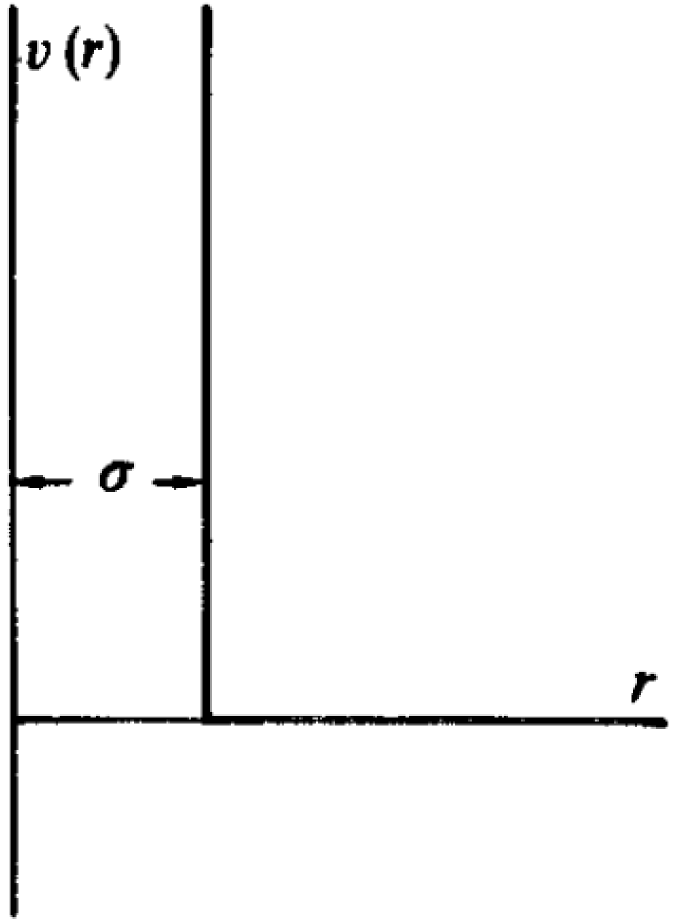
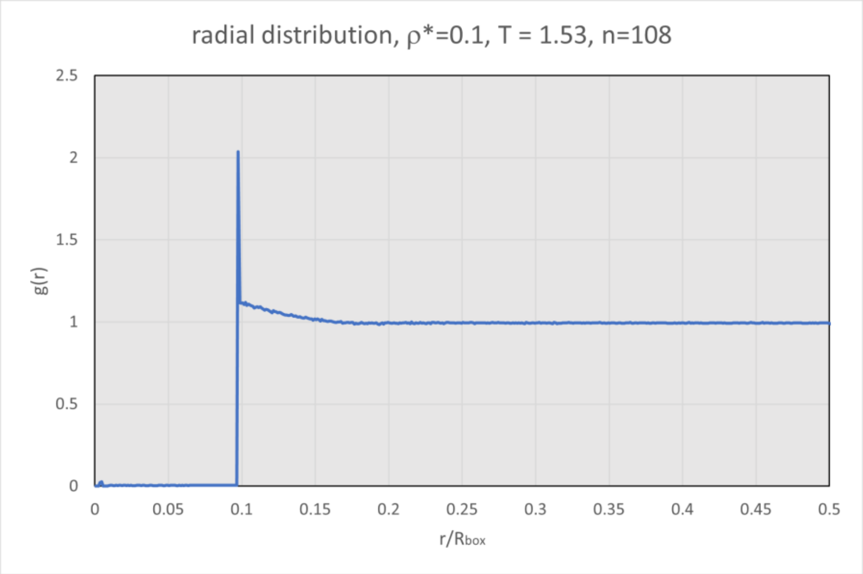
Hard sphere simulation

- ❑Compressibility factor
- ❑Radial distribution

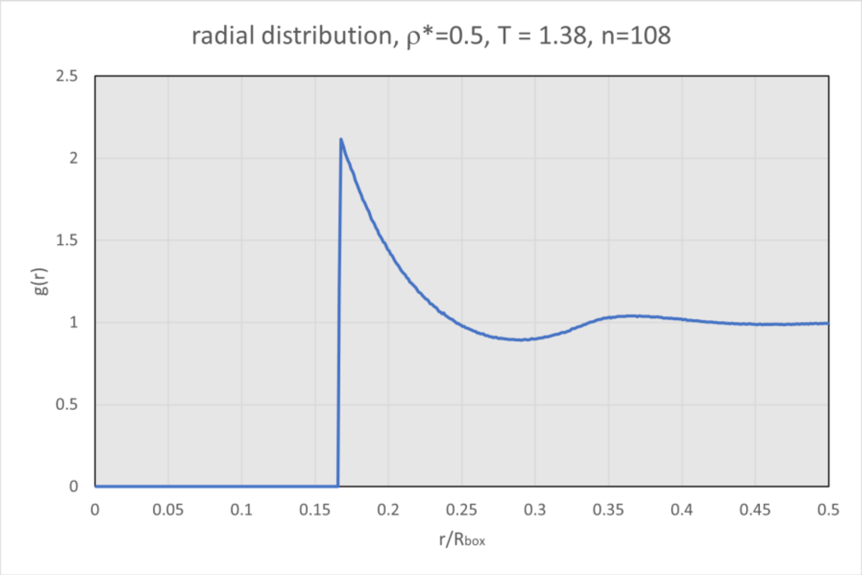


g(R) for hard spheres

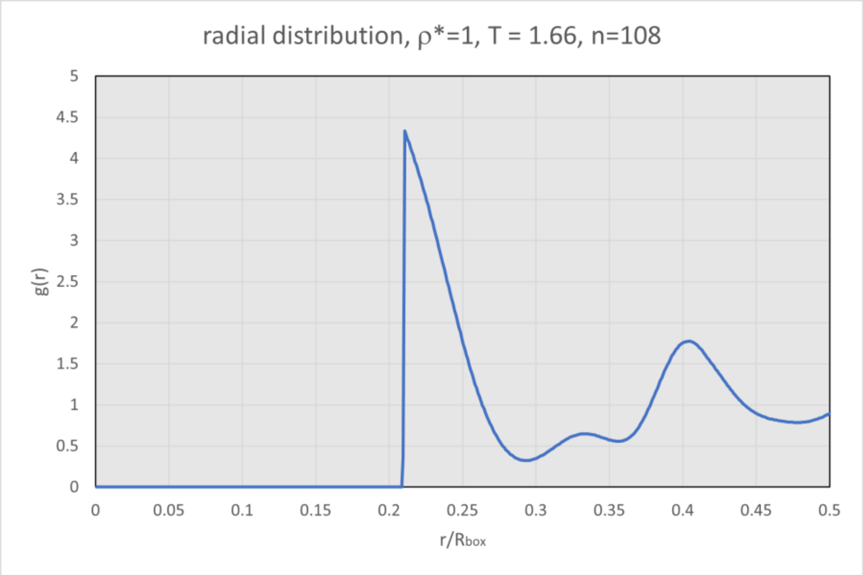
System size
- N = 108
- T ~ 1.5



Z = PV/NkT = 1.24477029



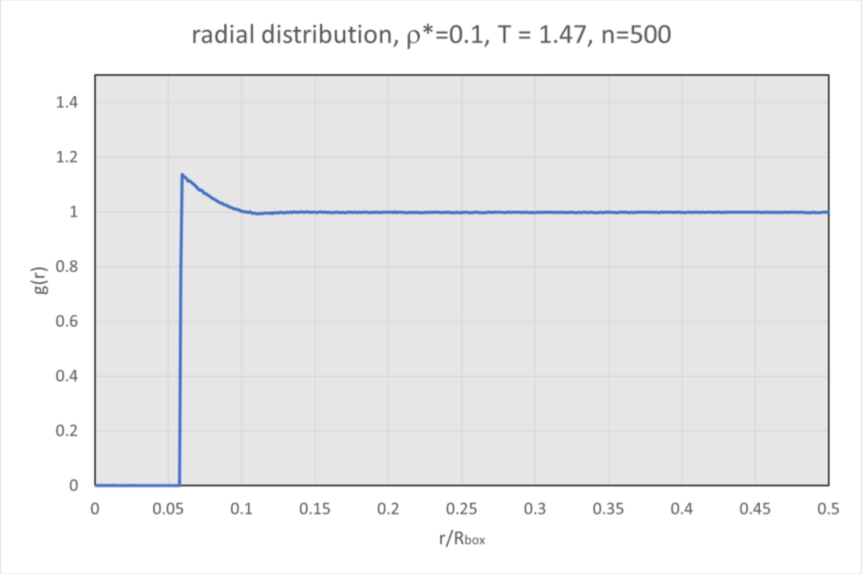
Z = PV/NkT = 3.28025508



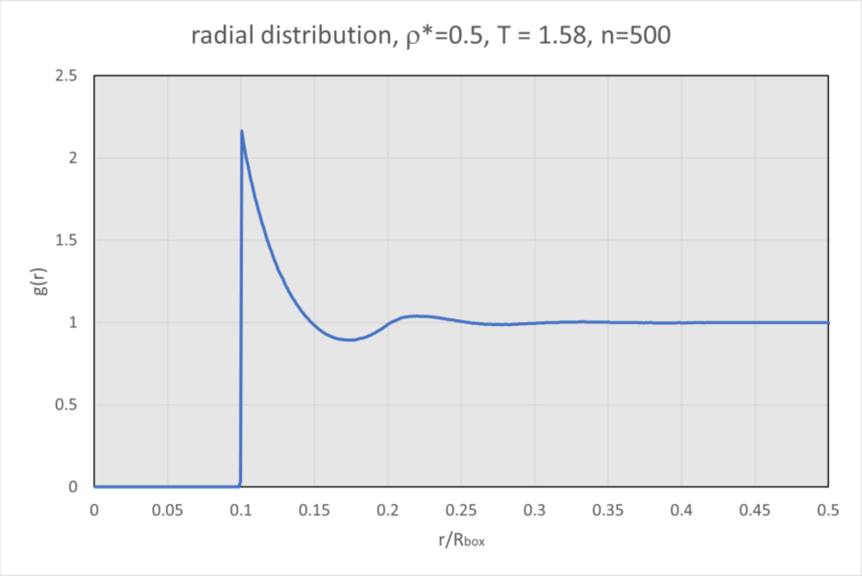
Z = PV/NkT = 10.21343231

g(R) for hard spheres

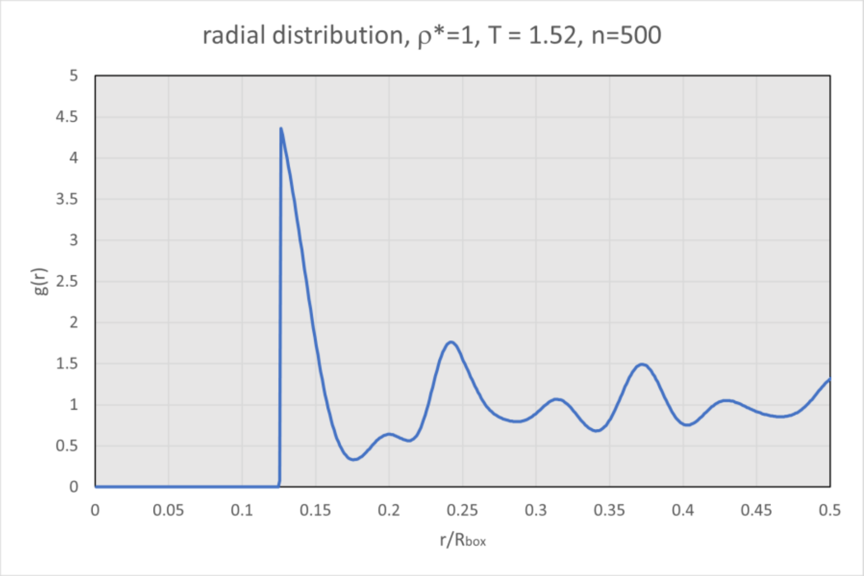
System size
- N = 500
- T ~ 1.5



$Z = PV/NkT = 1.23968816$



$Z = PV/NkT = 3.27309155$

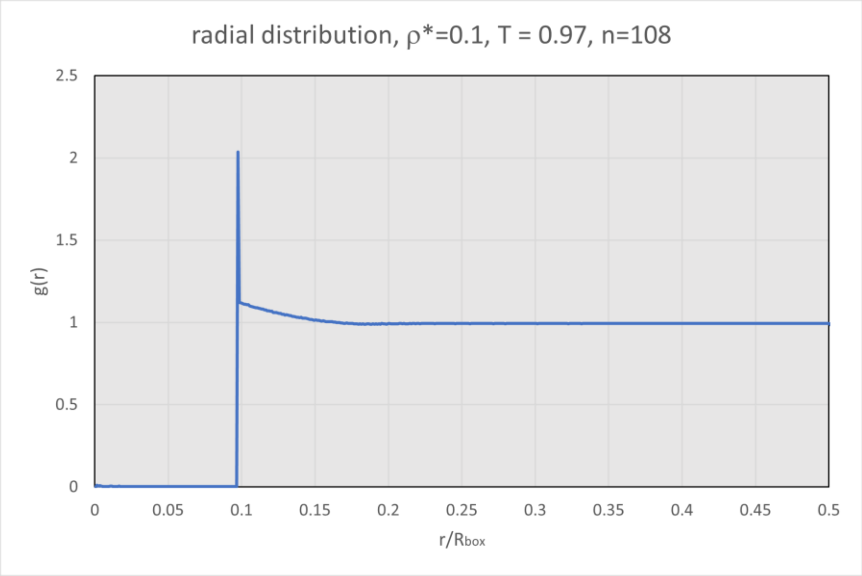


$Z = PV/NkT = 10.24549675$

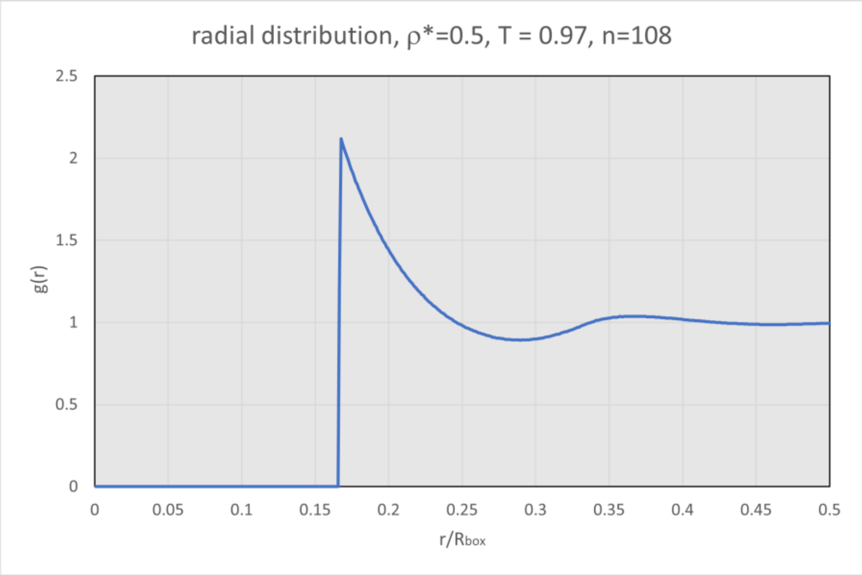
g(R) for hard spheres

System size

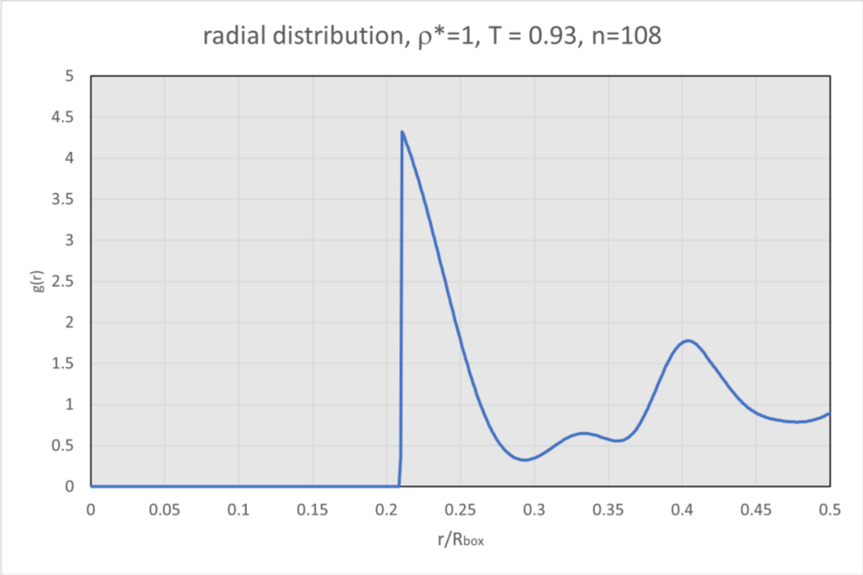
- N = 108
- T ~ 1



Z = PV/NkT = 1.24566603



Z = PV/NkT = 3.30094147



Z = PV/NkT = 10.32818508

Equation of State for Hard Spheres

Thiele (1963)

$$Z = \frac{PV}{NkT} = \frac{1 + y + y^2}{(1-y)^3}$$

$$y = \frac{\sqrt{2}}{6}\pi\frac{V_0}{V} = \frac{\sqrt{2}}{6}\pi\frac{\rho_0}{\rho}$$

- V = system volume
- V_0 = close packed volume = $\frac{N\sigma^3}{\sqrt{2}}$
- ρ= number density = $\frac{N}{V}$
- ρ_0 = close packed number density = $\frac{\sqrt{2}}{\sigma^3}$

Norman (1969)

$$Z = \frac{PV}{NkT} = \frac{1 + y + y^2 - y^3}{(1-y)^3}$$

Speedy (1997)

$$Z = \frac{3}{1 - \rho/\rho_0} - A\frac{\rho/\rho_0 - B}{\rho/\rho_0 - C}$$

A = 0.5921, B = 0.7072, C = 0.601

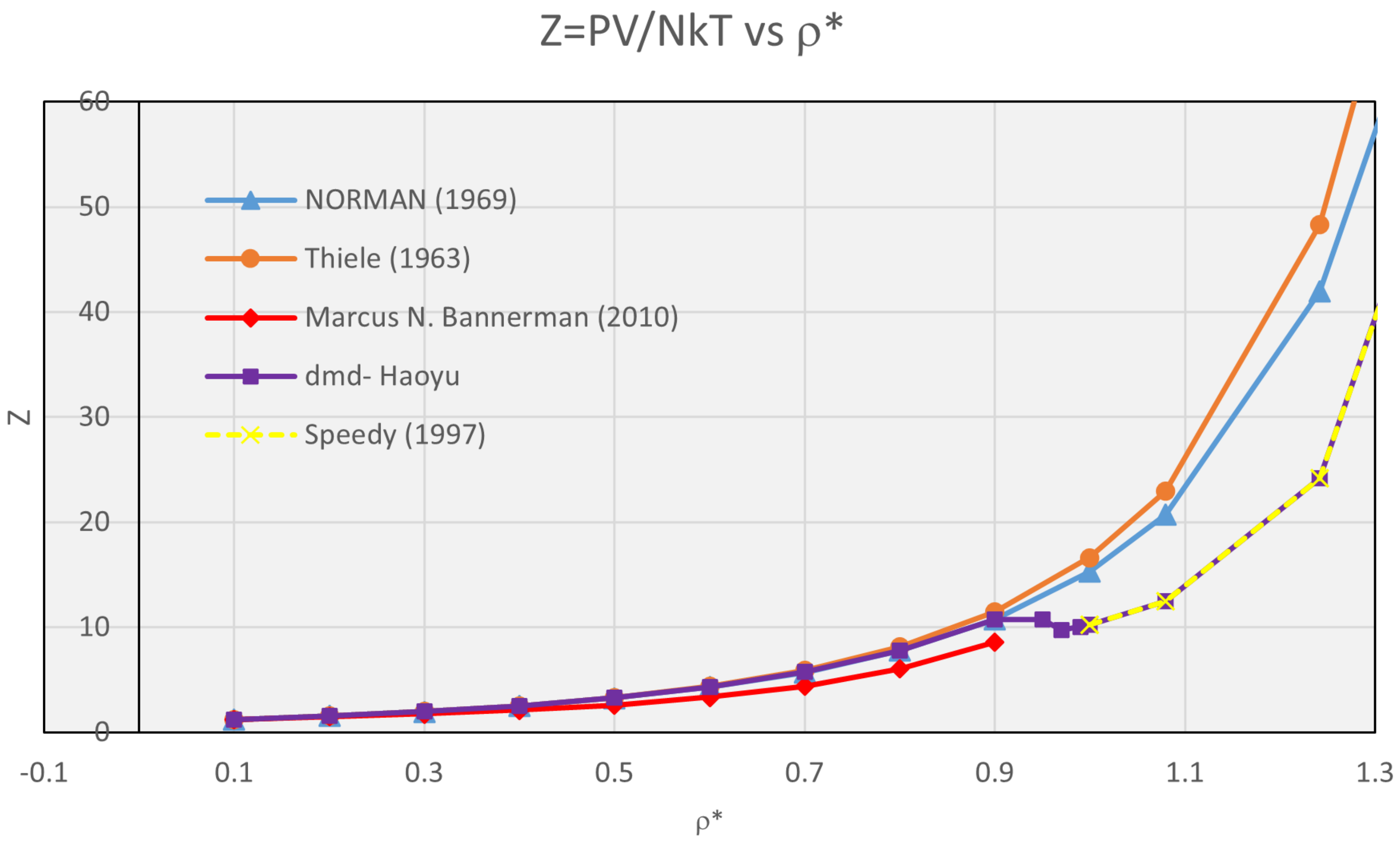
Marcus N. Bannerman (2010)

$$Z_{\text{fcc}} = \frac{3}{1 - \rho/\rho_0} - A\frac{\rho/\rho_0 - B}{\rho/\rho_0 - C},$$

$$Z = \frac{PV}{NkT} = 1 + \sum_{n=2}^{10} B_n\left(\frac{\rho}{\rho_0}\right)^{n-1} + \left(\frac{\rho}{\rho_0}\right)^{10} \times \left[\frac{B_{10}}{1-\frac{\rho}{\rho_0}} - \frac{A_1}{\left(1-\frac{\rho}{\rho_0}\right)^2}\right]$$

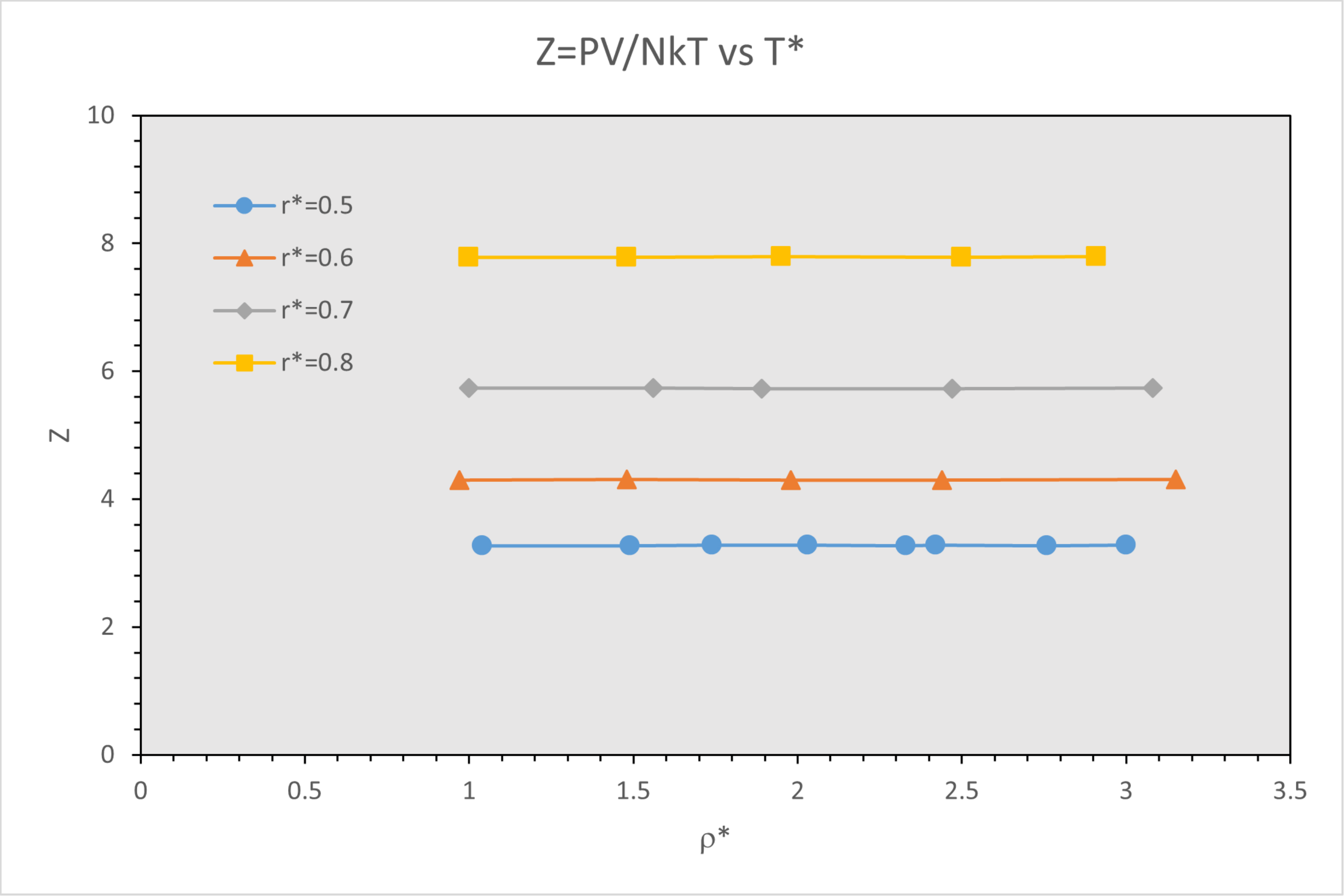
n	B_n
2	2.961921
3	5.483111
4	7.456345
5	8.485568
6	8.863719
7	8.793670
8	8.366104
9	7.756405
10	7.079543
A_1	0.68219

Compressibility factor for Hard Spheres



ρ^* = 0.9-1
Fluid-solid transition region

Compressibility factor for Hard Spheres under different T*



Equation for calculating g(r) for Hard-spheres

ρ* range: 0.2~0.9

Trokhymchuk (2005)

$$g(r) = \begin{cases} = \dfrac{A}{r} e^{\mu[r-\sigma]} + \dfrac{B}{r}\cos(\beta[r-\sigma]+\gamma)e^{\alpha[r-\sigma]} & \text{for } \sigma \leqslant r \leqslant r^{\star} \\ = 1 + \dfrac{C}{r}\cos(\omega r + \delta)e^{-\kappa r} & \text{for } r \geqslant r^{\star}. \end{cases}$$

$$\mu\sigma = \frac{2\eta}{1-\eta}\left(-1 - \frac{d}{2\eta} - \frac{\eta}{d}\right),$$

$$\gamma = \arctan\left\{-\frac{\sigma}{\beta_o}\left[(\alpha_o\sigma(\alpha_o^2+\beta_o^2) - \mu_o\sigma(\alpha_o^2+\beta_o^2)) \times \left(1+\frac{1}{2}\eta\right) + (\alpha_o^2+\beta_o^2-\mu_o\alpha_o)(1+2\eta)\right]\right\},$$

where

$$\alpha_o\sigma = \frac{2\eta}{1-\eta}\left(-1 + \frac{d}{4\eta} - \frac{\eta}{2d}\right)$$

$$\beta_o\sigma = \frac{2\eta}{1-\eta}\sqrt{3}\left(-\frac{d}{4\eta} - \frac{\eta}{2d}\right),$$

$$d = [2\eta(\eta^2 - 3\eta - 3 + \sqrt{3(\eta^4 - 2\eta^3 + \eta^2 + 6\eta + 3)})]^{1/3}.$$

Next are the coefficients parametrized by Roth *et al.*,[22]

$$\omega\sigma = -0.682\exp(-24.697\eta) + 4.720 + 4.450\eta,$$

$$\kappa\sigma = 4.674\exp(-3.935\eta) + 3.536\exp(-56.270\eta),$$

and those parametrized in present study,

$$\alpha\sigma = 44.554 + 79.868\eta + 116.432\eta^2 - 44.652\exp(2\eta),$$

$$\beta\sigma = -5.022 + 5.857\eta + 5.089\exp(-4\eta),$$

$$r^*/\sigma = 2.0116 - 1.0647\eta + 0.0538\eta^2,$$

$$g_m = 1.0286 - 0.6095\eta + 3.5781\eta^2 - 21.3651\eta^3 + 42.6344\eta^4 - 33.8485\eta^5.$$

After this, the remaining parameters can be expressed in the terms of known parameters,

$$B = \frac{g_m - (\sigma g_\sigma^{\text{expt}}/r^*)\exp\mu[r^*-\sigma]}{\cos(\beta[r^*-\sigma]+\gamma)\exp\alpha[r^*-\sigma] - \cos\gamma\exp\mu[r^*-\sigma]}r^*,$$

$$A = \sigma g_\sigma^{\text{expt}} - B\cos\gamma,$$

$$\delta = -\omega r^* - \arctan\frac{\kappa r^* + 1}{\omega r^*},$$

$$C = \frac{r^*[g_m - 1]\exp\kappa r^*}{\cos(\omega r^* + \delta)},$$

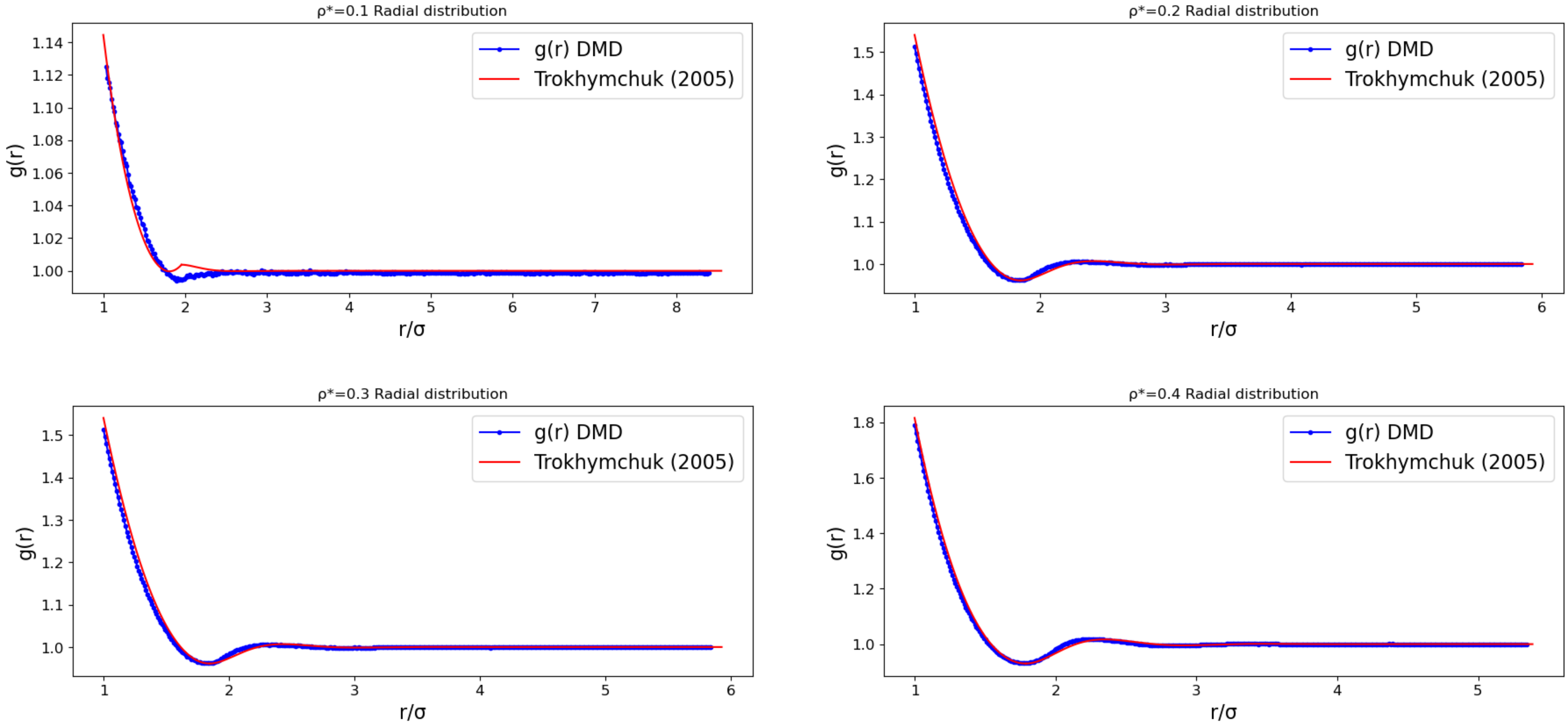
where

$$g_\sigma^{\text{expt}} = \frac{1}{4\eta}\left(\frac{1+\eta+\eta^2 - 2/3\eta^3 - 2/3\eta^4}{(1-\eta)^3} - 1\right).$$

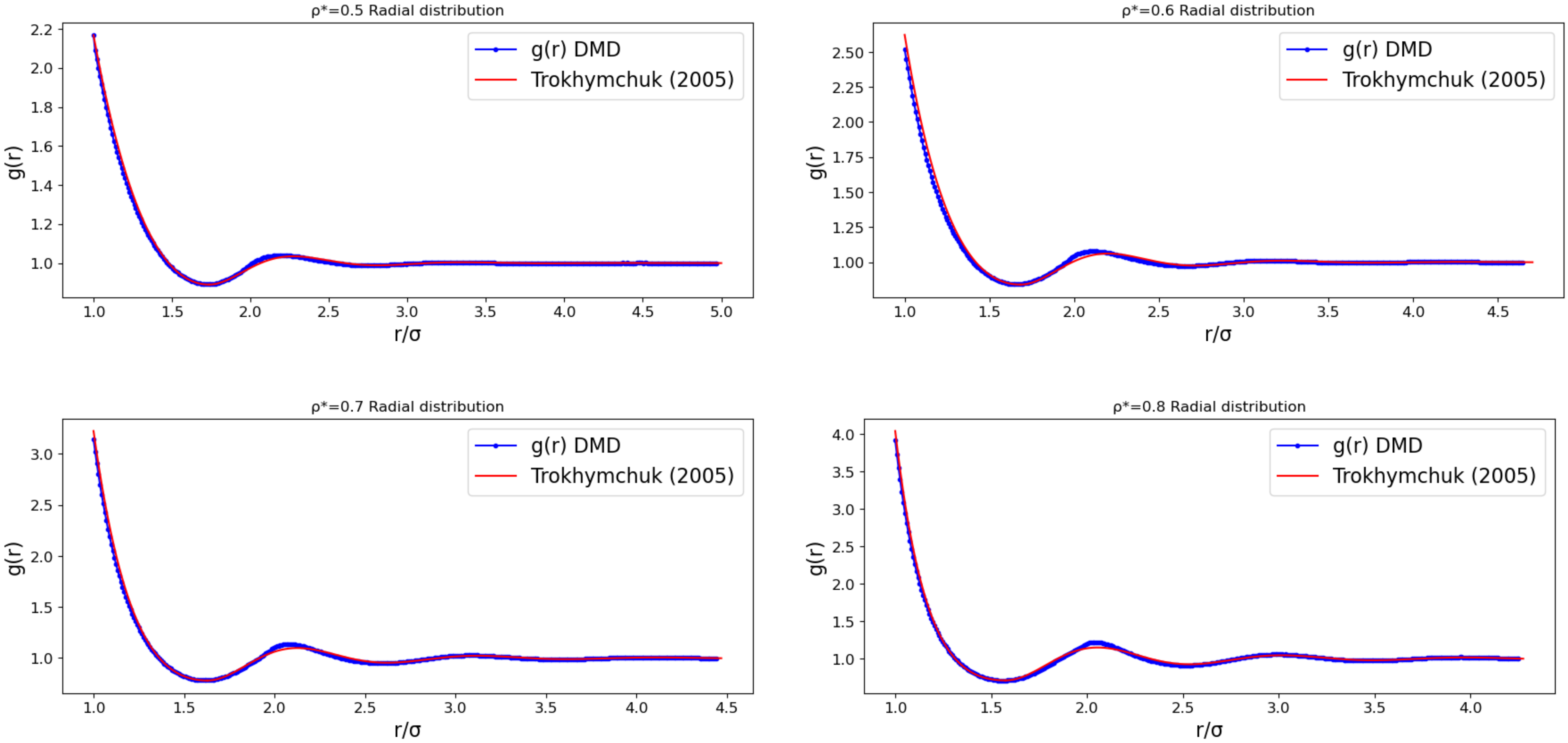
Finally, the RDF of the hard-sphere fluid in the range of densities $0.2 \leqslant \rho\sigma^3 \leqslant 0.9$ has the form,

$$g(r) = 0 \quad \text{for } r < \sigma$$

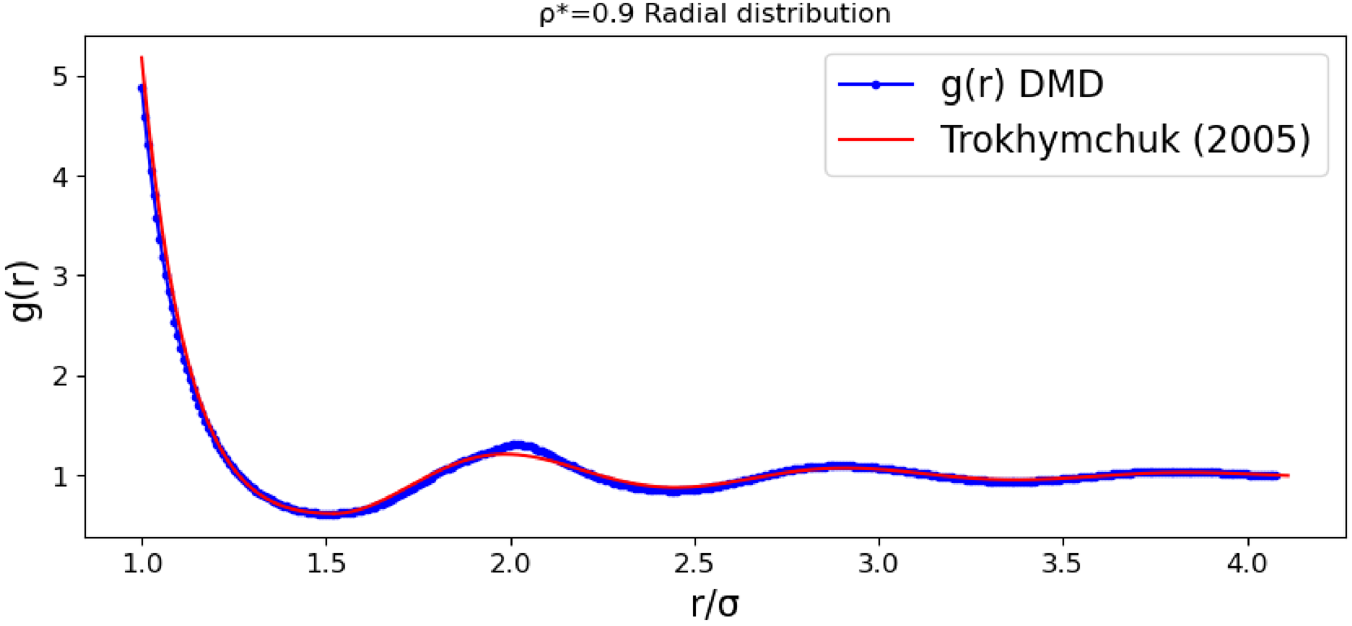
Comparison between g(r) for HS



Comparison between g(r) for HS



Comparison between g(r) for HS



g(r) for Hard-spheres solid ($\rho^* > 0.99$)

J. M. KINCAID (1977)

$$\tilde{g}^{HS}(R, \eta) = \frac{A}{R} \exp\left[-W_1^2(R-R_1)^2 - W_2^4(R-R_1)^4\right] + \frac{W}{24\eta\sqrt{\pi}} \sum_{i=2}^{\infty} \frac{n_i}{RR_i} \exp\left[-W^2(R-R_i)^2\right] \quad (2)$$

i	n_i	R_i
1	12	see table 3
2	6	$\sqrt{2}/(\eta/\eta_C)^{1/3}$
3	24	$\sqrt{3}/(\eta/\eta_C)^{1/3}$
4	12	$\sqrt{4}/(\eta/\eta_C)^{1/3}$
5	24	$\sqrt{5}/(\eta/\eta_C)^{1/3}$

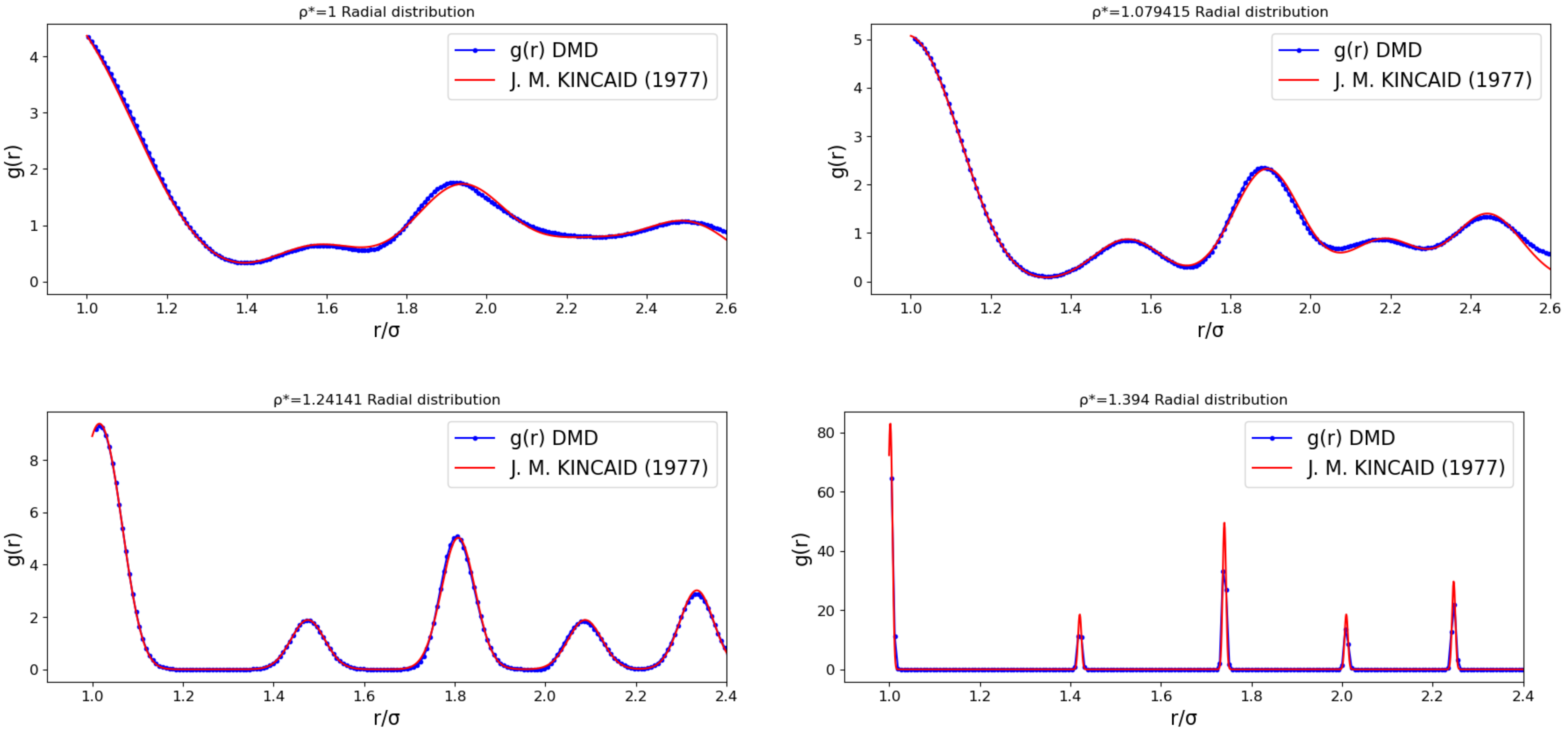
η	r.m.s. $\tilde{g}^{HS}$	r.m.s. $\tilde{g}_{WEIS}{}^{HS}$	R_1
0·73	0·9480		1·0026
0·71	0·1182		1·0073
0·68	0·0777		1·0135
0·65	0·0588	0·0838	1·0183
0·6171	0·0485	0·0508	1·0207
0·56518	0·0465	0·0464	1·00771
0·54	0·0447	0·0449	0·98281
0·52	0·1130	0·1080	0·94375

$$W_1(\eta) = 1{\cdot}5523/(\eta_C-\eta) - 2{\cdot}0303 \exp\left[5{\cdot}8331(\eta_C-\eta)\right] + 74{\cdot}8732(\eta_C-\eta)^2, \quad (8)$$

$$W_2(\eta) = (0{\cdot}95596 - 5{\cdot}8550(\eta_C-\eta) + 39{\cdot}7466(\eta_C-\eta)^2 - 109{\cdot}6264(\eta_C-\eta)^3)/(\eta_C-\eta), \quad (9)$$

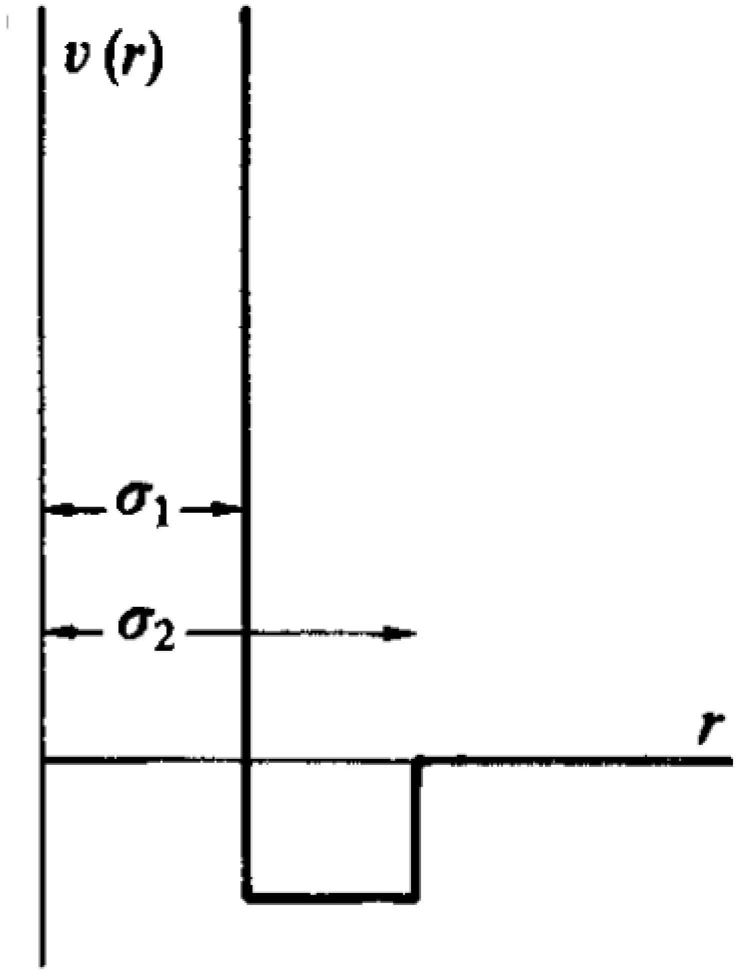
$$W(\eta) = (1{\cdot}0 - 10{\cdot}5896(\eta_C-\eta)^{2{\cdot}543})/[0{\cdot}694(\eta_C-\eta)]^{1{\cdot}072}. \quad (10)$$

Comparison between g(r) for HS solid



Square-well potential sphere simulation

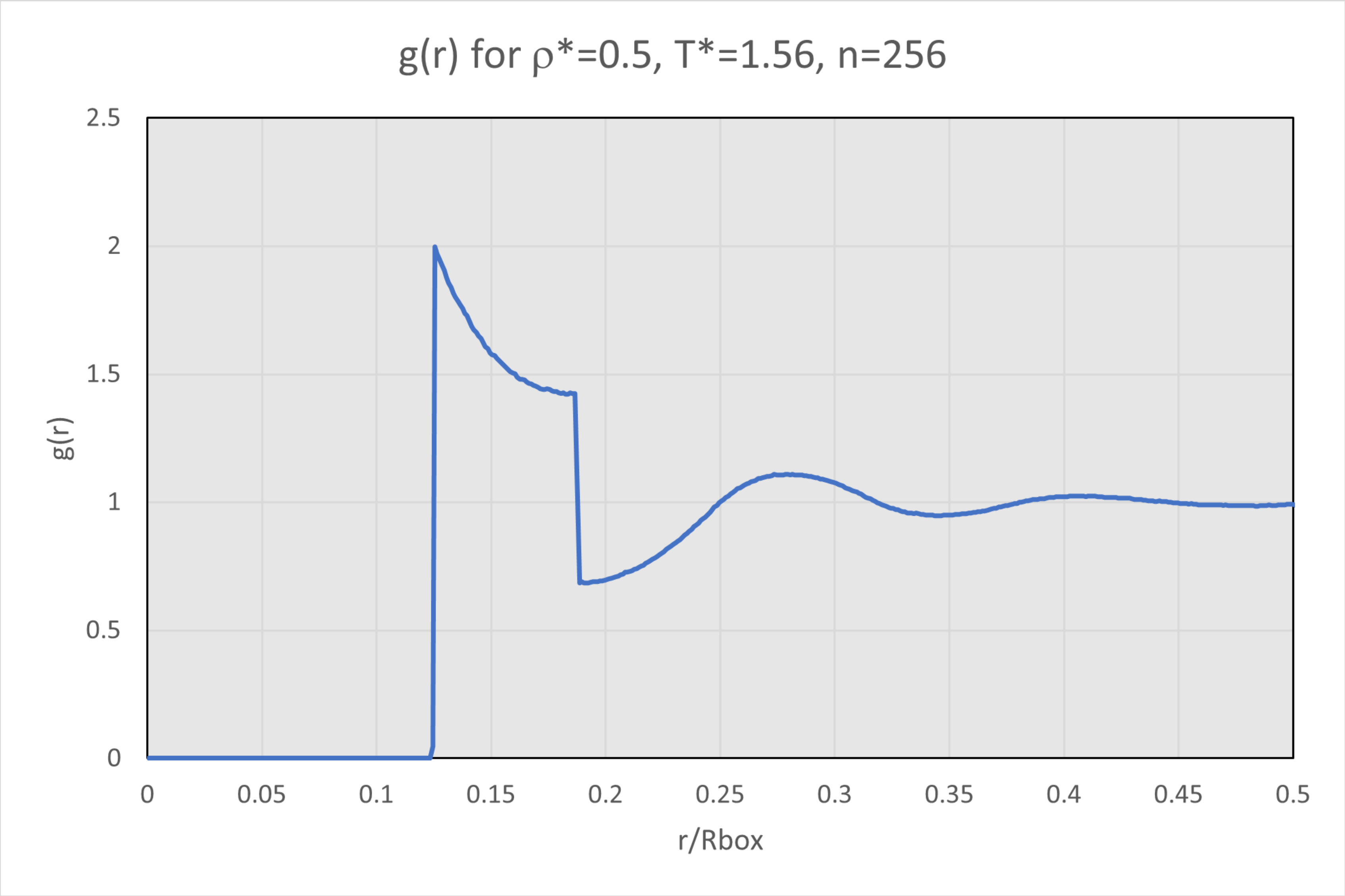
- ❑Compressibility factor
- ❑Radial distribution



g(r) for SW spheres

System size

- N = 256
- T ~ 1.5
- ρ ~ 0.5



Equation of State for Square-well Spheres

R. J. LEE and K. C. CHAO (1988)

$$Z = Z^{HS} - \frac{z_0}{2\alpha}\left[\frac{\Omega\left(\frac{\rho^*\alpha'}{T^*}+1\right)-1}{1+\rho^*(\Omega-1)} + \left(\frac{0.57}{1+0.57\rho^*} - \frac{\alpha'}{\alpha}\right)\ln(1+\rho^*(\Omega-1))\right]$$

Parameters

$$z_0 = \frac{4\pi}{3}(\lambda^3 - 1)(1+0.57\rho^*)\rho^*$$

$$\Omega = \exp\left(\frac{\alpha\varepsilon}{kT}\right)$$

$$\alpha' = 0.1044 - 5.6983\,\rho^* + 7.1355{\rho^*}^2$$

$$\alpha = 1 + 0.1044\,\rho^* - 2.8469\,{\rho^*}^2 + 2.3785{\rho^*}^3$$

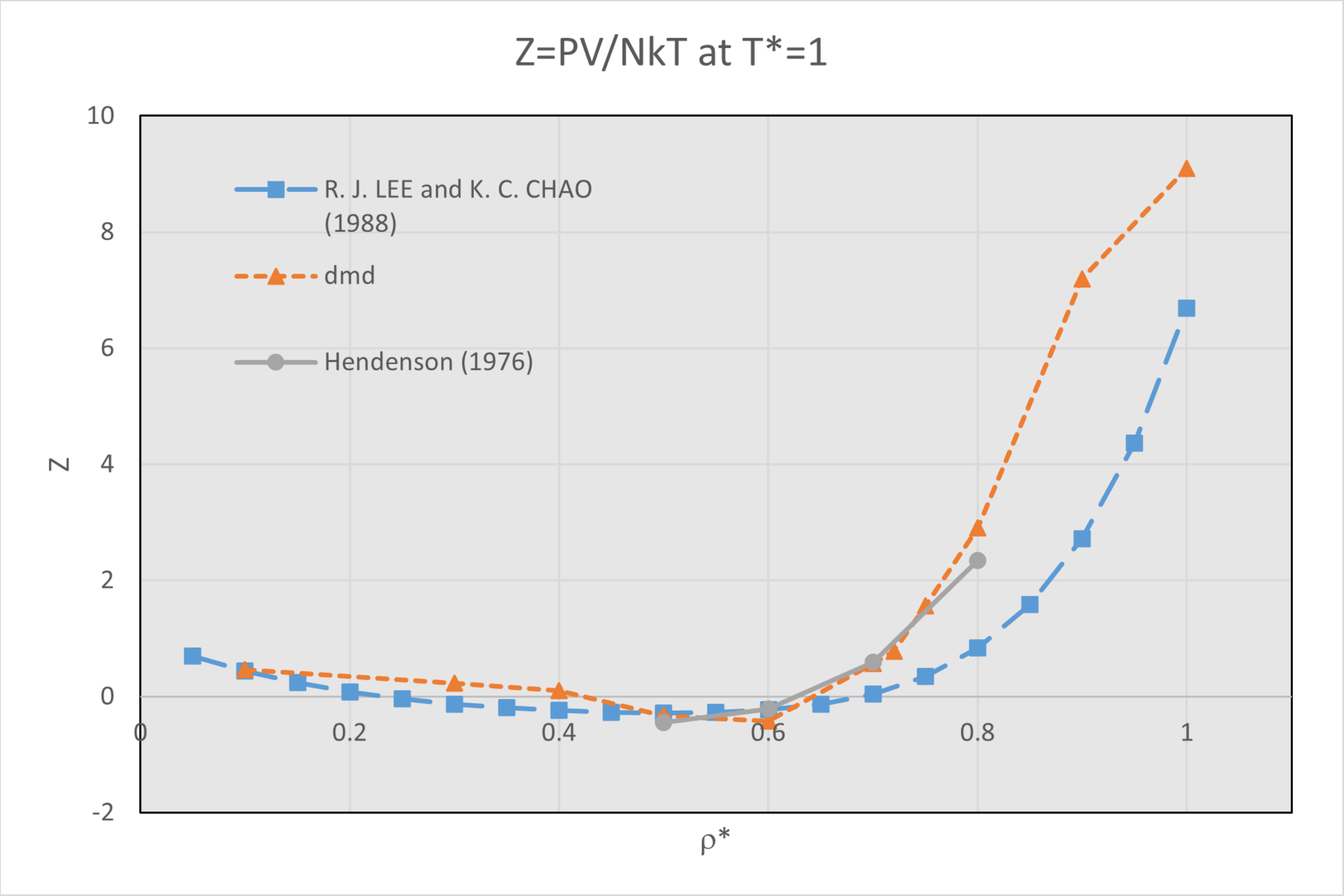
$$Z^{HS} = \frac{1+y+y^2}{(1-y)^3}$$

$$y = \frac{\sqrt{2}}{6}\pi\frac{V_0}{V} = \frac{\pi}{6}\rho^*$$

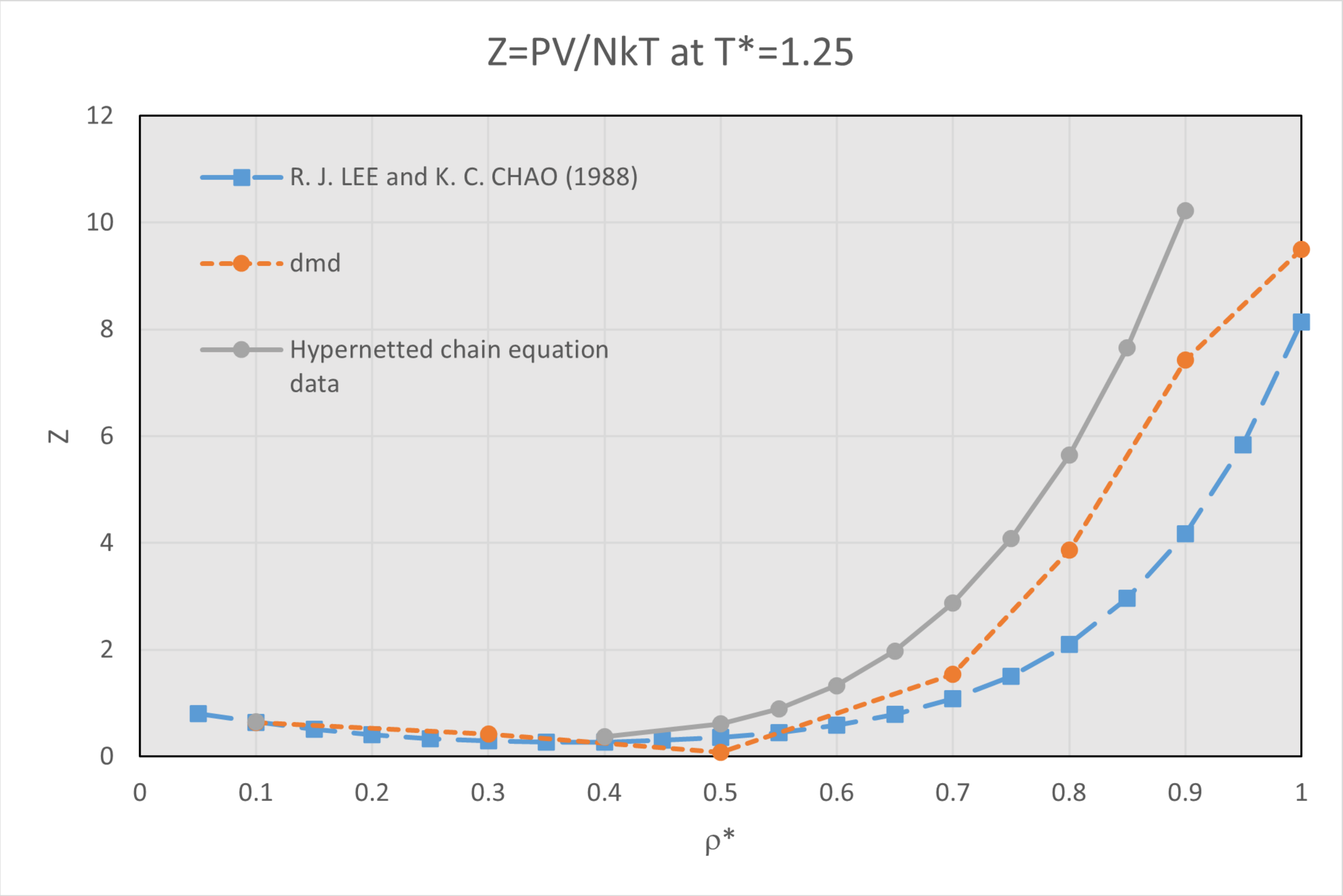
$$T^* = \frac{kT}{\varepsilon}$$

$$\rho^* = \rho\sigma^3$$

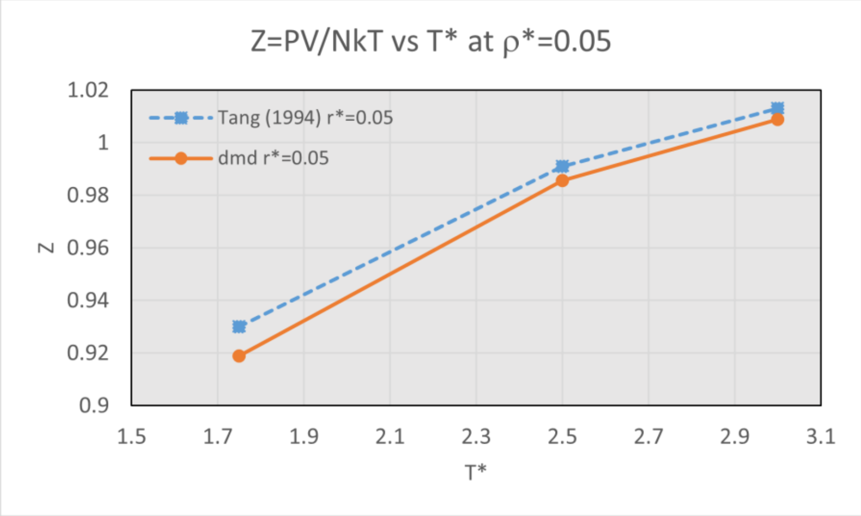
Compressibility factor for SW Spheres at T* = 1, λ = 1.5

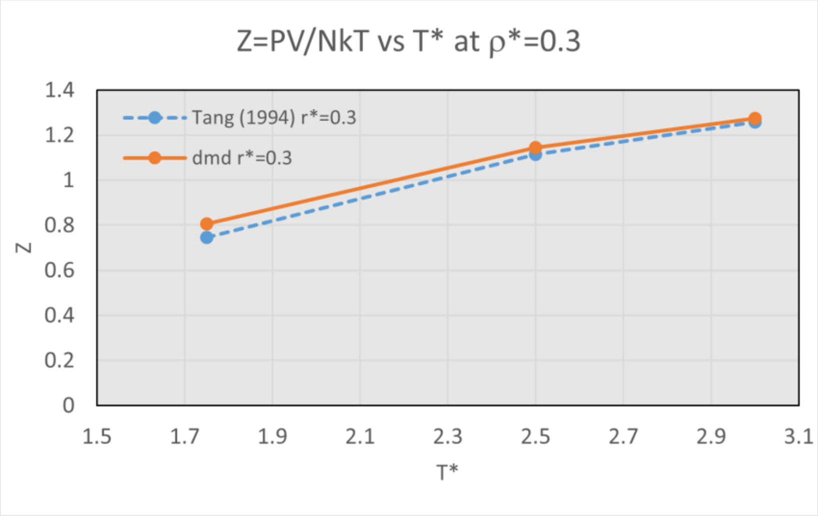


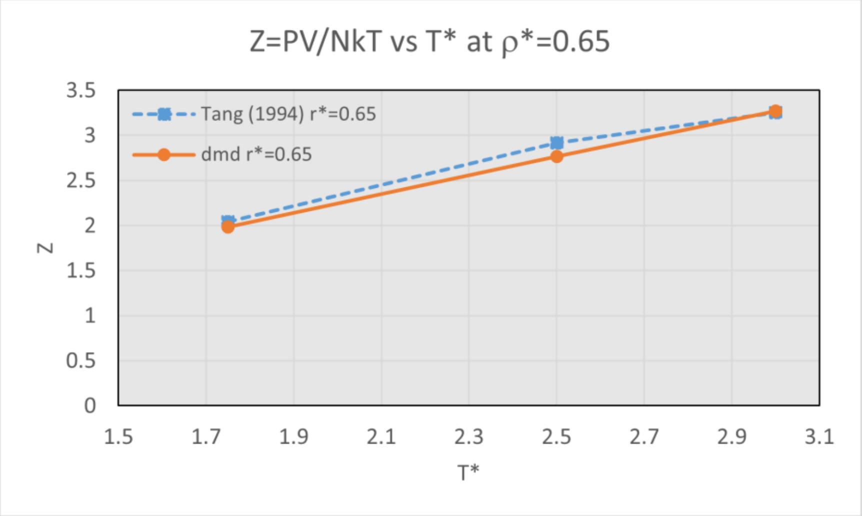
Compressibility factor for SW Spheres at T* = 1.25, λ = 1.5

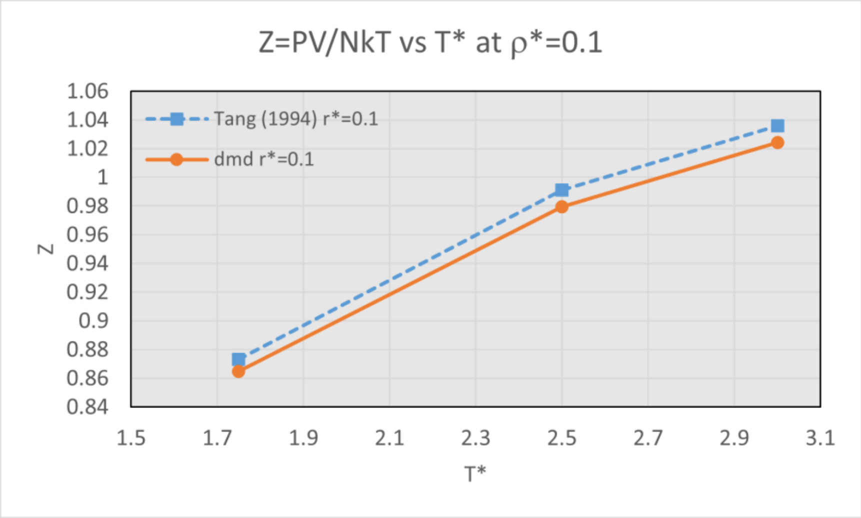


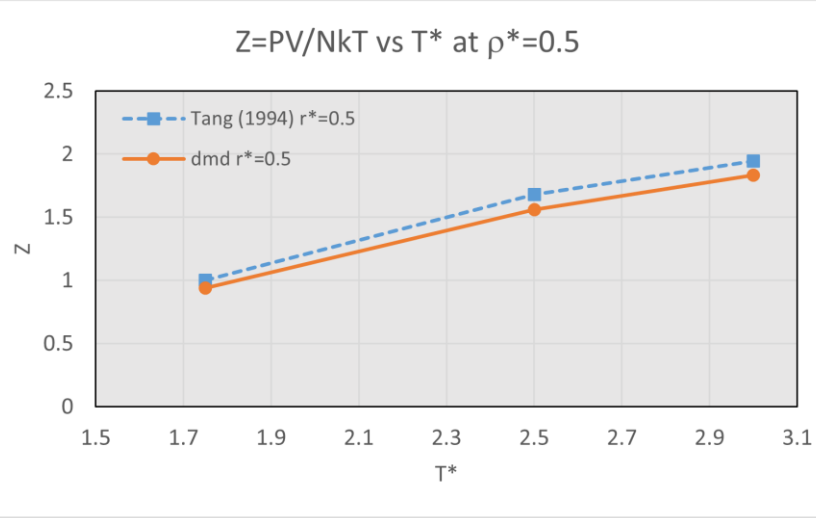
Compressibility factor for SW Spheres under different T*

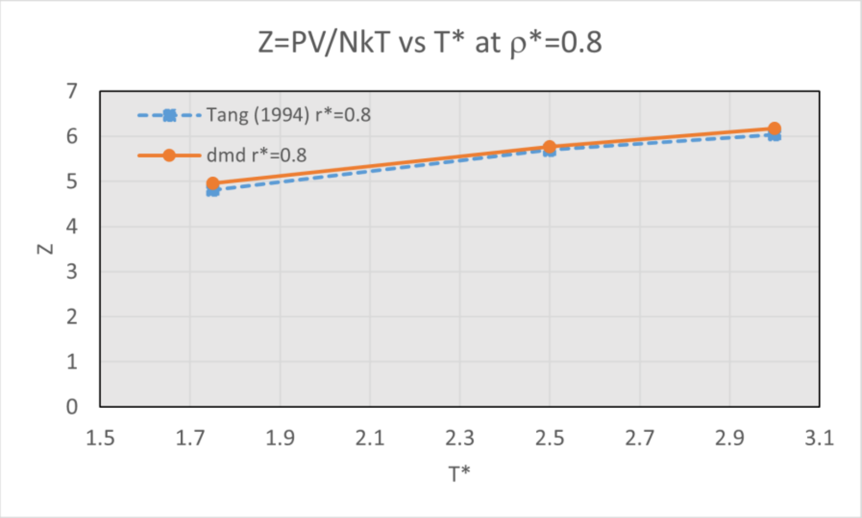




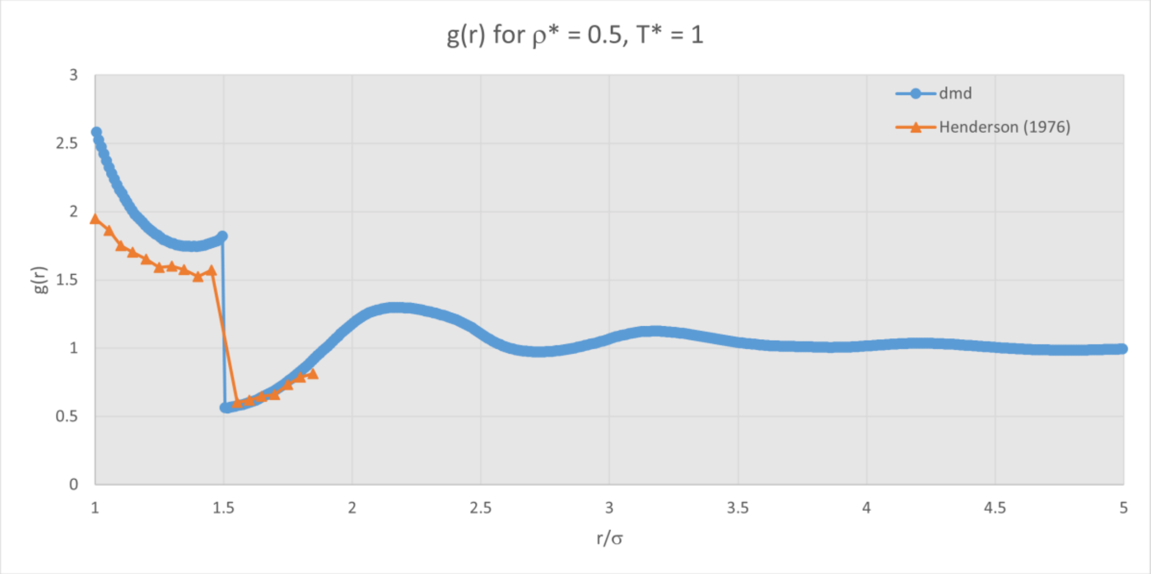


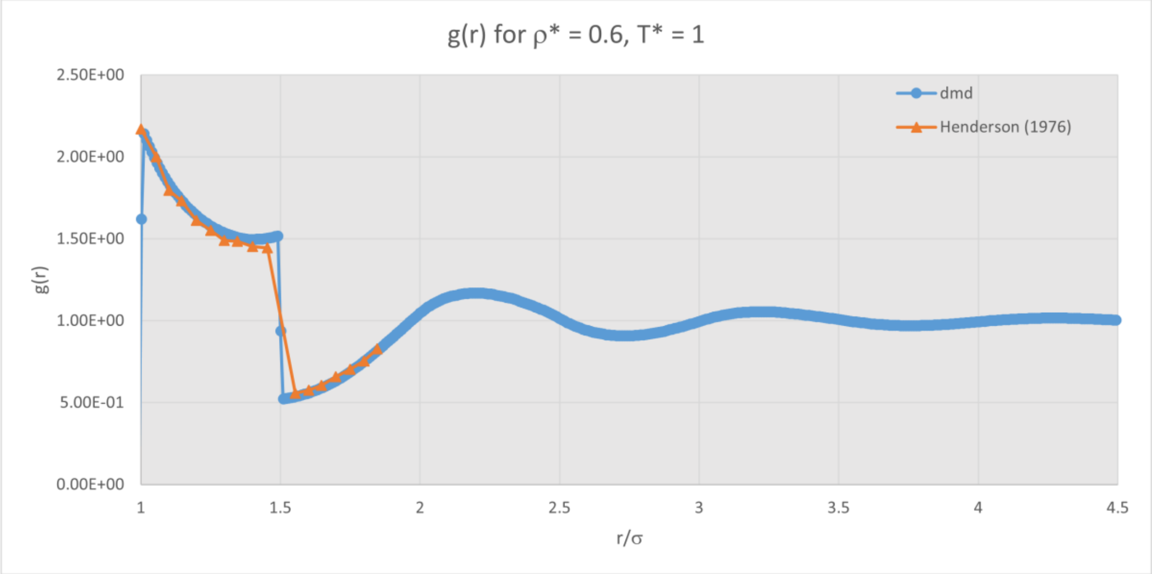


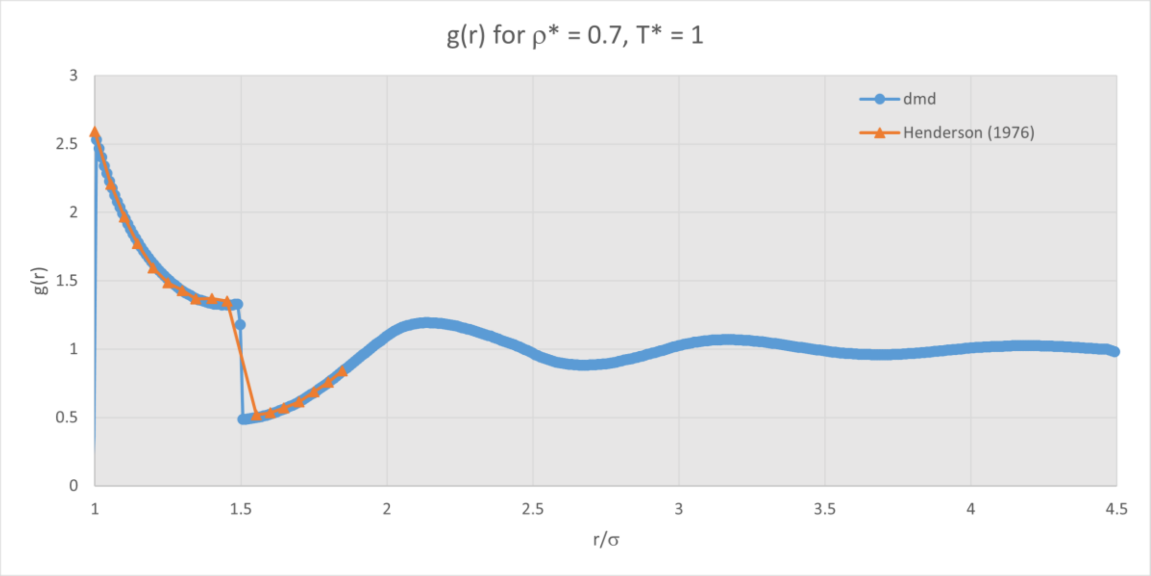


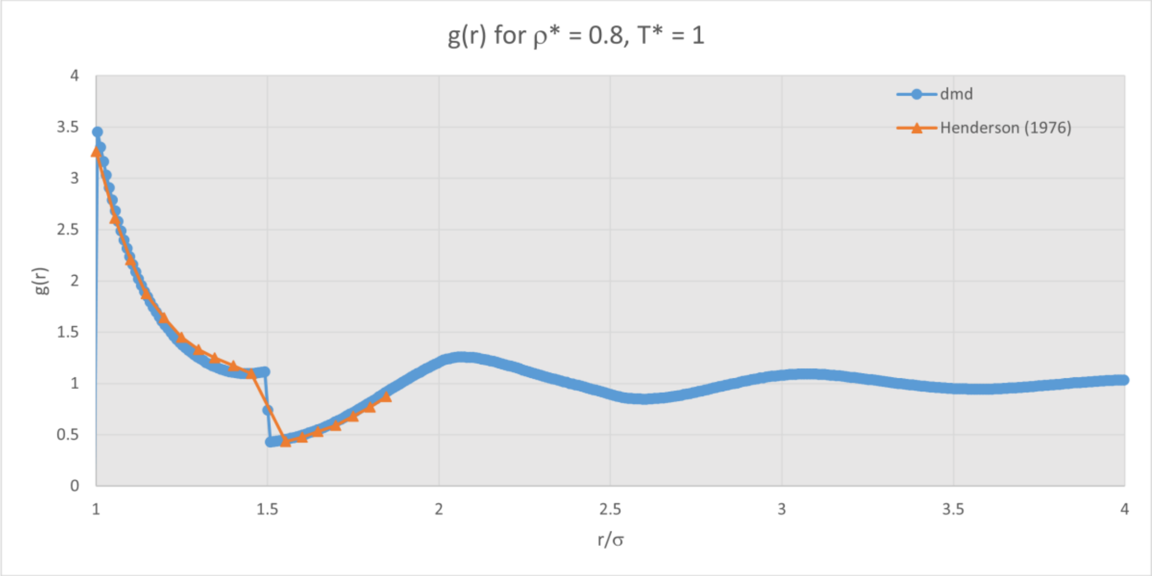


Comparison between g(r) for SW spheres at T* = 1, λ = 1.5

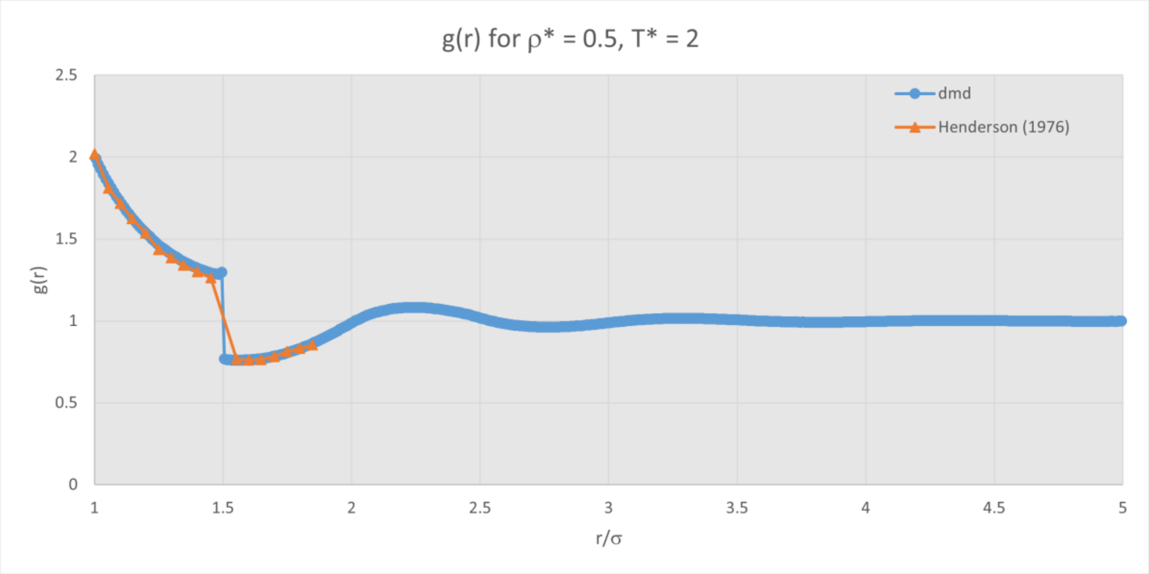


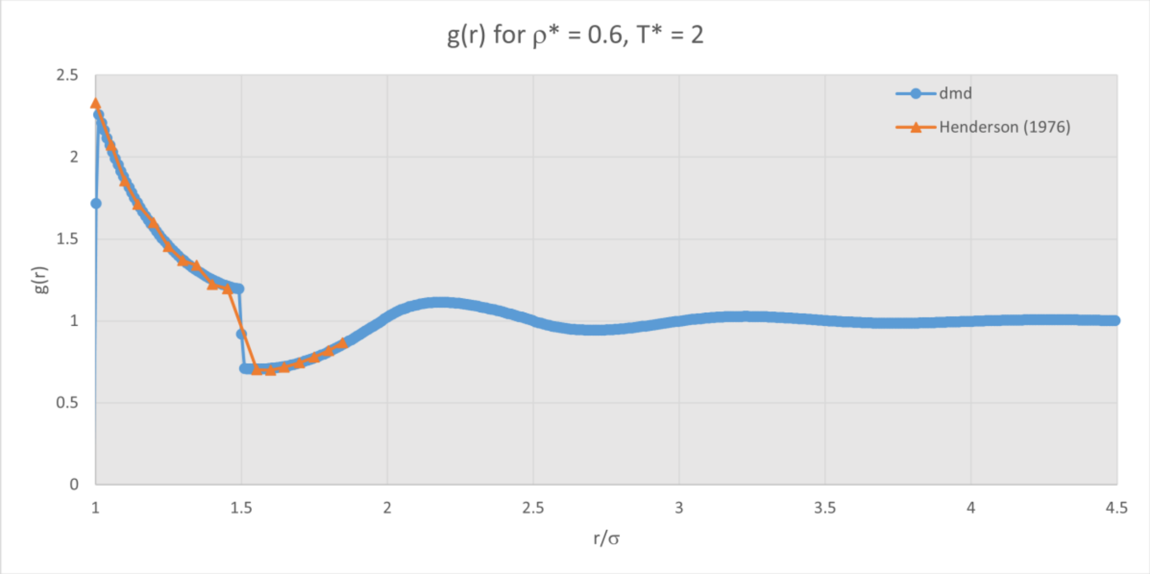


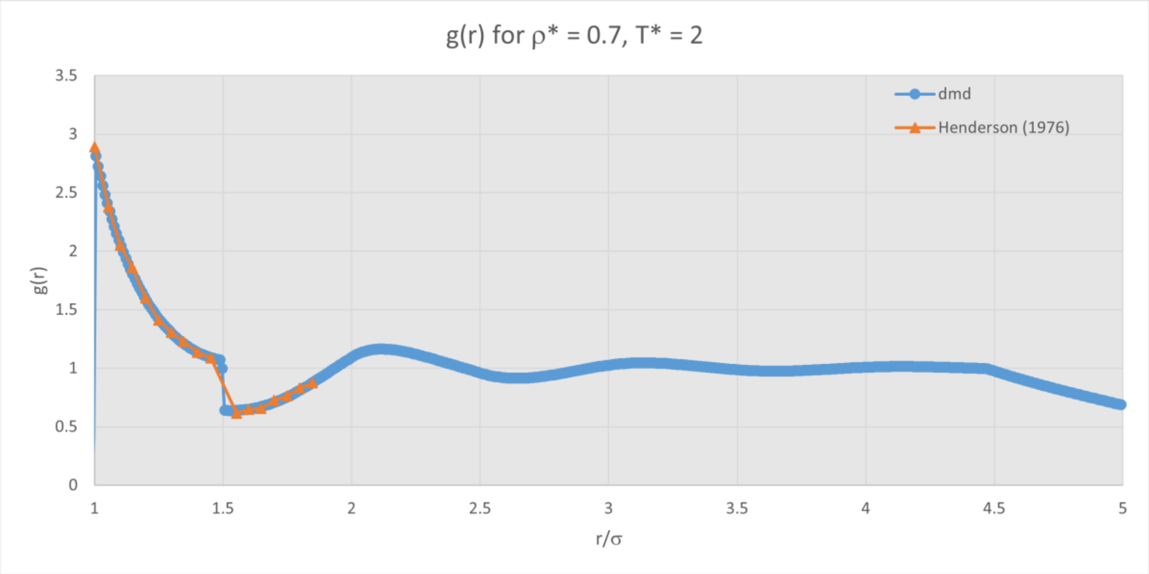


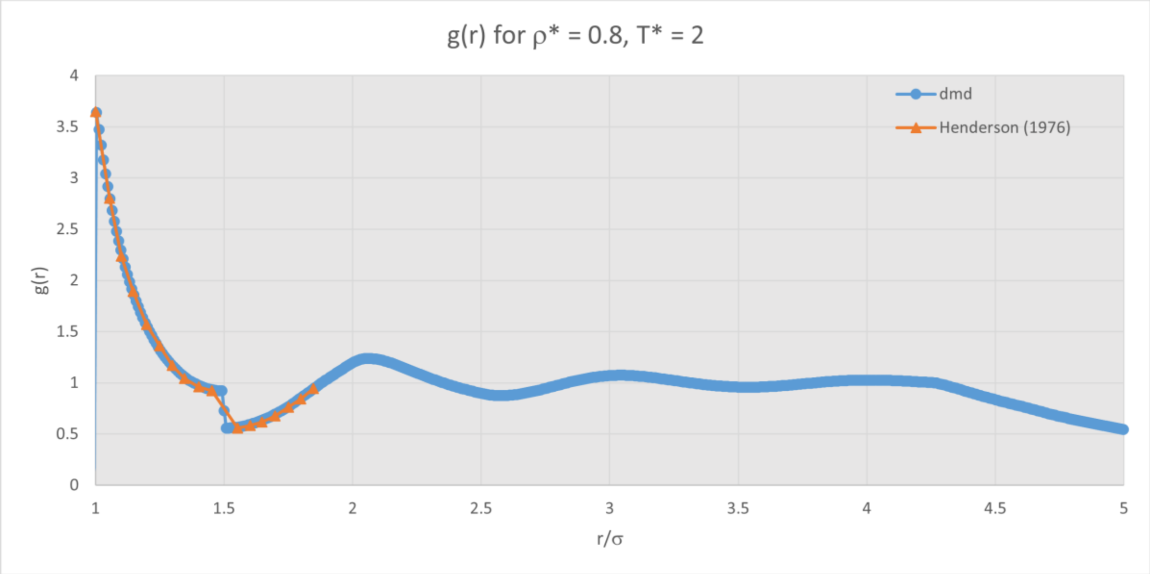


Comparison between g(r) for SW spheres at T* = 2, λ = 1.5









Square-well chains simulation

potential between two spheres from two chains

$$u_{ij}(r)\begin{cases}\infty, & r < \sigma \\ -\varepsilon, & \sigma \le r \le \quad \sigma \\ 0, & \lambda\sigma < r\end{cases}$$

potential between two bonded spheres in one chain

$$u_{i,i+1}(r)\begin{cases}\infty, & r < (1-\delta)\sigma \\ 0, & (1-\delta)\sigma \le r \le (1+\delta)\sigma \\ \infty, & (1+\delta)\sigma < r\end{cases}$$

Parameters:
δ = 0.01 (bond range)
λ = 1.5 (potential range)
ε = 1.0 (potential value)

Simulation condition
Burn in time: 0 - 12 million collisions with high temperature
N = 256

EOS for SW monomer and dimer are calculated by second order perturbation theory

$$Z = Z_H(n,\eta) - \frac{1}{T^*} Z^{(1)}(n,\eta) - \left(\frac{1}{T^*}\right)^2 Z^{(2)}(n,\eta)$$

n = chain length (mer)

$$Z_H(1\mathrm{mer},\eta) = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$$

$$Z_H(2\mathrm{mer},\eta) = \frac{1+2.45696\eta+4.10386\eta^2-3.75503\eta^3}{(1-\eta)^3}$$

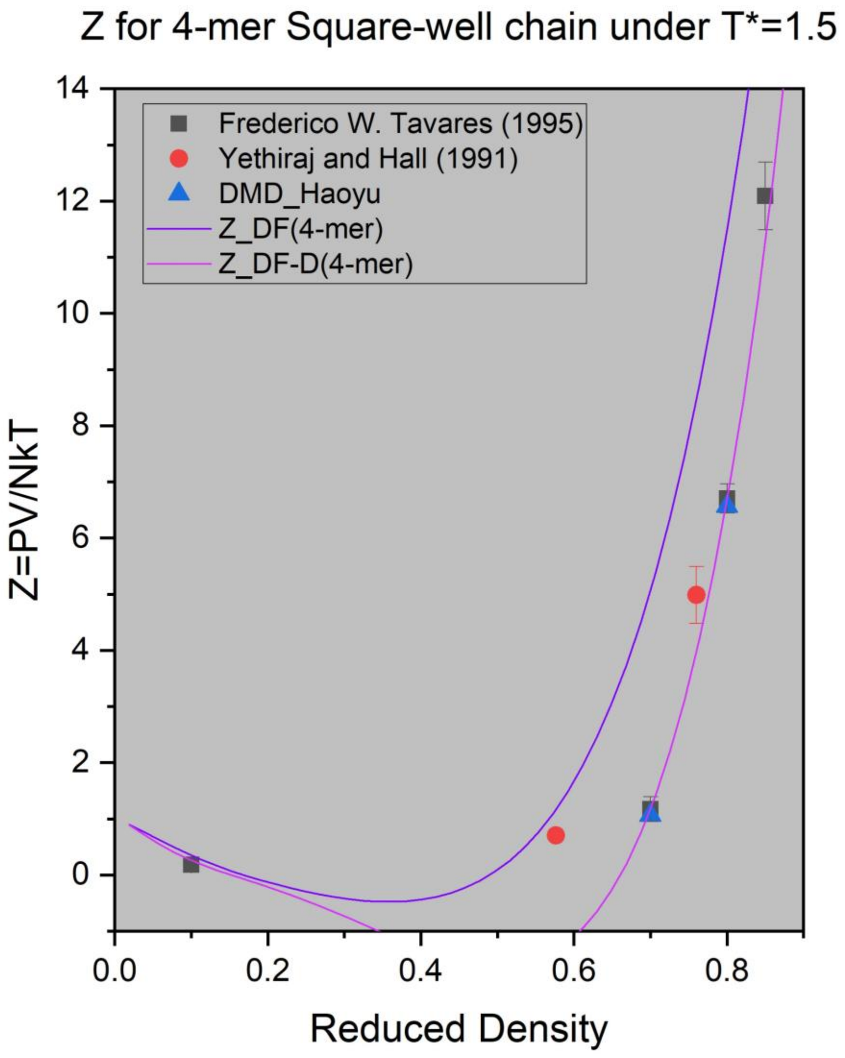
$$Z^{(1)}(1\mathrm{mer},\eta) = 9.5\eta\frac{1-1.13086\eta-5.72921\eta^2+9.50043\eta^3-2.37511\eta^4}{(1-\eta)^4}$$

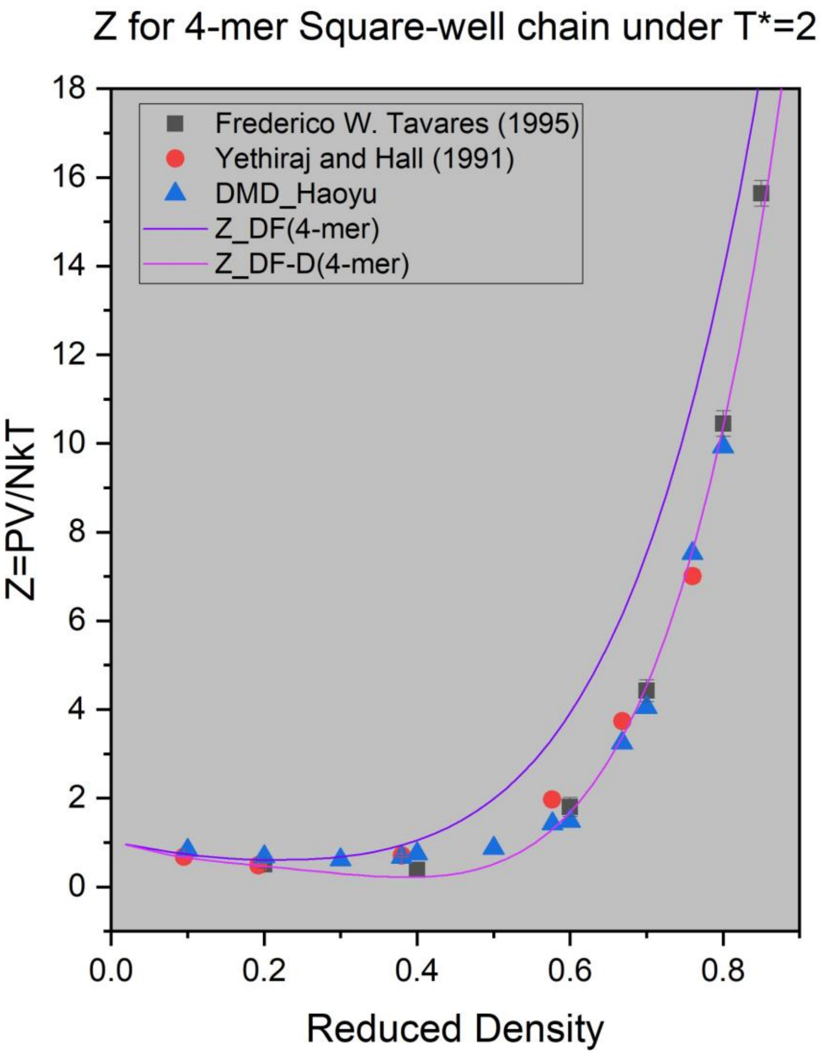
$$Z^{(2)}(1\mathrm{mer},\eta) = 288.15745\eta^2\frac{(1-5.4019\eta)}{(1+6.75237\eta)^4}$$

$$Z^{(1)}(2\mathrm{mer},\eta) = 12.00332\eta\frac{1+1.56564\eta-15.12892\eta^2+19.14672\eta^3-4.78668\eta^4}{(1-\eta)^4}$$

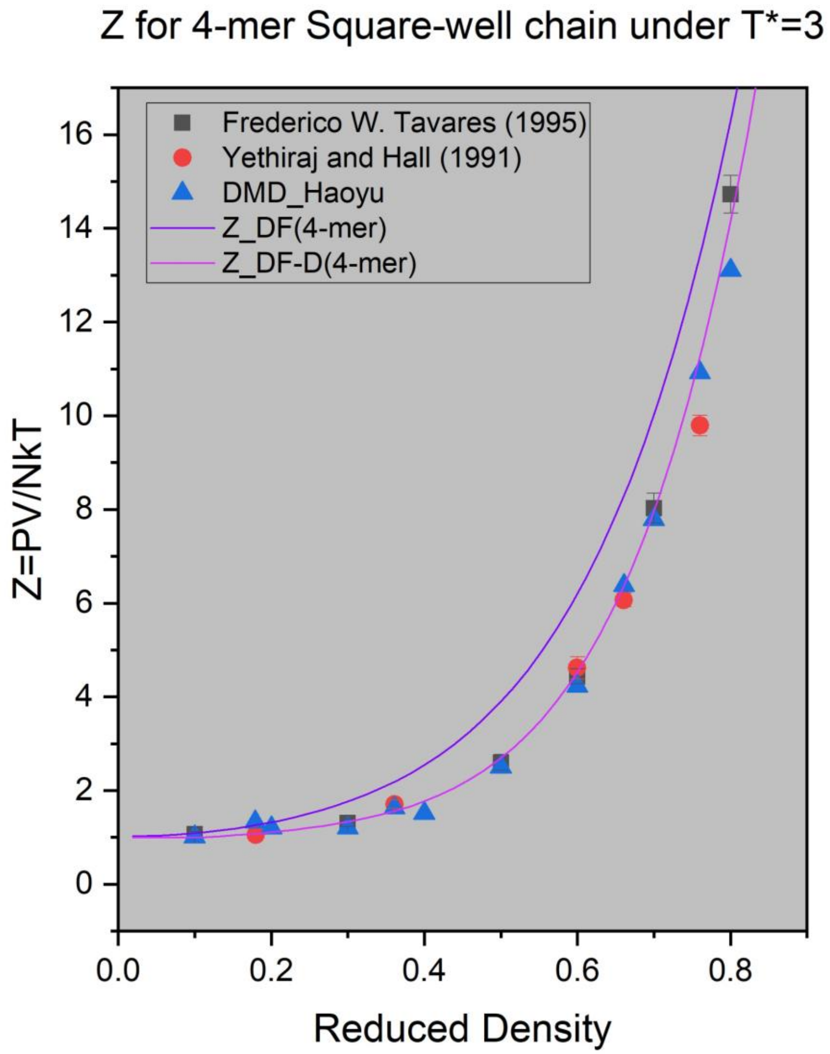
$$Z^{(2)}(2\mathrm{mer},\eta) = 492.36296\eta^2\frac{(2-12.31907\eta)}{(1+8.26765\eta)^4}$$

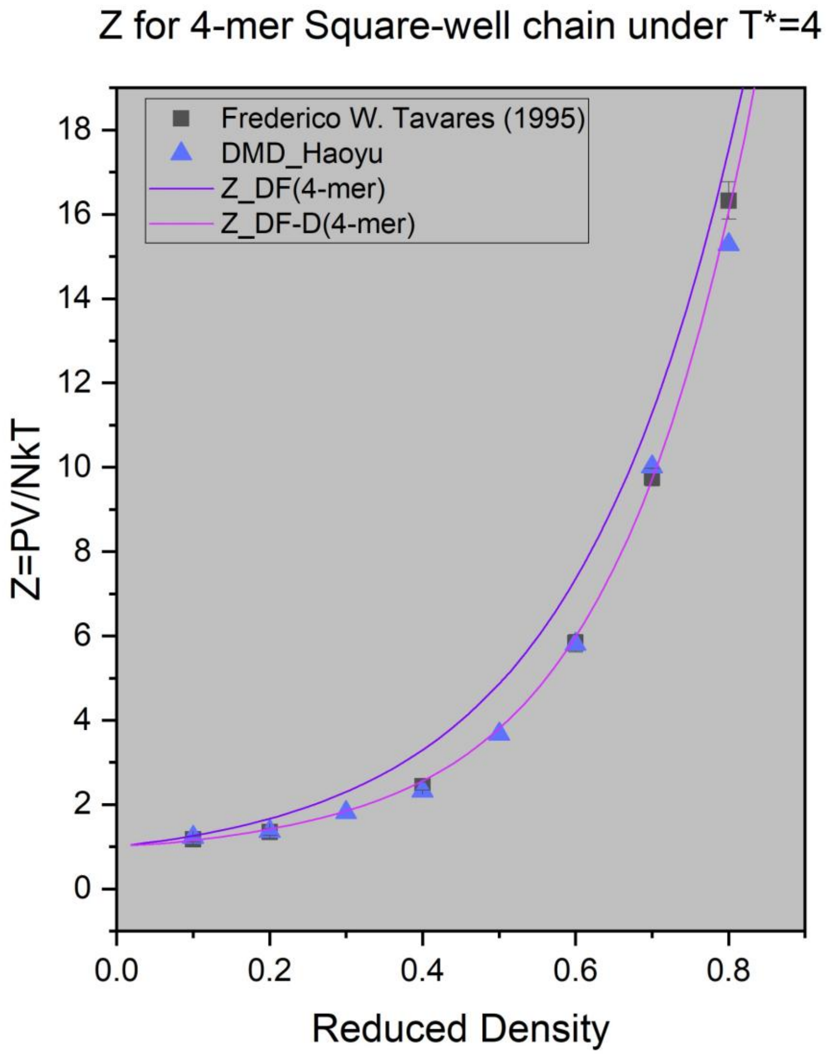
4-mer compressibility factor



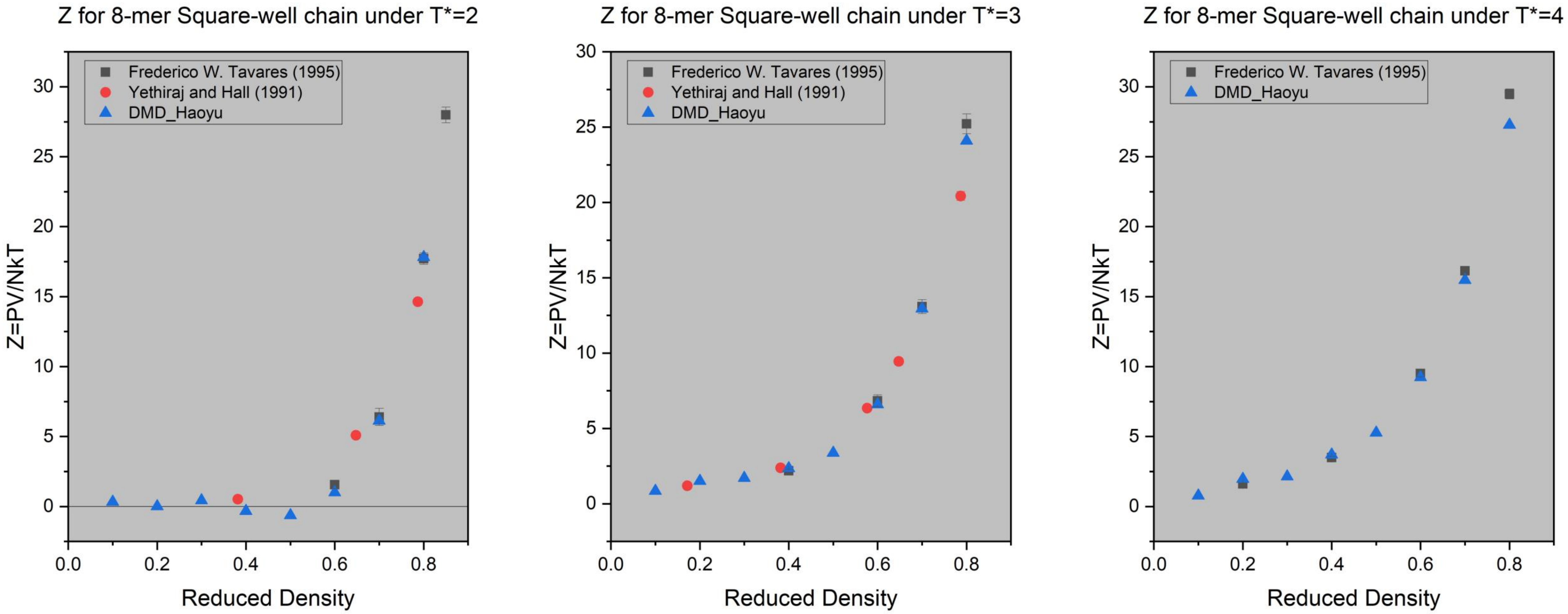


4-mer compressibility factor

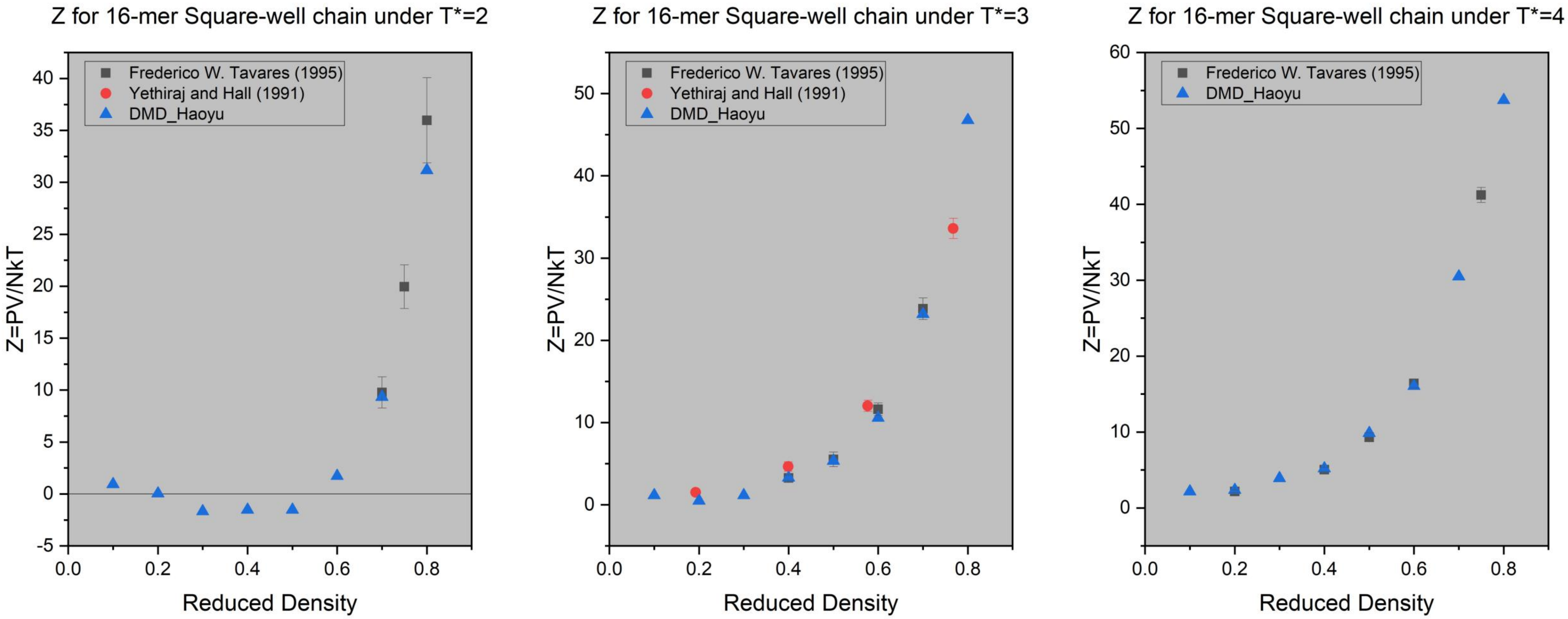




8-mer compressibility factor

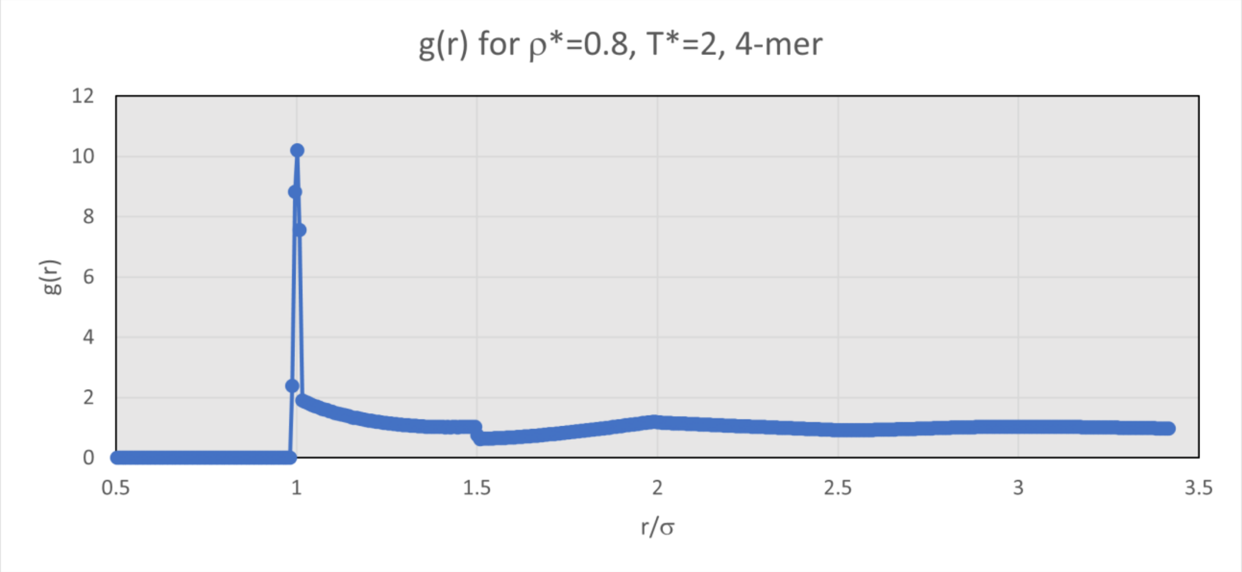


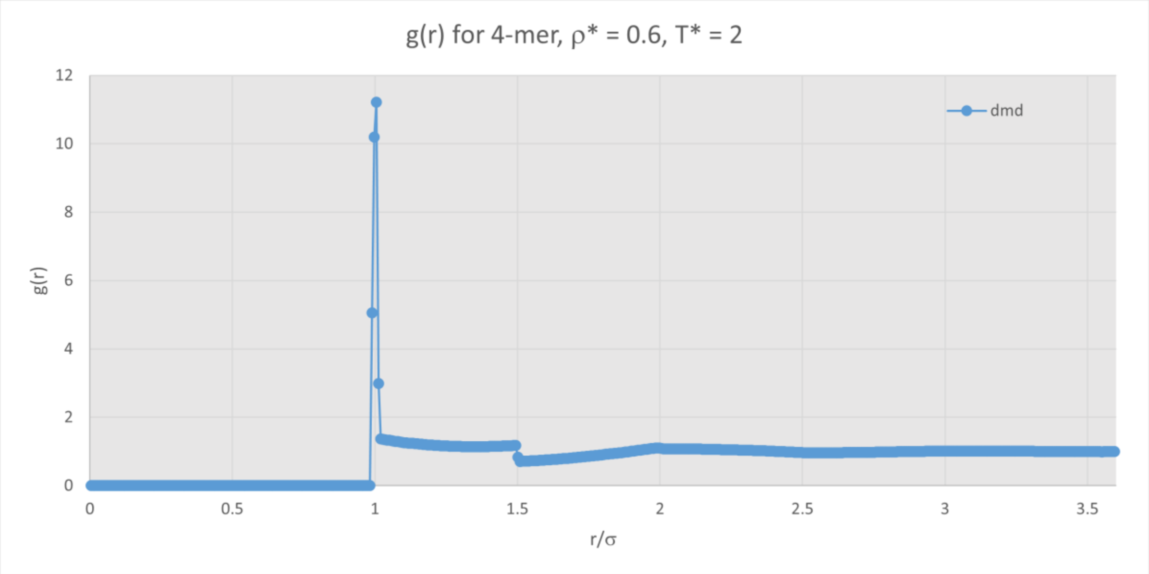
16-mer compressibility factor

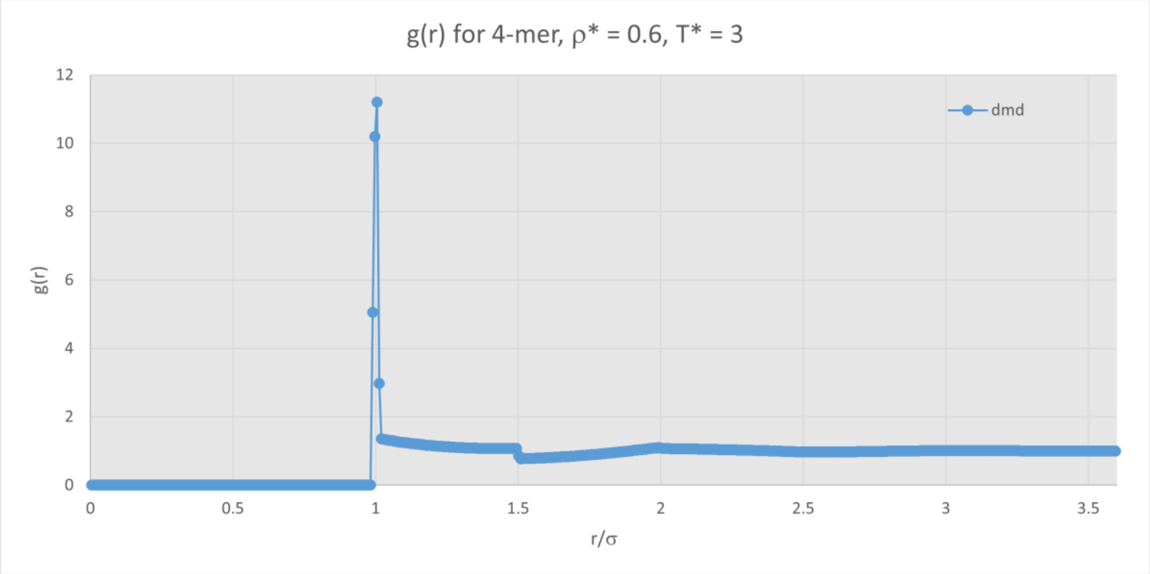


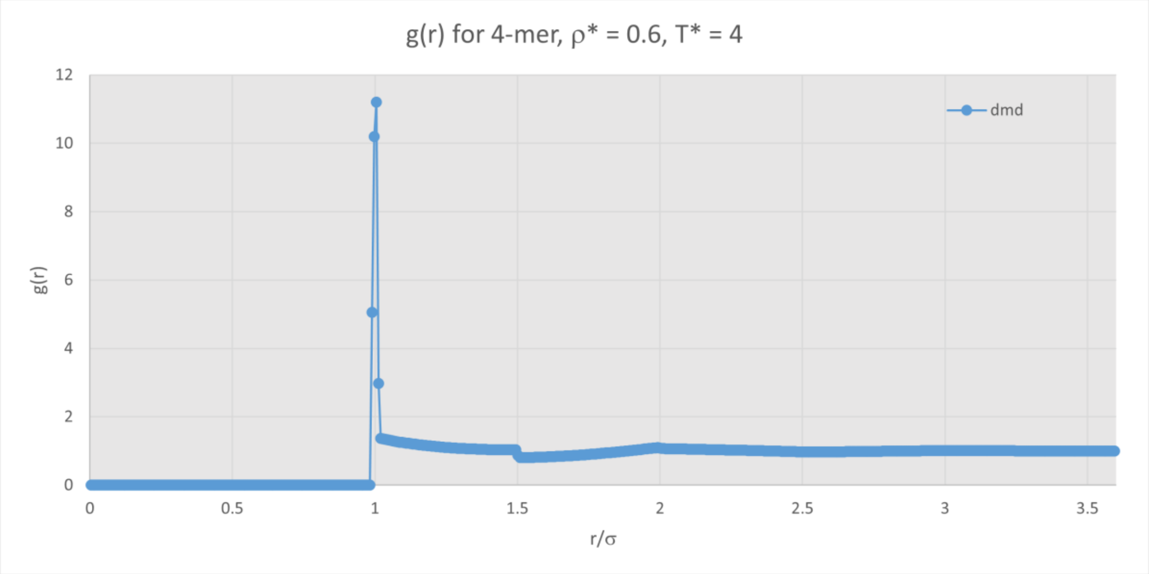
Some Radial distribution g(r) for square-well chains

These g(r) are calculated from an equation based on single spheres.



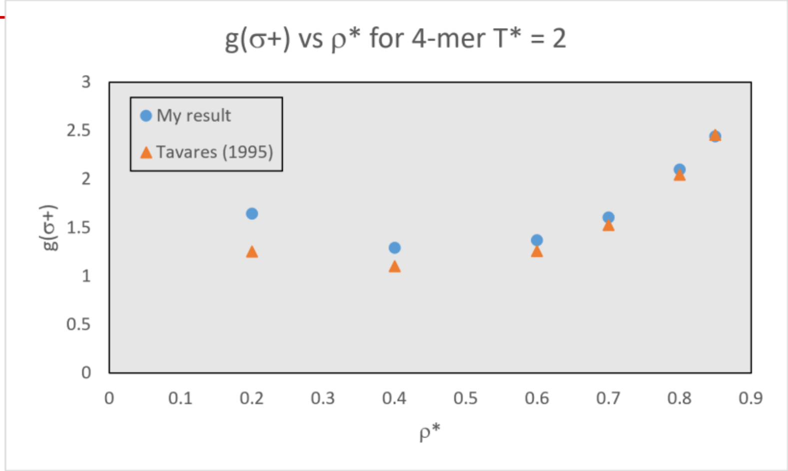


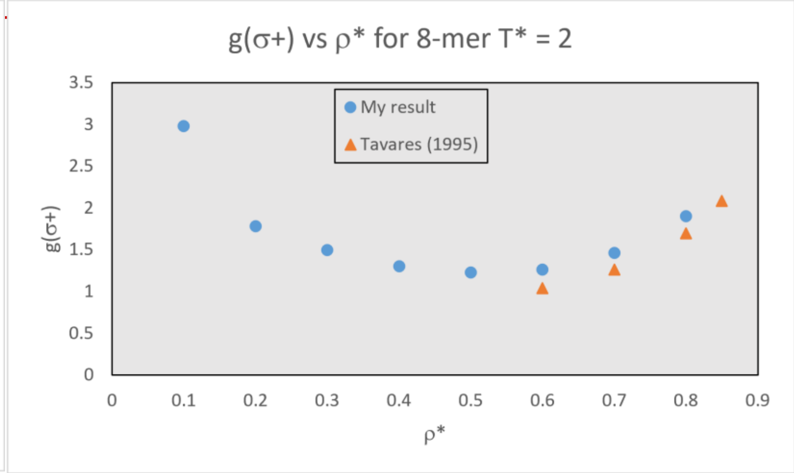


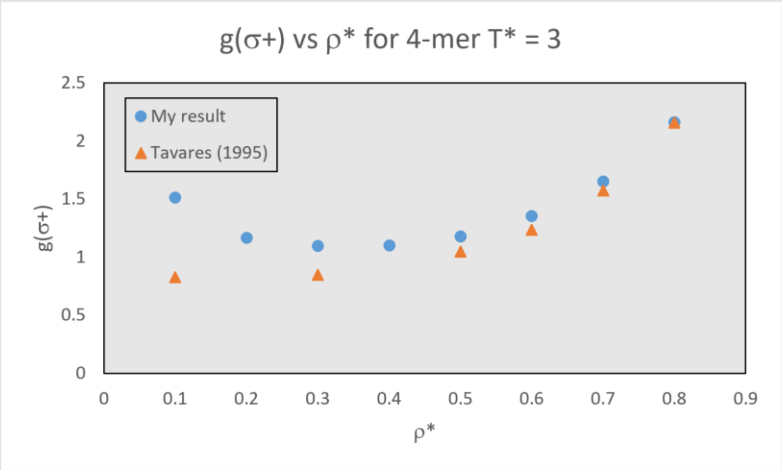


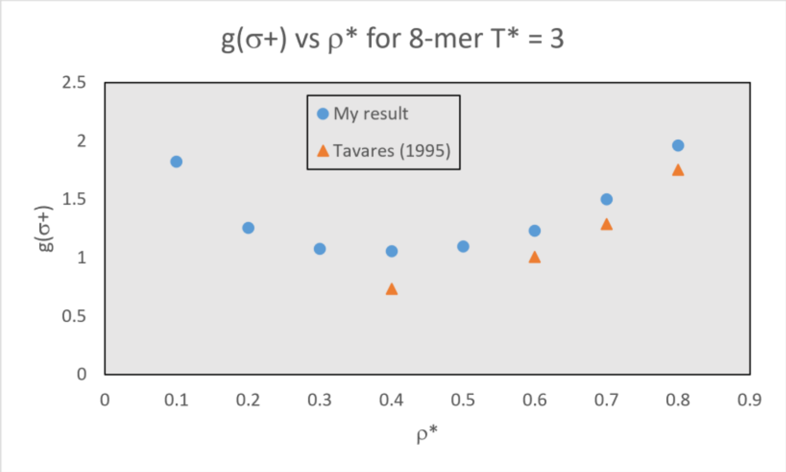
radial distribution at contact

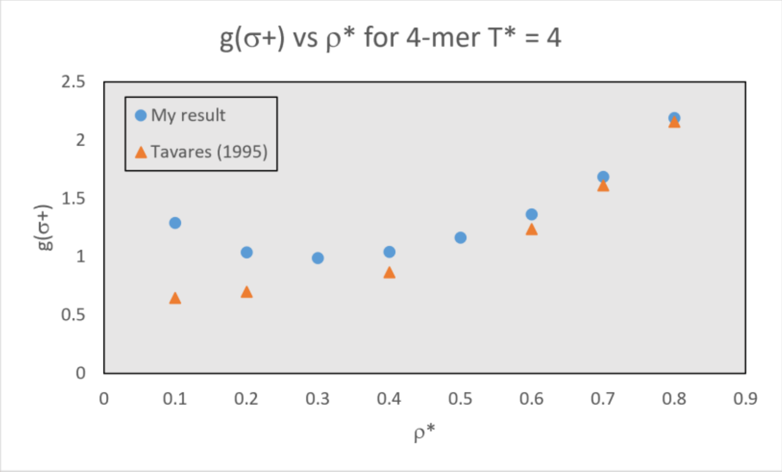
These g(r) are calculated from an equation based on single spheres.

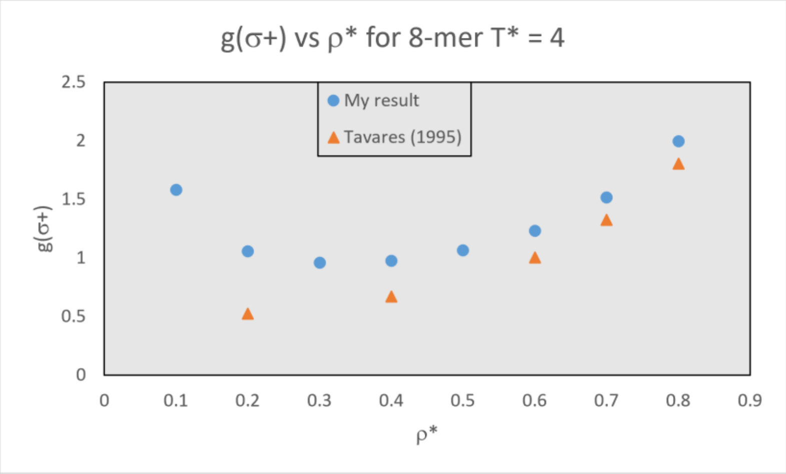




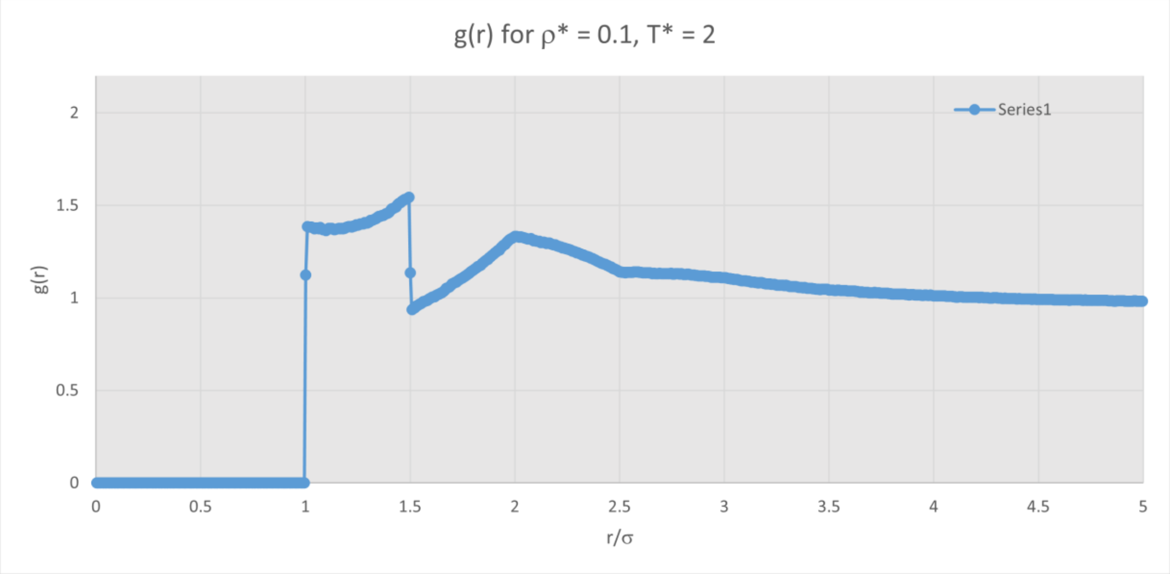


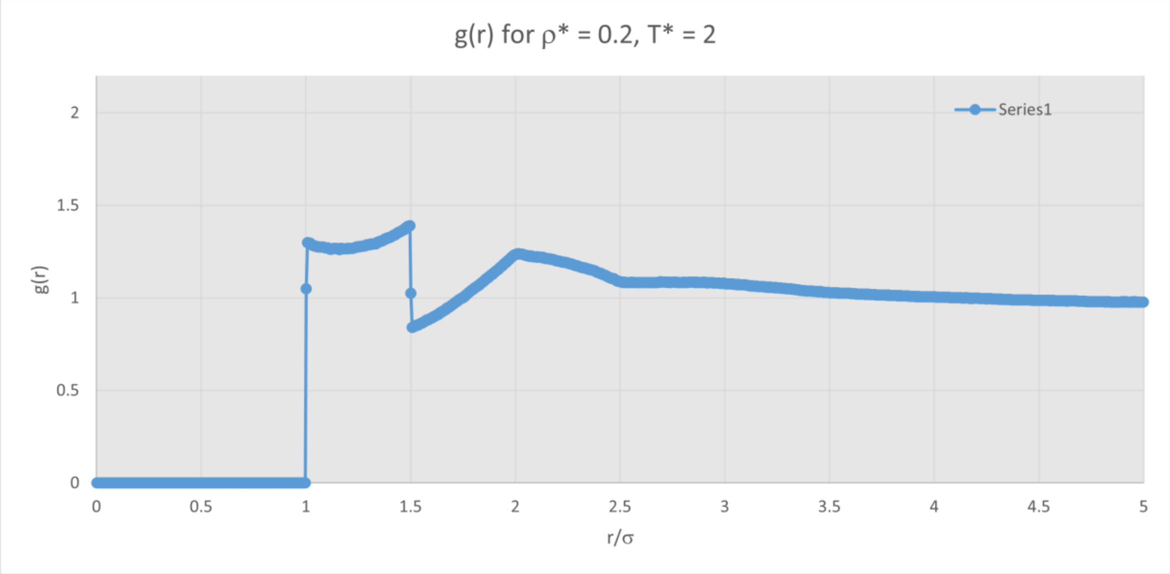


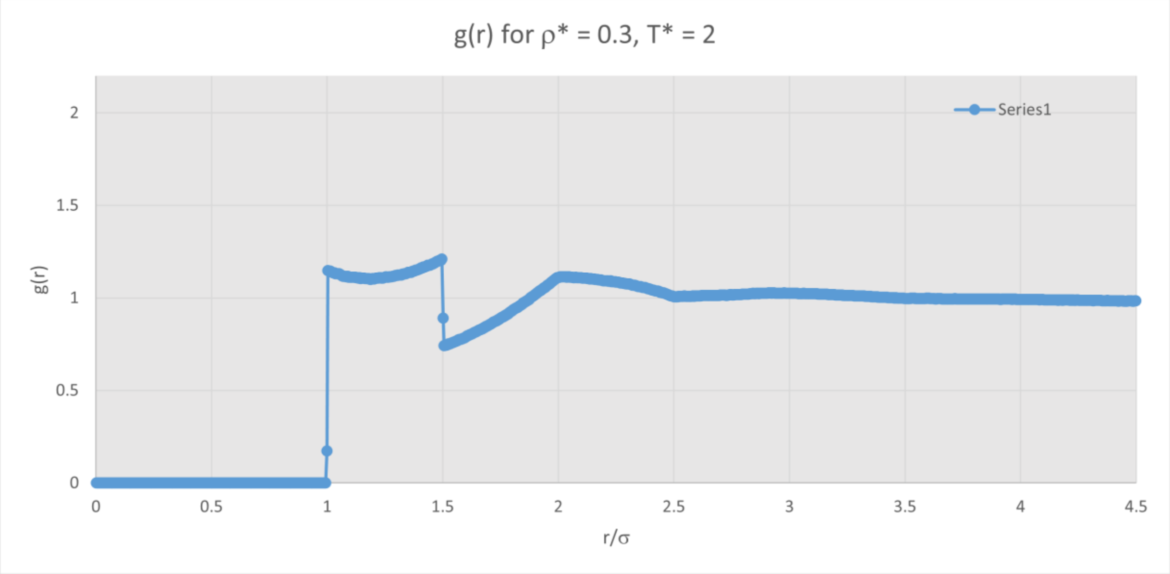


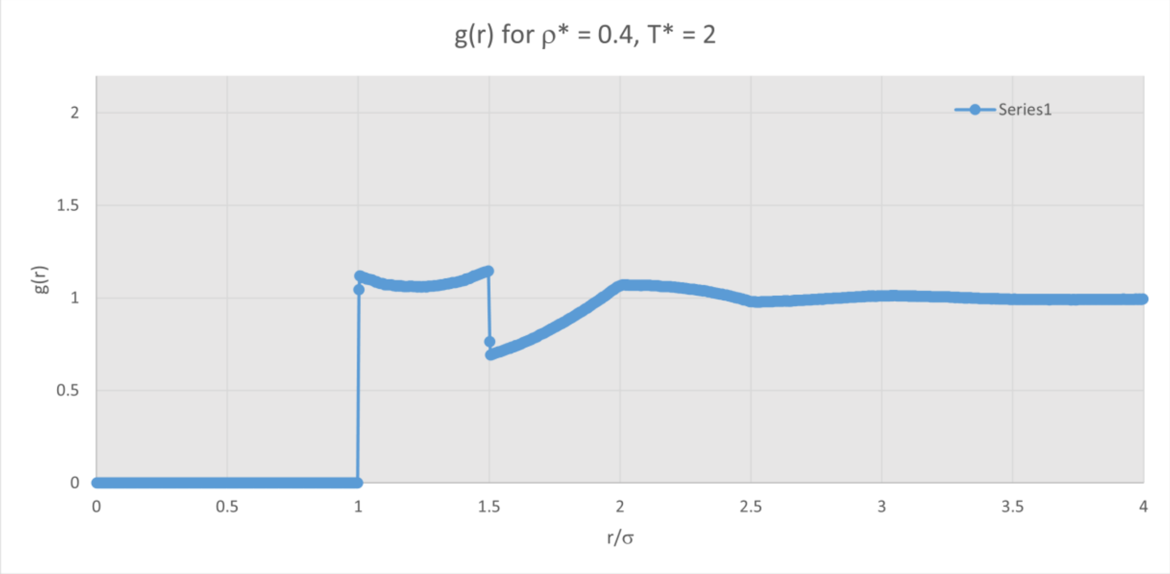


Some Radial distribution g(r) for 4-mer square-well chains

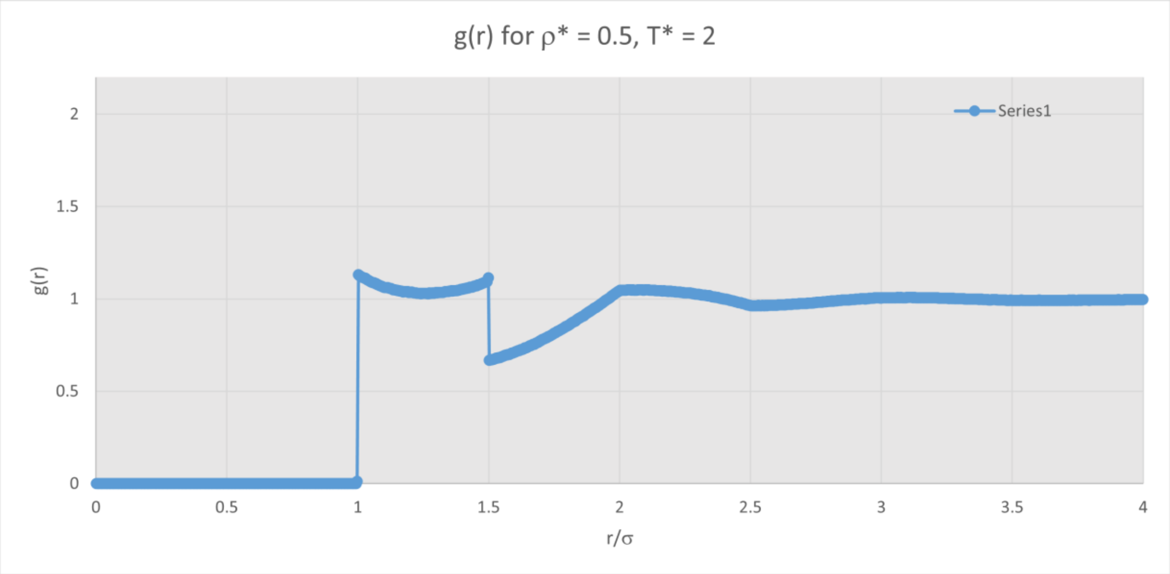


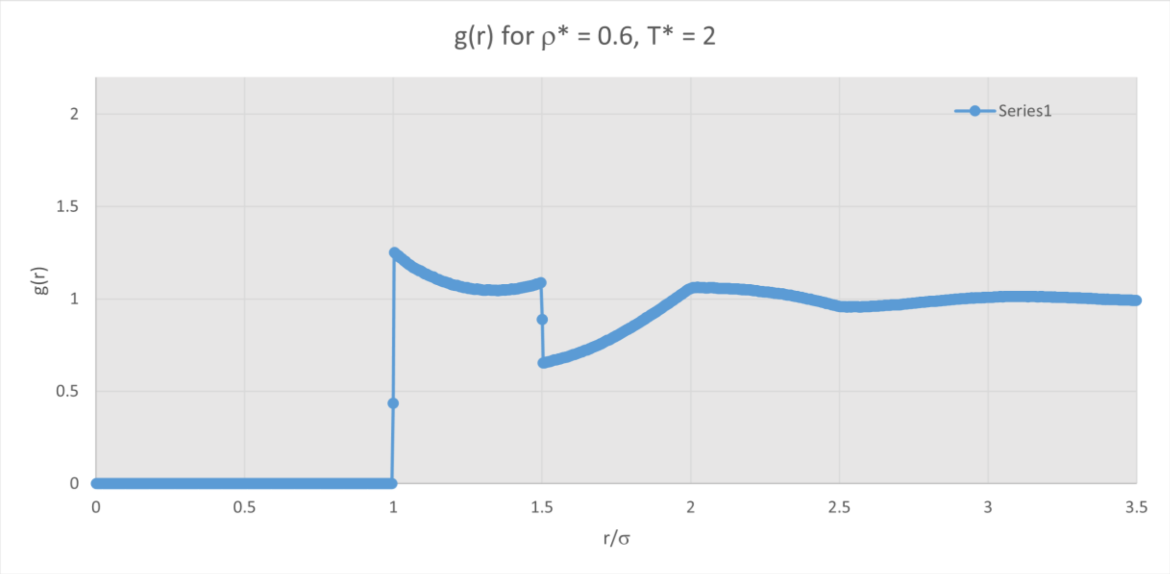


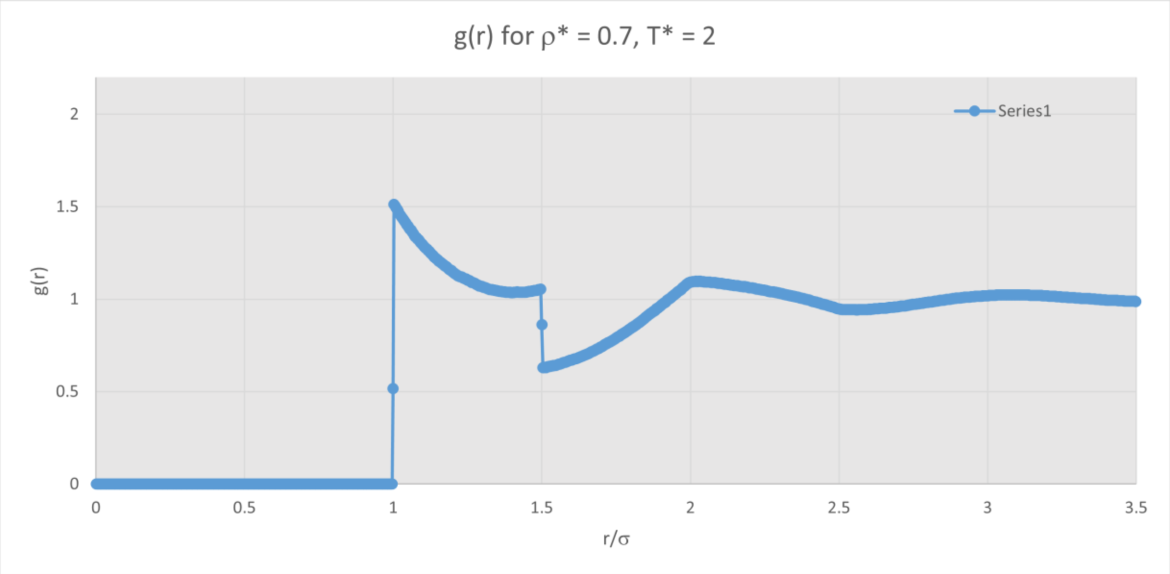


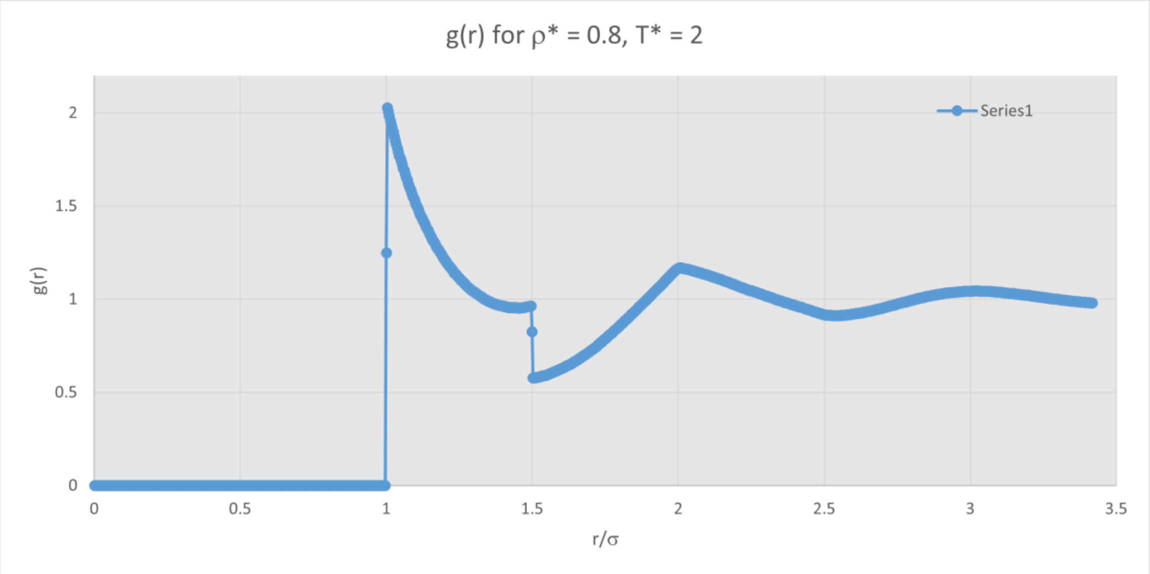


Some Radial distribution g(r) for 4-mer square-well chains



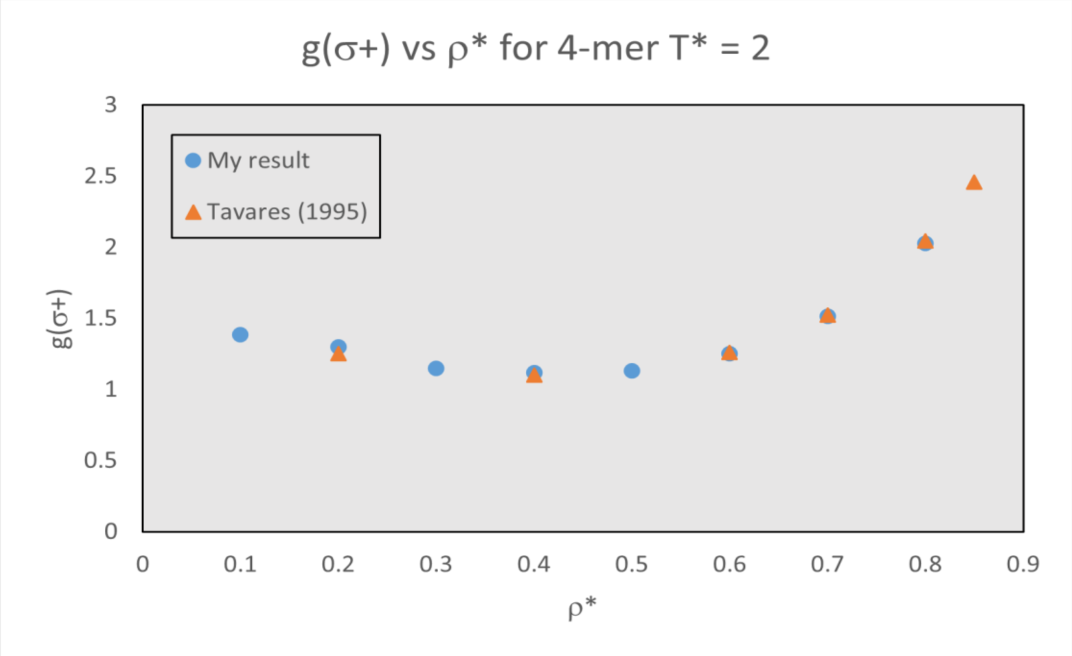


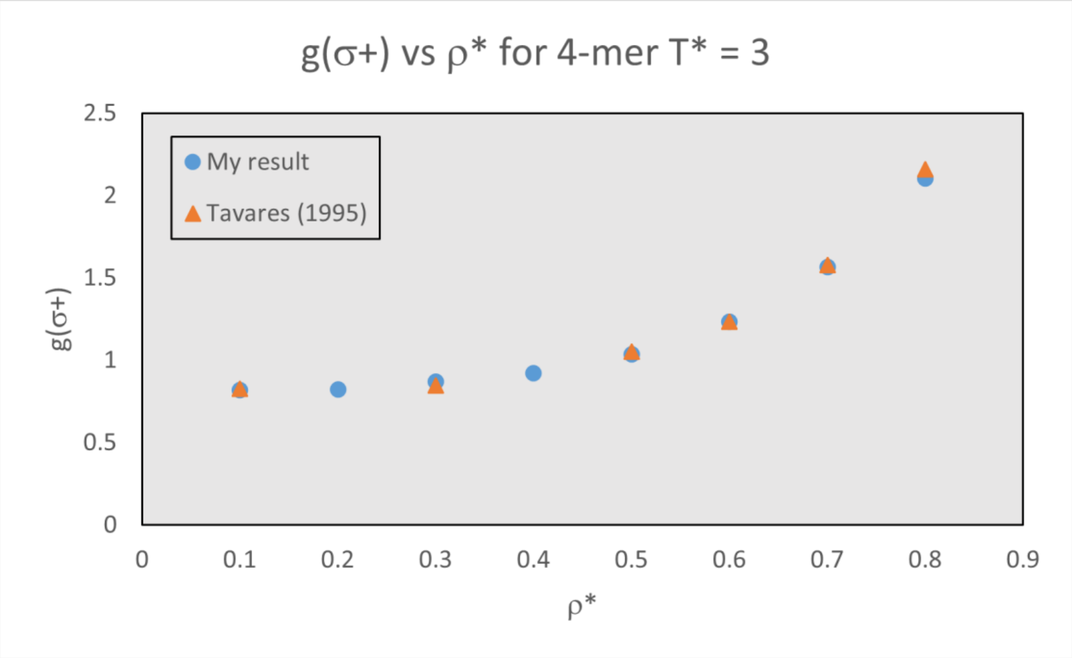


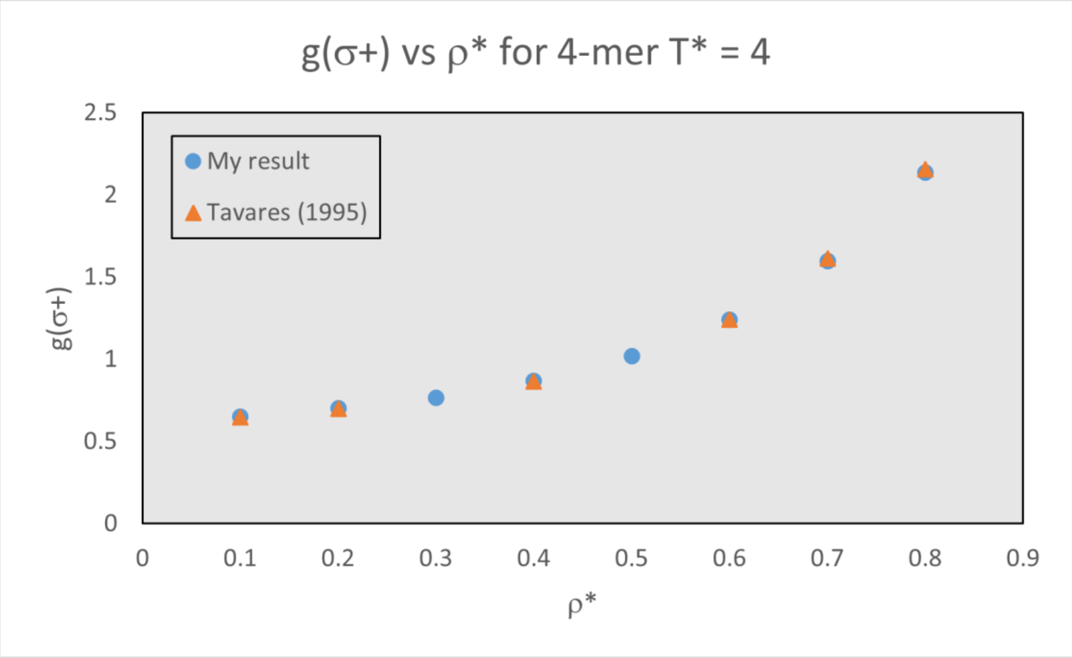


radial distribution g(r) at contact Updated

Good agreement with literature







Generalized Flory equations of state for square-well chains

$$Z_{GF} = 1 + \frac{v_e(n)}{v_e(1)}(Z_1 - 1)$$

$$Z_{GF-D} = \left[\frac{v_e(n) - v_e(1)}{v_e(2) - v_e(1)}\right] Z_2 - \left[\frac{v_e(n) - v_e(2)}{v_e(2) - v_e(1)}\right] Z_1$$

$v_e(n)$ = excluded volume of the n-mer

$$v_e(n) = v_e(3) + (n-3)[v_e(3) - v_e(2)]$$

$$v_e(1) = \frac{4}{3}\pi\sigma^3$$

$$v_e(2) = \frac{9}{4}\pi\sigma^3$$

$$v_e(3) = 9.82605\sigma^3$$

A. Yethiraj, C.K. Hall, Generalized Flory equations of state for square-well chains, The Journal of Chemical Physics 95 (1991) 8494–8506.