\langle\phi\rangle_0 + \Delta A_1 + \Delta A_2$$



POTOFF, J. J., & PANAGIOTOPOULOS, A. Z. (2000). SURFACE TENSION OF THE THREE-DIMENSIONAL LENNARD-JONES FLUID FROM HISTOGRAM-REWEIGHTING MONTE CARLO SIMULATIONS. *THE JOURNAL OF CHEMICAL PHYSICS*, *112*(14), 6411-6415.
CAILLOL, J. M. (1998). CRITICAL-POINT OF THE LENNARD-JONES FLUID: A FINITE-SIZE SCALING STUDY. *THE JOURNAL OF CHEMICAL PHYSICS*, *109*(12), 4885-4893.