Maximum of the Thermodynamic Property, the Heat Capacity, in a Lennard-Jones Fluid: A Theoretical Study Based on Molecular Integral Equations and Molecular Dynamics

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Background

It is well known that the constant-pressure heat capacity, Cp, diverges (increasing without limit) at the critical point of gas-liquid coexistence line. However, it is not clear how Cp behaves at other temperatures and pressures away from criticality. In this study, for a Lennard-Jones potential, the isotherms of Cp, at reduced temperatures T* = 1.6 and 3.0 along a range of densities (for reduced densities ρ* from 0.1 to 0.36), was examined.

The Lennard-Jones Potential is a mathematical model that is used to estimate the interaction potential between two molecules. The curve for a simple Lennard-Jones fluid is shown below in Figure 1.

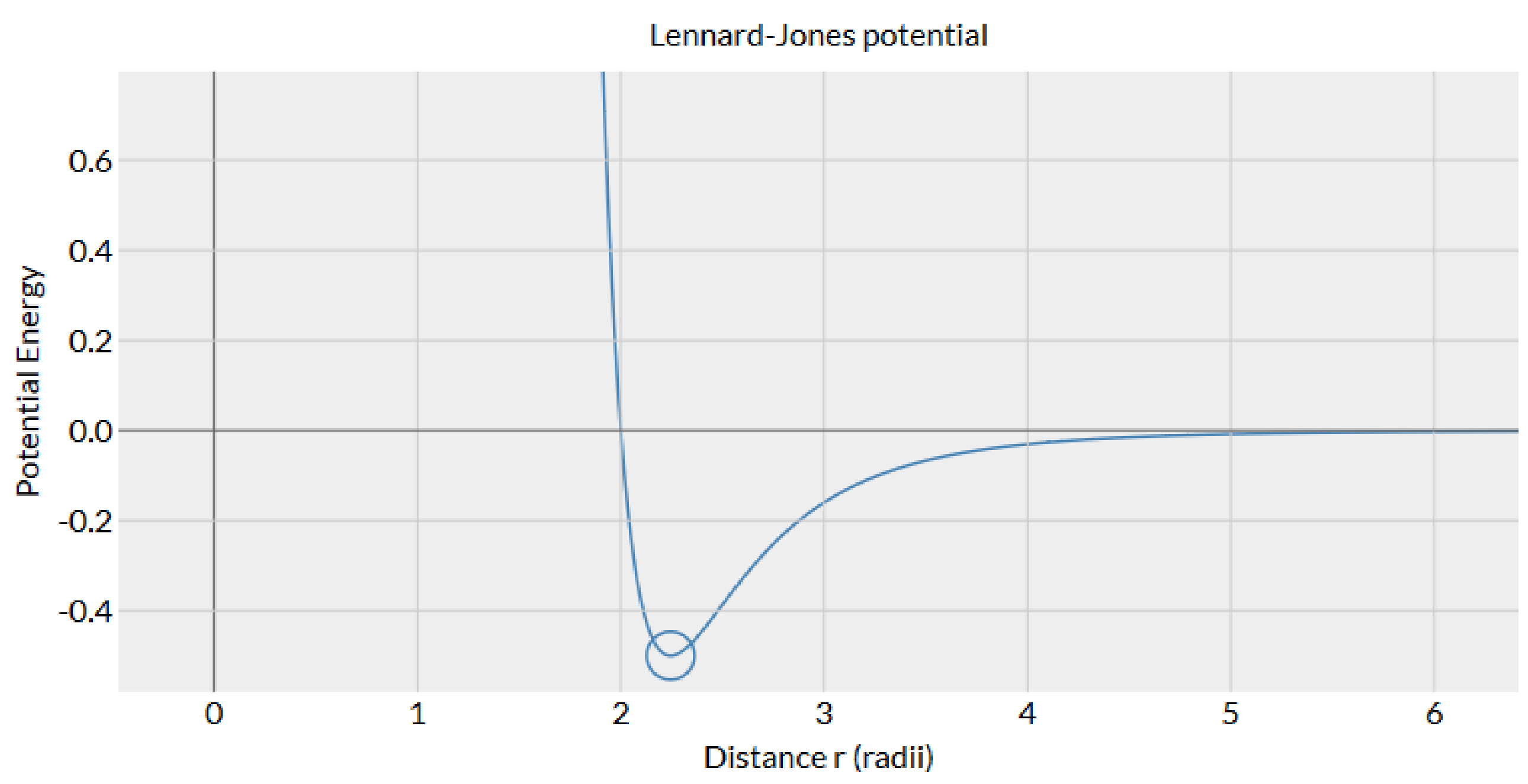

Figure 1: Potential curve for common Lennard-Jones fluids

The Lennard-Jones potential has been used in the past to model quite accurately many different realistic gases. The relation for a Lennard-Jones potential is shown below.

$$\mathrm{u}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

Where u is the potential, ε is the well depth, r is the distance between particles and σ is the van der Waals radius.

In this study, we use the Ornstein Zernike (OZ) integral equation, shown below, to model the heat capacity behavior of the Lennard-Jones fluid.

$$\gamma(r) = h(r) - C(r) = \rho \int dr' h(r') C(|r - r'|) \tag{2}$$

Where ρ is density, and h, C, and γ are probability functions showing different aspects of the colloidal structure.

However, since there are too many unknowns in the OZ integral equation, an additional closure relation must be used therefore, in this study, the zero-separation (ZSEP) closure relation, which satisfies the zero-separation theorems on the cavity functions, is used.

$$B(\gamma^*) = -\frac{\zeta\gamma^{*2}}{2}\left(1 - \frac{\varphi\alpha\gamma^*}{(1+\alpha\gamma^*)}\right) \tag{3}$$

The internal energy of a fluid can be expressed utilizing molecular dynamics using the following relation.

$$\frac{U}{NkT} = \frac{3}{2} + \rho \int_0^\infty \frac{4\pi r^2 g(r) u(r)}{kT} dr \tag{4}$$

Where U is the potential energy, u is the Lennard-Jones Potential, and g is the radial distribution function.

This, along with the previous relations, can be used to model the heat capacity behavior of a Lennard-Jones fluid, as is done in this study. This study is the result of the first time that integral equations (IET) have been used to search for heat capacity maxima, as insofar, only molecular dynamics simulations (MD) and equation of states (EOS) considerations have been used.

Interestingly, in the literature, at the isotherm T* =3.0, maxima or minima are not observed in the temperature density curve. Yet, at the isotherm T* = 1.6, a clearly defined maxima of Cv and Cp are observed at the density value ρ* near 0.3.

Objective

To verify if there are maxima in heat capacity behavior for realistic industrial fluids.

Experimental Procedure:

This project was performed using FORTRAN code based on iterative calculations based on the Picard method to solve for the OZ equation. Once the equation was solved, the outputs were checked for certain thermodynamic consistencies shown below. If the equation was not found to be consistent, then new variables were entered for the ZSEP closure, and the program was re-run. Once the equation was found to be consistent, values of Cv and Cp were calculated using excel.

Results

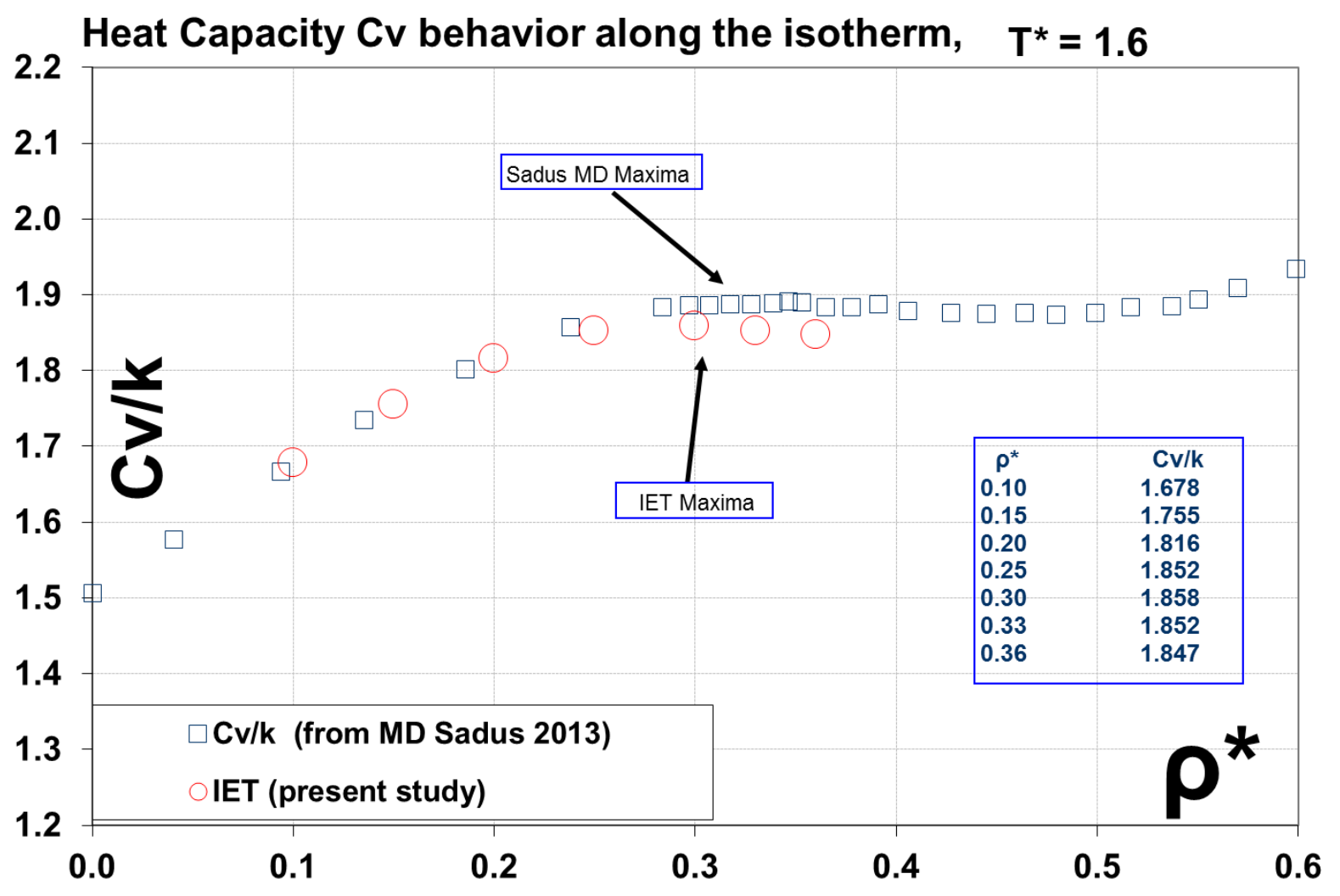

Figure 2: Heat Capacity Cv behavior along the isotherm T*=1.6

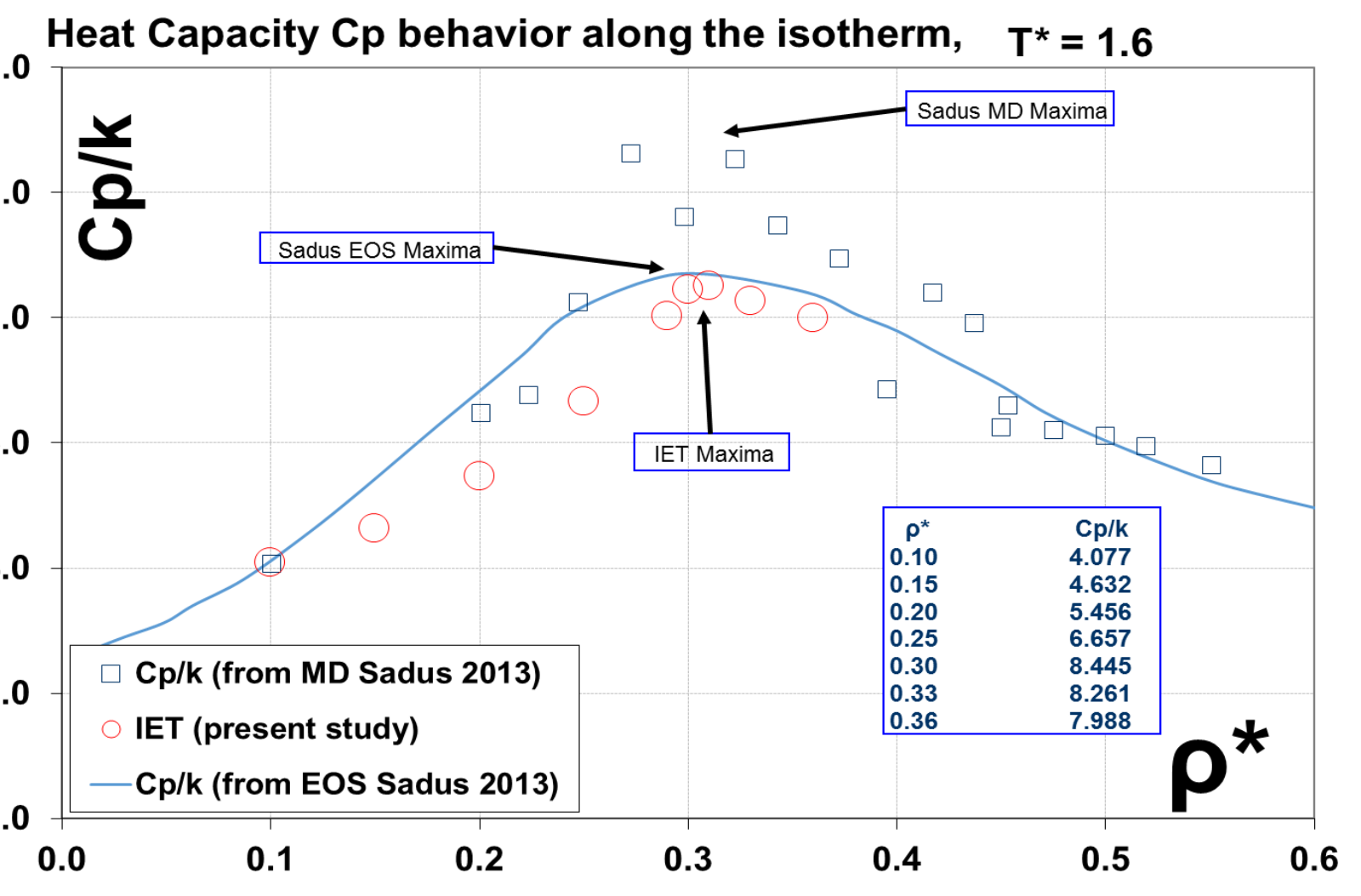

Figure 3: Heat Capacity Cp behavior along the isotherm T*=1.6

As can be seen above in Figures 2 and 3, there are local maxima for both the constant pressure and constant volume heat capacity at around the reduced density value ρ*=0.3. In order to explain why this phenomena may exist, the g-distribution function, a function of density with respect to radius, was calculated using the integral equation technique and is plotted below in Figure 4.

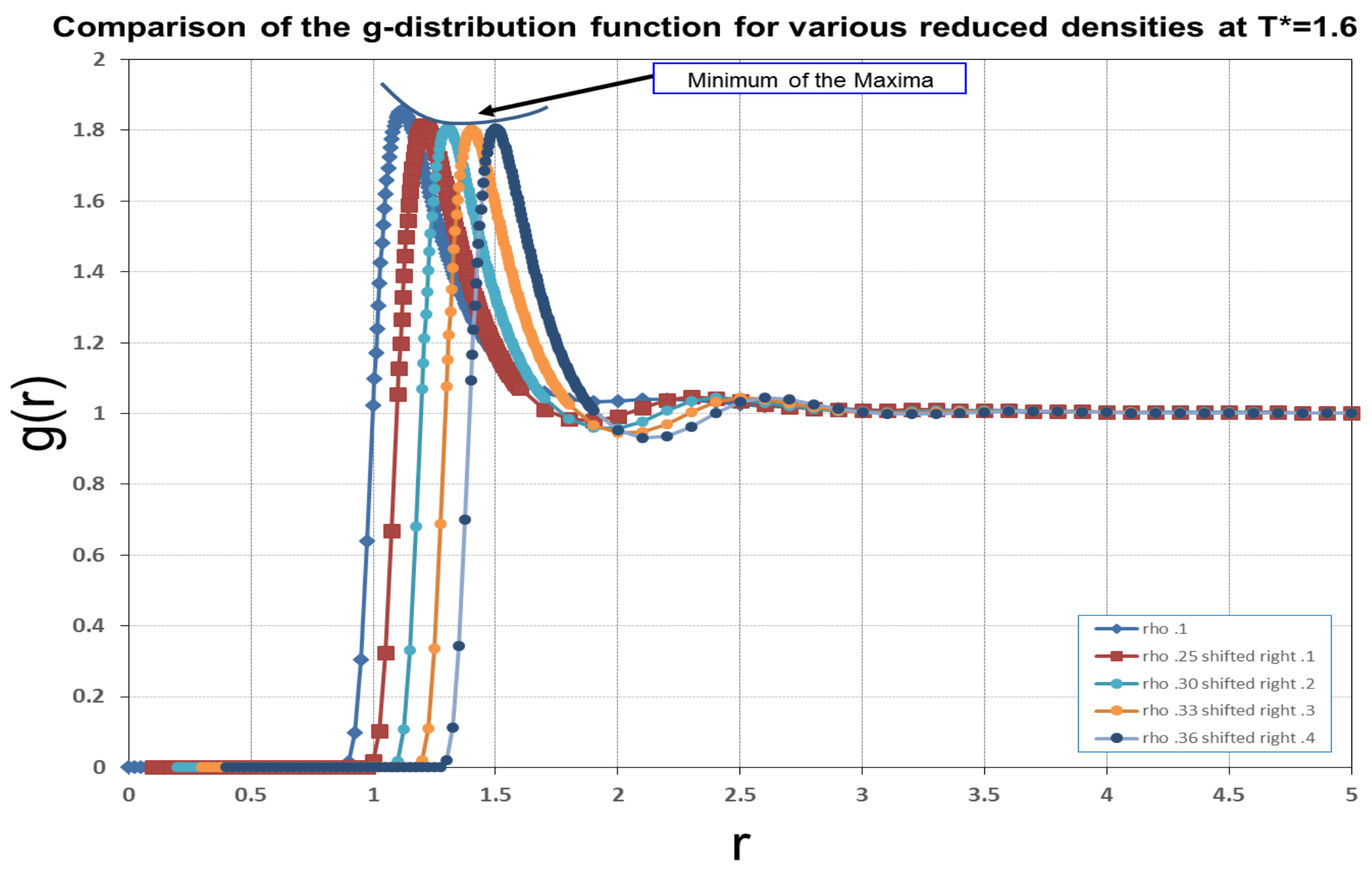

Figure 4: g-distribution function of multiple densities along T*=1.6

This shows that at the same reduced density at which the heat capacity maxima is found, at ρ* ≈ 0.3, there is a minimum in the peak of the g-distribution function. This gives rise to potential structural reasons as to why the maxima that have been found exist. By looking at Equation 4, one can see that as the g-distribution function becomes lower, there is a result of a higher heat capacity as the second term becomes less negative.

Conclusions

We find that there are actually heat capacity maxima for realistic industrial fluids and that the maxima are found in the same area as found in the literature using molecular dynamics and equations of state, yet this data has been found using Integral Equations, which are a less expensive way to compute fluid properties than molecular dynamics.

The critical point for a Lennard-Jones fluid is at T* = 1.326 and ρ* = .316. It is well known that heat capacity diverges to infinity near the critical point and this heat capacity maxima may be because of the proximity to the critical point.

It is also important to note that when there are heat capacity maxima, at that same density there are lower peaks in the g-distribution function, which gives rise to the interesting notion that heat capacities are related to how particles in a fluid are arranged.

Future Considerations

In the literature, heat capacity maxima at other conditions have been found, for these cases integral equations can be used to verify these maxima as well as to potentially search for new heat capacity maxima.

Also, as there is not currently experimental verification because of the difficulty associated with the low temperature of around 192 K, experiments can be run to further verify these maxima and see if they occur in real life.

References

1. L.L. Lee, D. Ghonasgi, and E. Lomba, *Fluid structures for soft-sphere potentials via the zero-separation theorems on molecular distribution functions,* Journal of Chemical Physics, 104, 8058-8067 (1996).
2. L.L. Lee, *The potential distribution-based closures to the integral equations for liquid structure: The Lennard-Jones fluid*, J.Chemical Physics 107, 7360-7370 (1997).
3. R. Sadus, J. Mairhofer, *Thermodynamic properties of supercritical n-m Lennard-Jones fluids and isochoric and isobaric heat capacity maxima and minima,* Journal of Chemical Physics 139, 154503-154509 (2013).