9.C.3. Higher-Order Virial Coefficients

Read Reichl's text.

With [see Ex.9.2, §9.C.2]

$$f_{12}(q)_{HS} = \begin{cases} -1 & q < \sigma \\ 0 & q \geq \sigma \end{cases}$$

we can use (9.49) to calculate the hard sphere gas B_j for arbitrary j.

For example, see Exercise 9.3 of §S.9.C for the calculation of B_3.

After much blood, sweat and tears, one gets

$B_2(T)$	$B_3(T)$	$B_4(T)$	$B_5(T)$	$B_6(T)$
b_0	$\frac{5}{8} b_0^2$	$0.29\, b_0^3$	$0.11\, b_0^4$	$0.04\, b_0^5$

$$b_0 = \frac{2}{3} \pi \sigma^3$$

The equation of state (9.43) thus becomes

$$\frac{P V}{N k_B T} = 1 + b_0 \frac{N}{V} g(T)$$

where

$$g(T) = \frac{V}{B_2(T) N} \sum_{n=2}^{\infty} B_n(T) \left(\frac{N}{V}\right)^{n-2}$$

$$\approx 1 + \frac{5}{8} b_0 \frac{N}{V} + 0.29 \left(b_0 \frac{N}{V}\right)^2 + 0.11 \left(b_0 \frac{N}{V}\right)^3 + 0.04 \left(b_0 \frac{N}{V}\right)^4 + \ldots \quad (9.64a)$$

The convergence of this series is rather slow, as can be seem in Reichl's Fig.9.5.

Fortunately, there is a well-known method, called the Pade approximation, for accelerating the convergence of a power series

$$P(x) = a_0 + a_1 x + \ldots + a_M x^M \quad (9.64)$$

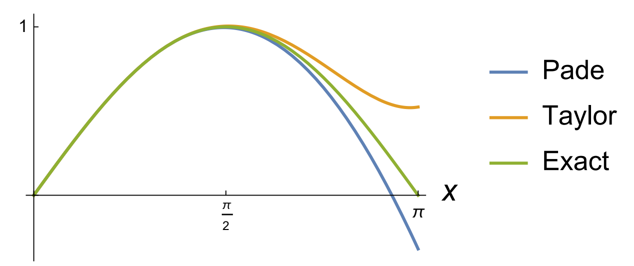
by replacing it with a rational polynomial

$$R(x) = \frac{b_0 + b_1 x + \ldots + b_m x^m}{c_0 + c_1 + \ldots + c_n x^n} \quad (9.65)$$

For example, the Taylor series for $\sin x$ with $M = 5$ and the Pade approximation with $m = 3$, $n = 2$ are [see §Code]

$$P(x) = x - \frac{x^3}{6} + \frac{x^5}{120} \qquad R(x) = \frac{x - \frac{7 x^3}{60}}{1 + \frac{x^2}{20}}$$

They are compared with the exact function $\sin x$ in the following graph.



Note that only powers up to x^3 is required in the Pade approximation while the Taylor series is up to x^5. Yet the former is the better approximation.

The Pade approximation to (9.64a) is [see §Code]

$$\frac{1.+\frac{0.175489\,N\,b_0}{V}+\frac{0.0416287\,N^2\,b_0^2}{V^2}}{1.-\frac{0.449511\,N\,b_0}{V}+\frac{0.0325733\,N^2\,b_0^2}{V^2}} \qquad (9.66a)$$

The difference between (9.66v) and Reichl's (9.66) may be attributed to the inferior precison of the data in (9.66a).

In order to produce the curves in Reichl's Fig.9.5a, we need to determine the excluded volume V_0, more accurately.

Reminder: In Exercise 9.2, we have made the casual assumption the $V_0 = N\,b_0$ based on the physical interpretation of the equation of state.

Since the radius of the spheres is $\frac{\sigma}{2}$, the total volume of the spheres is

$$\frac{4\,\pi}{3}\,N\left(\frac{\sigma}{2}\right)^3 = \frac{1}{4}\,N\,b_0$$

which is the theoretical value for V_0 in the gas phase.

In the condensed (fluid or solid) phase, V_0 is considerably larger than $\frac{1}{4}\,N\,b_0$ because, due to the inevitable space between spheres, packing a set of N balls of volume b_0 each requires a box much larger than $N\,b_0$. The smallest volume is achieved if the balls form a face-centered cubic lattice. For particles with hard core radius σ (or spheres with radius $\sigma/2$), the lattice constant of the f.c.c. lattice is easily found to be $a = \sqrt{2}\,\sigma$. Since there are 4 lattice sites in the unit cell, we have

$$V_0 = \frac{2^{3/2}}{4}\,N\,\sigma^3 = \frac{3\sqrt{2}}{4\,\pi}\,N\,b_0 \approx \frac{1}{2.96}\,N\,b_0 \approx 0.34\,N\,b_0$$

as the theoretical value for the excluded volume in the condensed phase.

In which case, (9.64a) becomes

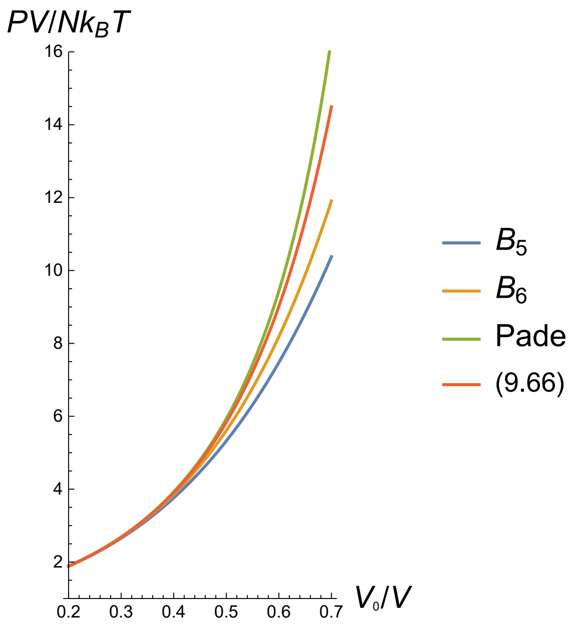
$$\frac{P\,V}{N\,k_B\,T} = 1 + \frac{4\,\pi}{3\sqrt{2}}\,\frac{V_0}{V}\,g(T)$$

$$g(T) \approx 1 + \frac{1.8512\,V_0}{V} + \frac{2.54416\,V_0^2}{V^2} + \frac{2.85834\,V_0^3}{V^3} + \frac{3.07861\,V_0^4}{V^4} \qquad (9.66b)$$

with a Pade approximation

$$g(T) \approx \frac{1.+\frac{0.519784\,V_0}{V}+\frac{0.365208\,V_0^2}{V^2}}{1.-\frac{1.33142\,V_0}{V}+\frac{0.285765\,V_0^2}{V^2}}$$

The following graph is our version of Reichl's Fig.9.5(a). The curve labeled (9.66) is the Pade approximation using Reichl's (9.66).



Code

Graphic outputs in this section are deleted to avoid repetition.

```
In[90]:= pe[x_, f_, n_, m_] := PadeApproximant[f[x], {x, 0, {n, m}}]
         ta[x_, f_, M_] := f[x] + O[x]^(M+1) // Normal

In[92]:= n = 3; m = 2; M = n + m;
         lst := {pe[x, f, n, m], ta[x, f, M], f[x]};

In[94]:= f = Sin[#] &;
         Plot[lst // Evaluate, {x, 0, π},
              AxesLabel → {"x", "sin x"},
              Ticks → {{0, π/2, π}, {0, 1}},
              PlotLegends → {"Pade", "Taylor", "Exact"}]

In[96]:= g6[x_] := 1 + 5/8 x + 0.29 x^2 + 0.11 x^3 + 0.04 x^4

In[97]:= g5[x_] := 1 + 5/8 x + 0.29 x^2 + 0.11 x^3

In[131]:= α = 4 π / (3. √2)

Out[131]= 2.96192

In[114]:= g6[x] /. x → b0 N/V
```

$$\text{Out[114]=}\ 1+\frac{5\,N\,b_0}{8\,V}+\frac{0.29\,N^2\,b_0^2}{V^2}+\frac{0.11\,N^3\,b_0^3}{V^3}+\frac{0.04\,N^4\,b_0^4}{V^4}$$

```
In[113]:= g6[α x] /. x -> V0/V
```

$$\text{Out[113]=}\ 1+\frac{1.8512\,V_0}{V}+\frac{2.54416\,V_0^2}{V^2}+\frac{2.85834\,V_0^3}{V^3}+\frac{3.07861\,V_0^4}{V^4}$$

In[127]:=
```
x =.;
pag[x_] = pe[x, g6[#] &, 2, 2]
```

Out[128]=
$$(1.000000000000000 + 0.175489\, x + 0.0416287\, x^2) / (1.000000000000000 - 0.449511\, x + 0.0325733\, x^2)$$

In[120]:=
```
pe[x, g6[#] &, 2, 2] /. x → b0 N/V // N
```

Out[120]=
$$\frac{1. + \frac{0.175489\, N\, b_0}{V} + \frac{0.0416287\, N^2\, b_0^2}{V^2}}{1. - \frac{0.449511\, N\, b_0}{V} + \frac{0.0325733\, N^2\, b_0^2}{V^2}}$$

In[121]:=
```
(pe[x, g6[α #] &, 2, 2] // N) /. x → V0/V
```

Out[121]=
$$\frac{1. + \frac{0.519784\, V_0}{V} + \frac{0.365208\, V_0^2}{V^2}}{1. - \frac{1.33142\, V_0}{V} + \frac{0.285765\, V_0^2}{V^2}}$$

In[103]:=
```
p66[x_] := (1 + 0.063507 x + 0.017329 x^2)/(1 - 0.561493 x + 0.081313 x^2)
```

In[129]:=
```
lse = {1 + α x g5[α x], 1 + α x g6[α x], 1 + α x pag[α x], 1 + α x p66[α x]};
Plot[lse // Evaluate, {x, .2, .7}, PlotRange → {1, 16},
    AxesLabel → {"V0/V", "PV/NkBT"},
    AspectRatio → 2,
    PlotLegends → {"B5", "B6", "Pade", "(9.66)"}]
```