Structure factors for 2D Lennard-Jones fluids

Haina Wang*

Department of Chemistry Torquato Lab, Princeton University, Princeton, NJ 08544, USA

E-mail: hainaw@princeton.edu

$S(0)$ from pressure virial expansions

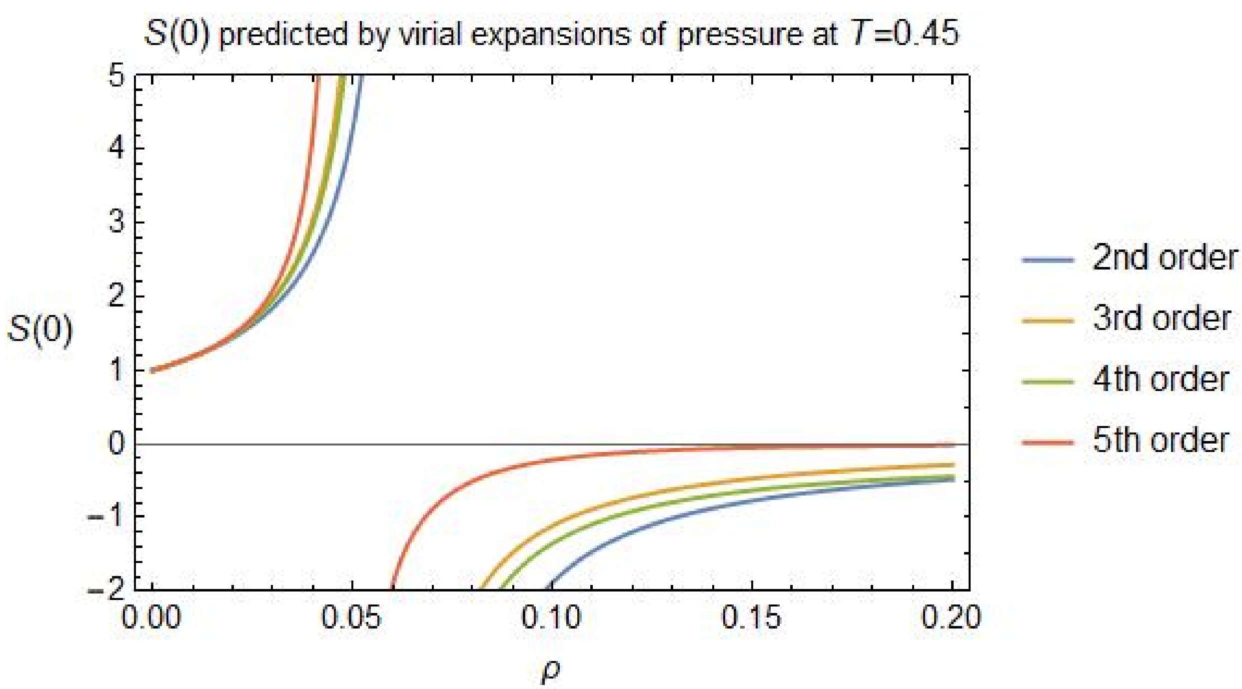
The virial expansion of pressure can be used to estimate $S(0)$ at low densities through the compressibility relationship, *i.e.*

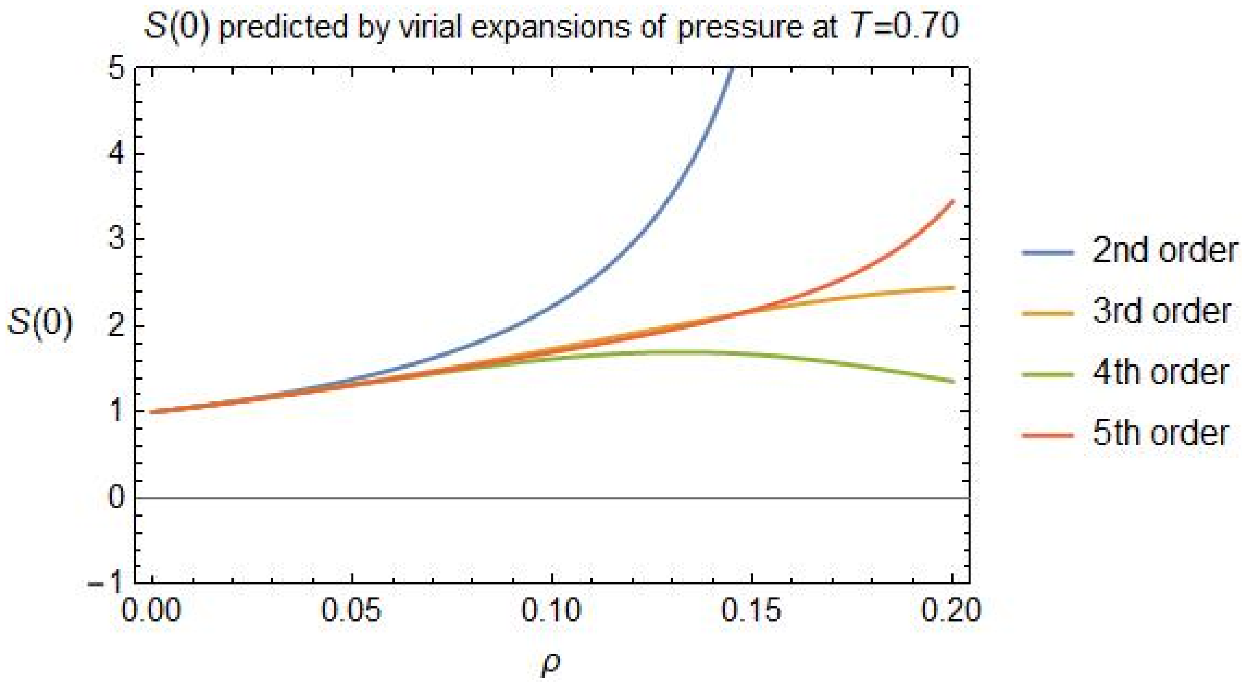
$$\begin{aligned}\rho kT\kappa_T = S(0) &= \left(\frac{\partial \frac{p}{kT}}{\partial \rho}\right)_T^{-1} \\ &= \left(1 + 2B_2(T)\rho + 3B_3(T)\rho^2 + 4B_4(T)\rho^3 + 5B_5(T)\rho^4 + ...\right)^{-1}\end{aligned} \tag{1}$$

We take virial expansions at one subcritical temperature, $T = 0.45$ and one supercritical temperature, $T = 0.70$, taking $T_c = 0.56$, as in Monte Carlo simulations. The virial coefficients up to the fifth order are given below.

T	B_2 [1]	B_3 [1]	B_4 [2]	B_5 [3]
0.45 ($0.8T_c$)	-7.6592	-12.29	39.89	186.26
0.70 ($1.25T_c$)	-2.7613	4.279	10.1924	-55.68

The dependence of $S(0)$ with ρ as predicted by pressure virial expansions at both temperatures are given below.





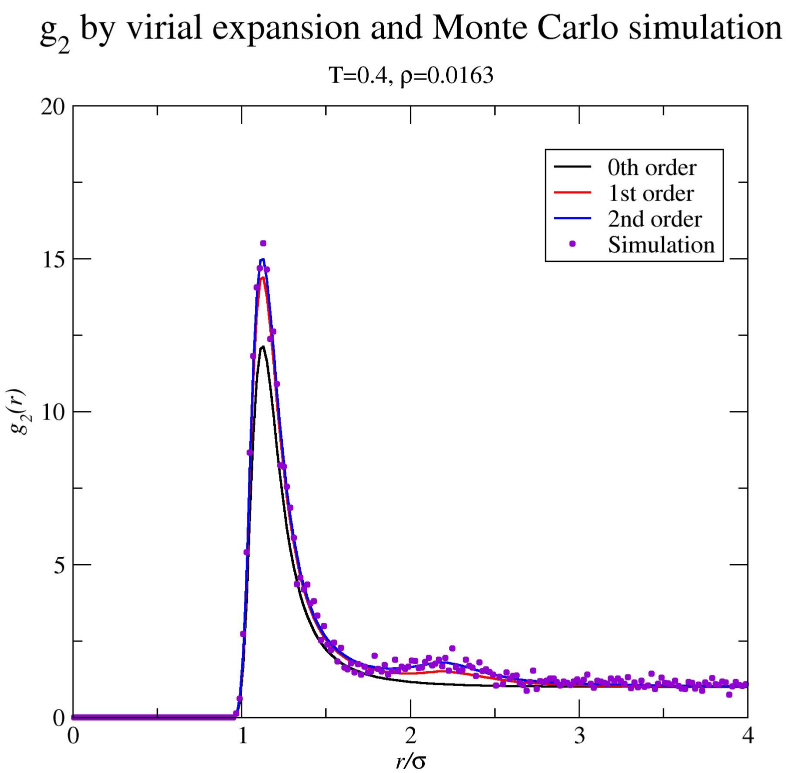
Both graphs suggests that $S(0)$ rises above 1 at low densities, starting from the second order expansion. The divergence of isothermal compressibility at $T = 0.45$ indicates a vapor-liquid phase transition. The 3rd, 4th and 5th virial expansions are able to predict the supercritical behavior at $T = 0.70$.

$S(k)$ from virial expansion of pair statistics

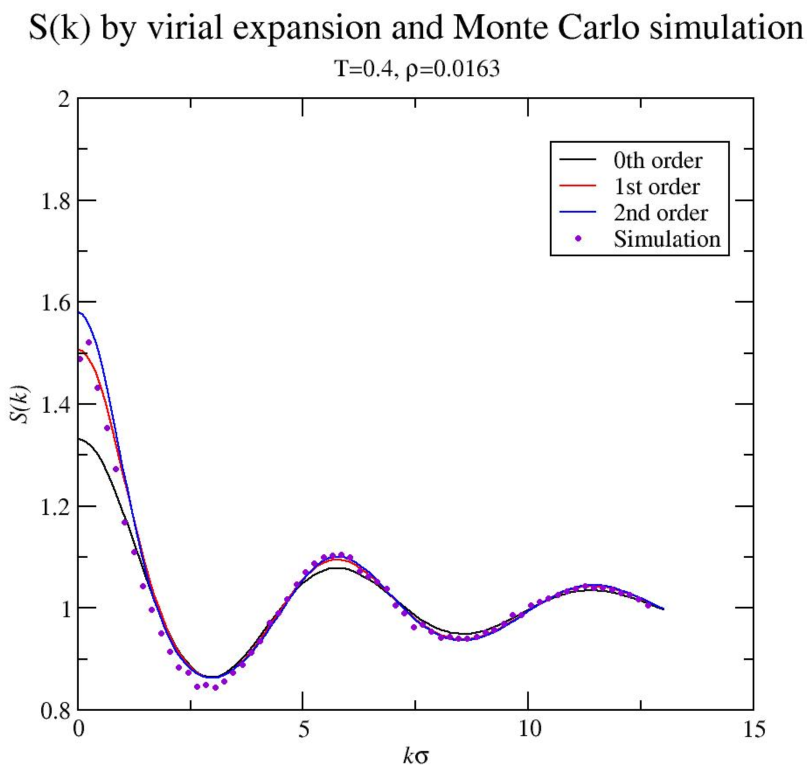
The radial distribution function $g_2(r)$ can be written in the power series

$$g_2(r) = e^{-\phi(r)/kT}\left(1 + \sum_{n=1}^{\infty} \rho^n y_n(r)\right) \tag{2}$$

The form of y_1 and y_2 at several temperatures are given in Ref. 2. The following graph shows the zeroth, first and second order expansion of g_2 at $\rho = 0.0163, T = 0.40$, as well as the Monte Carlo simulation results.



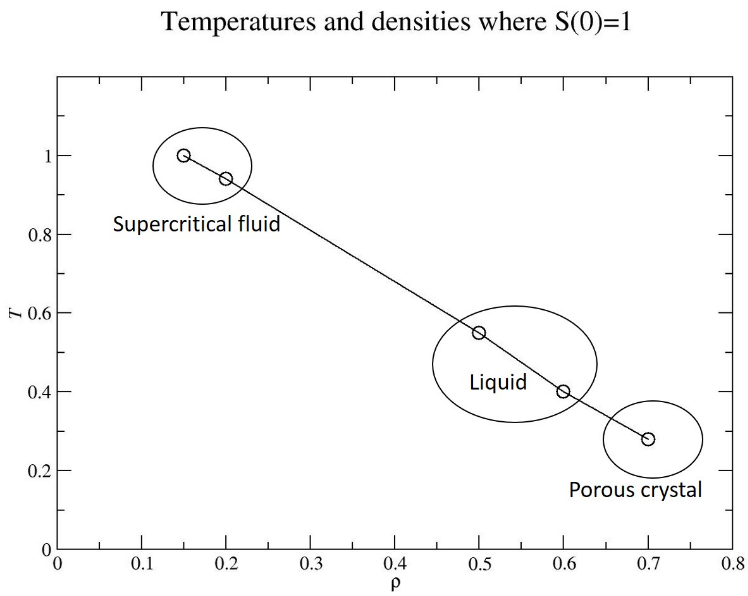
The following graph shows $S(k)$ obtained by Fourier transform of $g_2(r) - 1$ as well as the Monte Carlo simulation results at $\rho = 0.0163, T = 0.40$.



Therefore, at low densities, the first and second order virial expansion of g_2 are able to predict $S(k)$ relatively well, though they don't necessarily give a very accurate value of $S(0)$ because the functions $y_n(r)$ are not reported for $r \geq 4.0$ in the literature.

Temperatures and densities at which $S(0) = 1$

The following graph shows the temperature at which $S(0) = 1$, with 400 simulation particles. The linearity is excellent ($R^2 = 0.9995$) with the equation $T = -1.31\rho + 1.2$ even as the states shown here range from supercritical fluids to liquids to (porous) crystals. The implications are still to be explored.



References

(1) Morrison, I. D.; Ross, S. The second and third virial coefficients of a two-dimensional gas. *Surface Science* **1973**,

(2) Glandt, E. D. The fourth virial coefficient for a Lennard-Jones fluid in two dimensions. *The Journal of Chemical Physics* **1978**,

(3) Barker, J. A.; Henderson, D.; Abraham, F. F. Phase diagram of the two-dimensional Lennard-Jones system; Evidence for first-order transitions. *Physica A: Statistical Mechanics and its Applications* **1981**,