

3.6 Hard Sphere Gas

The interactions between the atoms or molecules of a real gas comprise a strong repulsion at short distances and a weak attraction at long distances. Both of these are important in determining how the properties of the gas differ from those of an ideal (non-interacting) gas. We quote from Chaikin and Lubensky¹: “Although this seems like an immense trivialisation of the problem, there is a good deal of unusual and unexpected physics to be found in hard-sphere models.”

The hard-sphere interaction is

$$U(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$

where σ is the hard core diameter. It is indeed a simplification of a real inter-particle interaction – but what behaviour does it predict? What properties of real systems can be understood in terms of the short-distance repulsion? And, indeed, what properties cannot be understood from this simplification?

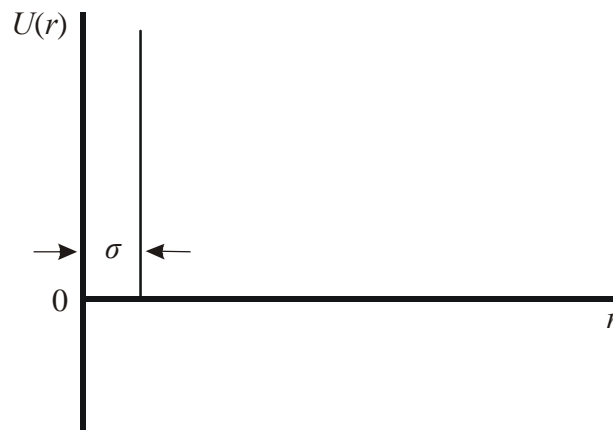


Fig. 3.1? *Hard core potential*

The direct way of solving the problem of the hard sphere fluid would be to evaluate the partition function; everything follows from that. Even for an interaction as simple as this, it turns out that the partition function cannot be evaluated analytically except in one dimension: the so-called Tonks ‘hard stick’ model. This leads to the Clausius equation of state. Certainly in two and three dimensions no explicit solution is possible.

(Question – is ‘excluded volume’ treatment a mean-field treatment – and so is the excluded volume argument then valid for four and higher dimensions? This can be tested using the virial coefficients calculated by Clisby and McCoy for four and higher dimensions.)

Arguments about why the partition function (really the configuration integral) is so difficult to evaluate are given in Reif. The point is that the excluded volumes appear in nested integrals.

Accepting that no analytic solution is possible, there is a number of approaches that might be considered: 1) mean field, 2) virial expansion, 3) molecular dynamics.

3.6.1 Mean field treatment

The mean field treatment of the hard sphere gas results in the Clausius equation of state: the ideal gas equation, but with an excluded volume term. This follows by analogy with our treatment of the van der Waals gas, where now there is no attractive term in the interaction. See also Problem 3.8.

3.6.2 Hard Sphere Equation of state

The equation of state of a hard-sphere fluid has a very special form. Recall that the Helmholtz free energy F is given in terms of the partition function Z by

$$F = -kT \ln Z .$$

We saw that the partition function for an interacting gas may be written as

$$Z = Z_{\text{id}} Q_N$$

where Z_{id} is the partition function for an ideal (non-interacting) gas

$$Z_{\text{id}} = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N$$

and Q_N is the configuration integral

$$Q_N = \frac{1}{V^N} \int e^{-\sum_{i<j} U_{ij}/kT} d^{3N} q .$$

To obtain the equation of state we must find the pressure, by differentiating the free energy

$$\begin{aligned} p &= - \left. \frac{\partial F}{\partial V} \right|_{T,N} \\ &= kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} \\ &= kT \left(\left. \frac{\partial \ln Z_{\text{id}}}{\partial V} \right|_{T,N} + \left. \frac{\partial \ln Q_N}{\partial V} \right|_{T,N} \right) . \end{aligned}$$

It is important, now, to appreciate that the configuration integral is independent of temperature. This must be so, since there is no energy scale for the problem; the interaction energy is either zero or it is infinite. Thus the ratio E/kT will be temperature-independent.

The pressure of the hard-sphere gas is then given by

$$p = kT \left(\frac{N}{V} + g(N/V) \right); \quad (\text{PP})$$

The function $g(N/V)$ is found by differentiating $\ln Q$ with respect to V . We know it is a function of N and V and in the thermodynamic limit the argument must be intensive. Thus the functional form and we have the low-density ideal gas limiting value $g(0) = 0$.

[Problem – show that the leading term in the expansion of $g(n)$ is in n^2 – i.e. show that there is no linear term.]

The important conclusion we draw from these arguments, and in particular from Eq. (PP) is that for a hard sphere gas the combination p/kT is a function of the density

N/V . This function must depend also on the only parameter of the interaction: the hard core diameter σ .

3.6.3 Virial Expansion

The virial expansion is written as

$$\frac{p}{kT} = \frac{N}{V} + B_2 \left(\frac{N}{V} \right)^2 + B_3 \left(\frac{N}{V} \right)^3 + \dots,$$

where the virial coefficients B_m are, in the general case, functions of temperature. However, as argued above, for the hard sphere gas the virial coefficients are temperature-independent.

The virial expansion may be regarded as a low-density approximation to the equation of state. Certainly this is the case when only a finite number of coefficients is available. If, however, all the coefficients were known, then provided the series were convergent, the sum would give p/kT for all values of the density N/V : the complete equation of state. Now although we are likely to know the values for but a finite number of the virial coefficients, there may be ways of guessing / inferring / estimating the higher-order coefficients. We shall examine two ways of doing this.

3.6.4 Virial Coefficients

The second virial coefficient for the hard sphere gas has been calculated; we found

$$B_2 = \frac{2}{3} \pi \sigma^3$$

where σ is the hard core diameter.

The general term of the virial expansion is $B_m (N/V)^m$, which must have the dimensions of N/V . Thus B_m will have the dimensions of (volume) $^{m-1}$. Now the only variable that the hard sphere virial coefficients depend on is σ . Thus it is clear that

$$B_m = \text{const} \times \sigma^{3(m-1)}$$

where the constants are dimensionless numbers – which must be determined.

It is increasingly difficult to calculate the higher-order virial coefficients; those up to sixth order were evaluated by Rhee and Hoover² in 1964, and terms up to tenth order were found by Clisby and McCoy³ in 2006. These are listed in the table below, in terms of the single parameter b :

$$b = B_2 = \frac{2}{3} \pi \sigma^3.$$

B_2/b	=	1
B_3/b^2	=	0.625
B_4/b^3	=	0.2869495
B_5/b^4	=	0.110252
B_6/b^5	=	0.03888198
B_7/b^6	=	0.01302354
B_8/b^7	=	0.0041832
B_9/b^8	=	0.0013094
B_{10}/b^9	=	0.0004035

Table 3.xx *Virial coefficients for the hard sphere gas*

Note/recall that the hard sphere virial coefficients are independent of temperature (Problem 3.7) and they are all expressed in terms of the hard core dimension.

We now consider ways of guessing / inferring / estimating the higher-order coefficients, so that the hard sphere equation of state may be approximated

3.6.5 Carnahan and Starling procedure

We start with the remarkable procedure of Carnahan and Starling⁴. They inferred a general (approximate) expression for the n^{th} virial coefficient, enabling them to sum the virial expansion and thus deduce an (approximate) equation of state. The virial expansion is written as

$$\frac{pV}{NkT} = 1 + B_2 \left(\frac{N}{V} \right) + B_3 \left(\frac{N}{V} \right)^2 + B_4 \left(\frac{N}{V} \right)^3 + \dots \quad (\text{HH})$$

This is written out for the known values of the virial coefficients:

$$\begin{aligned} \frac{pV}{NkT} = & 1 + b \frac{N}{V} + 0.625 \left(b \frac{N}{V} \right)^2 + 0.2869495 \left(b \frac{N}{V} \right)^3 + 0.110252 \left(b \frac{N}{V} \right)^4 + 0.03888198 \left(b \frac{N}{V} \right)^5 + \\ & + 0.01302354 \left(b \frac{N}{V} \right)^6 + 0.0041832 \left(b \frac{N}{V} \right)^7 + 0.0013094 \left(b \frac{N}{V} \right)^8 + 0.0004035 \left(b \frac{N}{V} \right)^9 + \dots \end{aligned}$$

In terms of the dimensionless density variable $y = Nb/4V$ this becomes

$$\begin{aligned} \frac{pV}{NkT} = & 1 + 4y + 10y^2 + 18.364768y^3 + 28.224512y^4 + 39.81514752y^5 + \\ & + 53.34441984y^6 + 68.5375488y^7 + 85.8128384y^8 + 105.775104y^9 + \dots \end{aligned} \quad (\text{BB})$$

Note only terms up to y^5 were known to Carnahan and Starling. And they observed that if these coefficients were rounded to whole numbers: 4, 10, 18, 28, 40, then the coefficient of y^n was given by $n(n+3)$. They then made the assumption that this expression would work for the higher-order terms as well. We can check this hypothesis with the newly-known virial coefficients; Carnahan and Starling's formula gives 54, 70, 88, 108; the actual rounded integers are 53, 69, 86, 106. The agreement is still quite good.

From this assumption, the general expression for the n^{th} virial coefficient is

$$B_n = \frac{(n-1)(n+2)}{4^{n-1}} b^{n-1}. \quad (\text{JJ})$$

These are tabulated below, together with the true values.

			C+S value
B_2/b	=	1	1
B_3/b^2	=	0.625	0.625
B_4/b^3	=	0.2869495	0.28125
B_5/b^4	=	0.110252	0.109375
B_6/b^5	=	0.03888198	0.0390625
B_7/b^6	=	0.01302354	0.0131836
B_8/b^7	=	0.0041832	0.00427246
B_9/b^8	=	0.0013094	0.00134277
B_{10}/b^9	=	0.0004035	0.000411987

If we now sum the infinite series of Eq. (HH), with the general B_n given by Eq. (JJ), we obtain

$$\frac{pV}{NkT} = 1 + \frac{4y + 2y^2}{(1-y)^3}.$$

In terms of the number density N/V this gives the equation of state as

$$\frac{p}{kT} = \frac{N}{V} \left\{ 1 + \frac{b \frac{N}{V} + \frac{b^2}{8} \left(\frac{N}{V} \right)^2}{\left(1 - \frac{b}{4} \frac{N}{V} \right)^3} \right\}. \quad (\text{AA})$$

Incidentally, the universal function $g(n)$ of Eq. (PP) is then given by

$$g(n) = n \frac{bn + (bn)^2/8}{(1-bn/4)^3}.$$

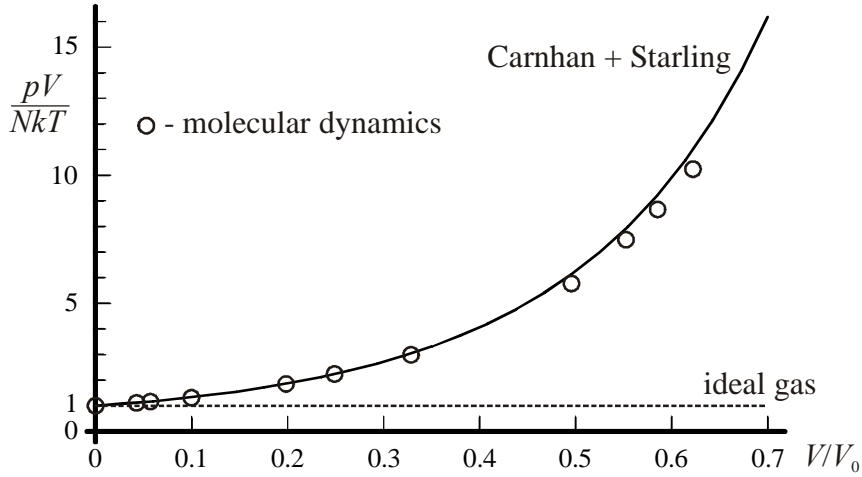
Conventionally the equation of state is expressed and plotted in terms of the ‘packing fraction’ V_0/V , where V_0 is the volume occupied by the hard spheres $V_0 = N\pi\sigma^3/4$ so that

$$\frac{V_0}{V} = \frac{\pi\sigma^3}{4} \frac{N}{V} = \frac{3b}{8} \frac{N}{V}.$$

Then we obtain

$$\frac{p}{kT} = \frac{N}{V} \left\{ 1 + \frac{\frac{8}{3} \frac{V_0}{V} + \frac{8}{9} \left(\frac{V_0}{V} \right)^2}{\left(1 - \frac{2}{3} \frac{V_0}{V} \right)^3} \right\}.$$

This is plotted in the figure below. For comparison we have also shown some data points obtained by molecular dynamics simulations⁵.



pV/NkT as a function of V_0/V

We note that a random assembly of spheres will pack to $V_0/V = 0.638$ so this is the greatest density possible for the fluid. However a close-packed lattice (fcc or hcp) will pack more densely, to 0.7405. Thus there should be a phase transition to a solid phase.

(I believe the lack of an attractive part of the inter-particle interaction means that there will be no gas-liquid transition. I think the attraction is needed to have a self-bound fluid phase coexisting with a dispersed gas phase.)

At higher densities the data points from molecular dynamics simulations fall consistently below the curve of Carnahan and Starling. This indicates the shortcoming of their method. Inspired as Eq. (JJ) is and as elegant as Eq. (AA) is, they are not quite correct. And the discrepancy is expected to become greater at the higher densities. Perhaps the problem is to be expected – after all, even the lower order virial coefficients have been approximated, when the coefficients of the powers of y in Eq. (BB) were truncated to integers.

A more systematic way at arriving at an equation of state is the Padé method.

3.6.6 Padé approximants

The equation of state of the hard sphere gas takes the form

$$\frac{pV}{NkT} = f(V_0/V)$$

where f is a universal function of its argument. So if the function is determined then the hard sphere equation of state is known.

The virial series gives f as a power series in its argument. And in reality one can only know a finite number of these terms. The Carnahan and Starling procedure takes the known terms, ‘guesses’ the (infinite number of) higher-order terms and then sums the series. The figure above indicates that the result is good, but it could be better.

For the Carnahan and Starling equation of state the function f may be written as

$$f(x) = \frac{1 + \frac{2}{3}x + \frac{20}{9}x^2 - \frac{8}{27}x^3}{1 - 2x + \frac{4}{3}x^2 - \frac{8}{27}x^3}.$$

In this form we observe that $f(x)$ is the quotient of two polynomials. And this leads us naturally to the Padé method.

One knows $f(x)$ to a finite number of terms. In the Padé method the function $f(x)$ is approximated by the quotient of two polynomials

$$f(x) \approx F_{n,m}(x) = \frac{P_n(x)}{Q_m(x)}.$$

Here $P_n(x)$ and $Q_m(x)$ are polynomials of degrees n and m respectively.

$$P_n(x) = p_0 + p_1x + p_2x^2 + \dots + p_nx^n,$$

$$Q_m(x) = q_0 + q_1x + q_2x^2 + \dots + q_mx^m.$$

Without loss of generality we may (indeed it is convenient to) restrict $q_0 = 1$.

The terms of $P_n(x)$ and $Q_m(x)$ may be determined so long as $f(x)$ is known to at least $n + m$ terms. In other words if $f(x)$ is known to $n + m$ terms, then $F_{n,m}(x)$ agrees with the known terms of the series for $f(x)$; moreover the quotient generates a series of higher order terms as well. The hope is that this series will be a good approximation to the true (but unknown) $f(x)$.

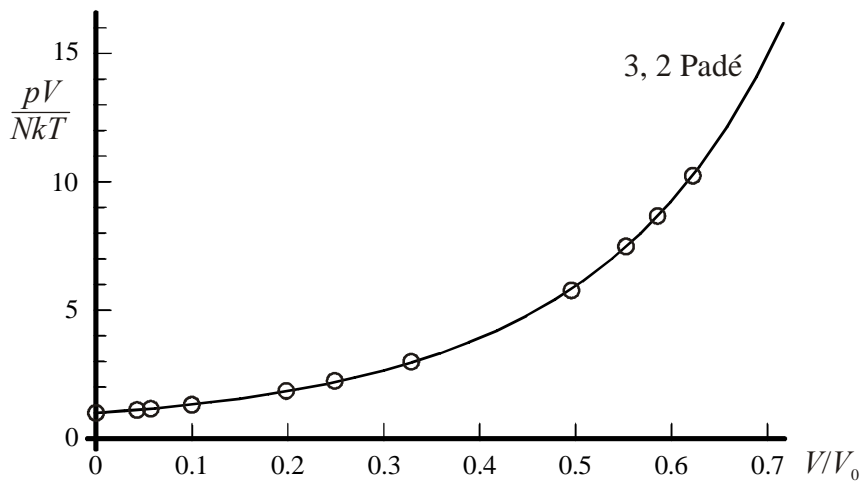
Power series of $f(x)Q_m(x) - P_n(x)$ begins with the term x^{m+n+1} .

One can construct approximants with different m, n subject to $m + n = N$. See Reichl for (some) details.

In this way Ree and Hoover (1964) – (i.e. before Clisby and McCoy’s extra virial coefficients) constructed the approximant:

$$\frac{pV}{NkT} = 1 + \frac{2.66667 \frac{V_0}{V} + 0.451605 \left(\frac{V_0}{V}\right)^2 + 0.328609 \left(\frac{V_0}{V}\right)^3}{1 - 1.49731 \frac{V_0}{V} + 0.578226 \left(\frac{V_0}{V}\right)^2}.$$

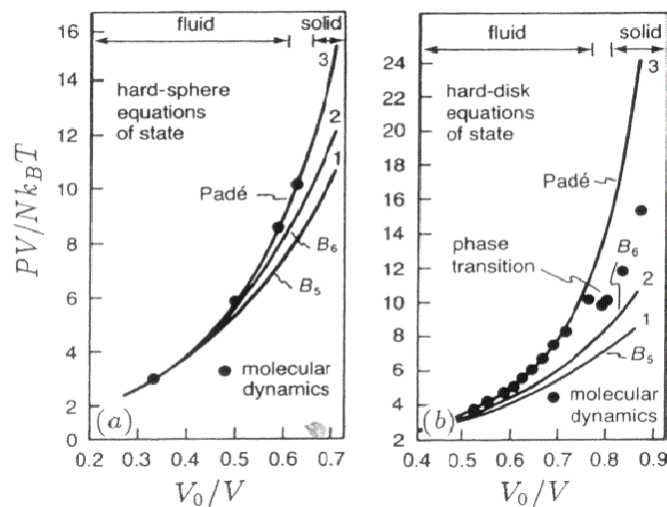
This is plotted in the figure below. Observe the agreement with the molecular dynamics simulation data is very good indeed; it is considerably better than the Carnhan and Starling equation of state.



Padé approximant to hard sphere equation of state

3.6.7 Phase transition

We note that a random assembly of spheres will pack to $V_0/V = 0.638$ so this is the greatest density possible for the fluid. However a close-packed lattice (fcc or hcp) will pack more densely, to 0.7405. Thus there should be a phase transition to a solid phase.



3d hard spheres

2d hard discs

(from Reichl)

The lack of an attractive part of the inter-particle interaction means that there will be no gas-liquid transition; attraction is needed to have a self-bound fluid phase coexisting with a dispersed gas phase. The transition to the solid phase is seen in the two-dimensional simulations.

¹ P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press, (1995).

² F. H. Rhee and W. G. Hoover, *J. Chem. Phys.* **40**, 939 (1964)

³ N. Clisby and B. McCoy, arXiv: cond-mat/0503525 v1 21 Mar (2005)

⁴ N. F. Carnahan, K. E. Starling, *J. Chem. Phys.* **51**, 635, (1969)

⁵ J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**, 321 (1984)