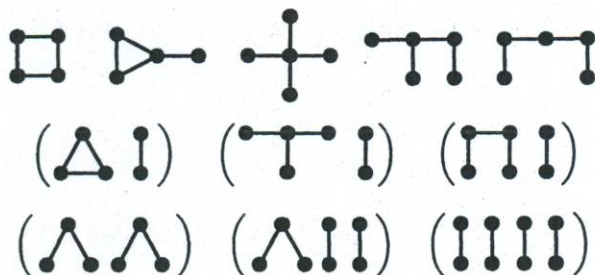The factor of 3! comes from the ways of interchanging the subdiagrams with each other, while the factor of 2^3 comes from the number of ways of reversing the individual sub-diagrams. Alternatively, we can count the number of ways of choosing six molecules to interact in disjoint pairs: $N(N-1)/2$ for the first pair, $(N-2)(N-3)/2$ for the second pair, $(N-4)(N-5)/2$ for the third pair, and then divide by 3! because any of the three pairs could have been chosen first, and either of the remaining two could have been chosen second.

Problem 8.2. Here are all the diagrams corresponding to four factors of f_{ij}:

$$\square \quad \triangleright\!\!-\!\!\cdot \quad +\!\!\!\cdot \quad \cdot\sqcap\,\cdot \quad \sqcap\!\!-\!\!\cdot$$

$$(\triangle\,\text{I}) \quad (\top\,\text{I}) \quad (\sqcap\,\text{I})$$

$$(\wedge\wedge) \quad (\wedge\,\text{II}) \quad (\text{IIII})$$

Problem 8.3. Expanding the exponential in a third-order Taylor series, we have

$$\exp\!\left(\text{I} + \triangle\right) = 1 + \left(\text{I} + \triangle\right) + \tfrac{1}{2}\left(\text{I} + \triangle\right)^2 + \tfrac{1}{3!}\left(\text{I} + \triangle\right)^3$$

$$= 1 + \text{I} + \triangle + \tfrac{1}{2}\left(\text{I}\right)^2 + \left(\text{I}\,\triangle\right) + \tfrac{1}{2}\left(\triangle\right)^2$$

$$+ \tfrac{1}{3!}\left(\text{I}\right)^3 + \tfrac{1}{2}\left[\left(\text{I}\right)^2\triangle\right] + \tfrac{1}{2}\left[\text{I}\left(\triangle\right)^2\right] + \tfrac{1}{3!}\left(\triangle\right)^3$$

Notice that wherever a diagram appears squared, there is an accompanying factor of 1/2. If we approximate $N = (N-1) = (N-2)\cdots$, then 1/2 times the square of a diagram is the same thing as a disconnected diagram in which the original diagram is duplicated:

$$\tfrac{1}{2}\left(\text{I}\right)^2 \approx \left(\text{I}\,\text{I}\right); \qquad \tfrac{1}{2}\left(\triangle\right)^2 \approx \left(\triangle\,\triangle\right).$$

In each case, the factor of 1/2 is implicit in the symmetry factor of the disconnected diagram. Similarly,

$$\tfrac{1}{3!}\left(\text{I}\right)^3 \approx \left(\text{I}\,\text{I}\,\text{I}\right); \qquad \tfrac{1}{3!}\left(\triangle\right)^3 \approx \left(\triangle\,\triangle\,\triangle\right).$$

With these approximations, therefore, the numerical factors in our formula completely disappear, leaving a simple sum of all possible diagrams, connected and disconnected, that can be constructed from up to three of the basic two-dot and triangle diagrams.

Similarly, using the results of the previous problem,

$$\bigwedge \sim \frac{N^3 v^2}{V^2}; \qquad \mathsf{T} \sim \frac{N^4 v^3}{V^3}; \qquad \Pi \sim \frac{N^4 v^3}{V^3}.$$

The disconnected diagrams, aside from their symmetry factors, are basically products of connected diagrams, so

$$\left(\mathsf{I}\,\mathsf{I}\right) \sim \frac{N^4 v^2}{V^2}; \qquad \left(\mathsf{I}\bigwedge\right) \sim \frac{N^5 v^3}{V^3}; \qquad \left(\mathsf{I}\,\mathsf{I}\,\mathsf{I}\right) \sim \frac{N^6 v^3}{V^3}.$$

The only remaining diagram in equation 8.20 is the triangle. If we imagine defining relative coordinates $\vec{r}_a = \vec{r}_1 - \vec{r}_2$ and $\vec{r}_b = \vec{r}_1 - \vec{r}_3$, then the arguments of the f-functions can be written as r_a, r_b, and $|\vec{r}_a - \vec{r}_b|$. A change of variables then leaves one overall integral that gives a factor of V, while the remaining two integrals, of a product of three f-functions, must evaluate to something of order v^2. Therefore,

$$\triangle \sim \frac{N^3 v^2}{V^2}.$$

Looking over these estimates, we should note that while V/v is greater than N in a low-density gas, it is normally greater by only a few orders of magnitude (perhaps a factor of a thousand). Thus, the basic two-dot diagram might be of order $N/1000$, which is a large number. Connected diagrams with three or more dots are suppressed by more factors of V/Nv, so at least they're smaller than the two-dot diagram. But the disconnected diagrams are much larger, since they have a greater excess of powers of N over powers of v/V. For example, the first disconnected diagram would typically be of order $(N/1000)^2$, while the third disconnected diagram would be of order $(N/1000)^3$. Because these diagrams are growing larger and larger, the series isn't going to converge until the symmetry factors also become quite large. Fortunately, exponentiating the series saves us from having to evaluate all the disconnected diagrams.

Problem 8.7. Let's carefully write out the quadratic term in the series 8.22:

$$\frac{1}{2}\left(\mathsf{I}\right)^2 = \frac{1}{2}\left(\frac{1}{2}\frac{N(N-1)}{V^2}\int d^3r_1\, d^3r_2\, f_{12}\right)^2 = \frac{1}{8}\frac{N^2(N-1)^2}{V^2}\left(\int d^3r\, f(r)\right)^2$$

$$= \left[\frac{1}{8}N^4 - \frac{1}{4}N^3 + \frac{1}{8}N^2\right]\frac{v^2}{V^2},$$

where v is defined to equal $\int d^3r\, f(r)$, a number that's on the order of the volume of a molecule. On the other hand, the diagrams in equations 8.18 and 8.19 are

$$\left(\mathsf{I}\,\mathsf{I}\right) = \frac{1}{8}\frac{N(N-1)(N-2)(N-3)}{V^4}\int d^3r_1\, d^3r_2\, d^3r_2\, d^3r_4\, f_{12}f_{34}$$

$$= \frac{1}{8}\frac{N^4 - 6N^3 + 11N^2 - 6N}{V^2}\left(\int d^3r\, f(r)\right)^2$$

$$= \left[\frac{1}{8}N^4 - \frac{3}{4}N^3 + \frac{11}{8}N^2 - \frac{3}{4}N\right]\frac{v^2}{V^2}$$

and

$$\bigwedge = \frac{1}{2}\frac{N(N-1)(N-2)}{V^3}\int d^3r_1\, d^3r_2\, d^3r_3\, f_{12}f_{23}$$

$$= \frac{1}{2}\frac{N^3 - 3N^2 + 2N}{V^2}\left(\int d^3r\, f(r)\right)^2$$

$$= \left[\frac{1}{2}N^3 - \frac{3}{2}N^2 + N\right]\frac{v^2}{V^2},$$

where I've written everything in terms of the same basic integral as in Problem 8.5. The sum of these two diagrams is therefore

$$(\text{|}\text{|}\text{|}) + \bigwedge = \left[\frac{1}{8}N^4 - \frac{1}{4}N^3 - \frac{1}{8}N^2 + \frac{1}{4}N\right]\frac{v^2}{V^2}.$$

Comparing this expression to the first one above, we find that

$$\frac{1}{2}(\text{|}\text{|})^2 = (\text{|}\text{|}\text{|}) + \bigwedge + \left[\frac{1}{4}N^2 - \frac{1}{4}N\right]\frac{v^2}{V^2}.$$

Now recall that for a low-density gas, V/v must be greater than N by at least a couple of orders of magnitude. This implies that the terms proportional to N^4 and N^3 in the preceding expressions are large, but the leftover terms proportional to N^2 and N are actually much less than 1, when we include the factor of $(v/V)^2$. These terms therefore contribute negligibly to the partition function. Alternatively, when we take the logarithm of the partition function to get the free energy, then differentiate with respect to V to get the pressure, the leading terms will give contributions that are intensive as desired (proportional to powers of N/V), but the leftover terms will have more powers of V in the denominator than powers of N in the numerator, so they will vanish in the thermodynamic limit.

Problem 8.8. Each diagram in equation 8.23, when evaluated, will give one overall factor of V, times an integral that is of order v^{n-1}, where v is the volume of a molecule and n is the number of dots in the diagram. Thus, a diagram with n dots is of order $N^n(v/V)^{n-1}$. When such a diagram is differentiated to obtain a contribution to the pressure (see equation 8.27), it then picks up another factor of V in the denominator. To obtain the corresponding term in the virial expansion, we factor out N/V, which gives an expression of order $(Nv/V)^{n-1}$. This expression has the form of the nth term in the virial expansion (equation 8.33), since it is a density-independent quantity times $(N/V)^{n-1}$. In particular, the third virial coefficient, $C(T)$, is determined entirely by the triangle diagram:

$$\bigtriangleup = \frac{1}{3!}\frac{N^3}{V^3}\int d^3r_1\, d^3r_2\, d^3r_3\, f_{12}f_{23}f_{31}.$$

Changing variables to $\vec{r}_a = \vec{r}_2 - \vec{r}_1$ and $\vec{r}_b = \vec{r}_2 - \vec{r}_3$, this becomes

$$\bigtriangleup = \frac{1}{6}\frac{N^3}{V^3}\int d^3r_1\left(\int d^3r_a\, d^3r_b\, f(r_a)f(r_b)f(|\vec{r}_a - \vec{r}_b|)\right)$$

$$= \frac{1}{6}\frac{N^3}{V^2}\int d^3r_a\, d^3r_b\, f(r_a)f(r_b)f(|\vec{r}_a - \vec{r}_b|).$$

The first line defines the constants r_0 and u_0, in units of ångstroms and electron-volts. (I started with the values 4.0 and 0.01, then adjusted the values by trial and error to obtain a good fit to the theoretical prediction.) The second line defines a list of t values, multiplying the kelvin temperatures by k/u_0 to convert them to the dimensionless quantity t. The third line defines a list of values of B, similarly scaled by a factor of r_0^3 for comparison to the theoretical plot. Note also the factor of 10^{-8} to convert ångstroms to centimeters, and the factor of Avogadro's number to convert the virial coefficient per mole to the virial coefficient per molecule. The fourth line combines the two lists of numbers and produces a plot of the data points. Finally, to show the theoretical curve and the data on the same graph, I gave the instruction Show[LJplot,N2plot], which produced the following:
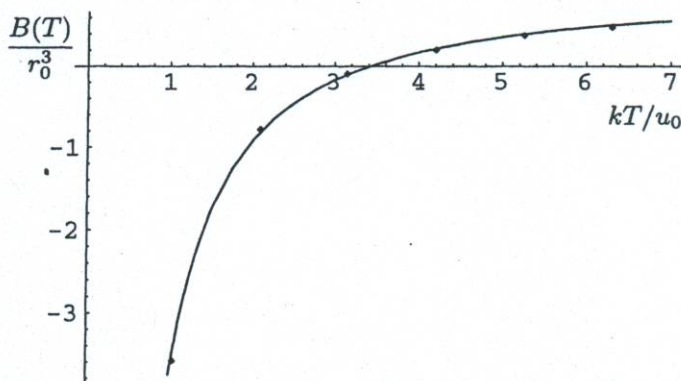
Although the fit isn't perfect, it's probably within the experimental error of the data points, and it's definitely much better than the fit to the van der Waals model in Problem 1.17.

Problem 8.11. The Mayer f-function is defined as $e^{-u(r)/kT} - 1$. For a gas of hard spheres, this would be zero when $r > r_0$ (and $u(r) = 0$) and -1 when $r < r_0$ (and $u(r) = \infty$). Here is a plot:
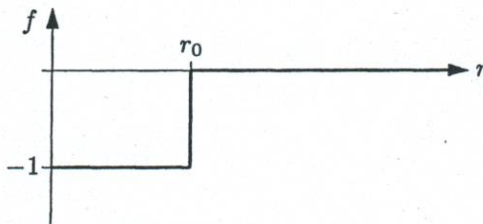
The second virial coefficient for this gas would therefore be

$$B(T) = -2\pi \int_0^\infty r^2 f(r) \, dr = +2\pi \int_0^{r_0} r^2 \, dr = \frac{2\pi r_0^3}{3}.$$

This is just a constant, independent of temperature. Therefore, at low densities, the pressure of the gas should be greater than NkT/V by a fraction equal to $NB/V = N(2\pi r_0^3/3)/V$. Although the precise numerical factor is hard for me to interpret, this result is sensible because the fractional increase in pressure is of the same order as the fraction of the total volume occupied by the molecules themselves.

Problem 8.12. Taking $u(r)$ to be infinite for $r < r_0$, the integral (8.36) for $B(T)$ conveniently splits into two pieces:

$$B(T) = -2\pi \int_0^\infty r^2 (e^{-\beta u(r)} - 1)\, dr = -2\pi \int_0^{r_0} r^2 (e^{-\beta u(r)} - 1)\, dr - 2\pi \int_{r_0}^\infty r^2 (e^{-\beta u(r)} - 1)\, dr.$$

In the first piece, $e^{-\beta u(r)} = e^{-\infty} = 0$, so the integral evaluates to $-r_0^3/3$ as in Problem 8.11. In the second piece, we are to assume that $|u(r)|$ is no greater than u_0 and that $kT \gg u_0$, so we can expand $e^{-\beta u(r)} \approx 1 - \beta u(r)$. Canceling the 1's, we obtain

$$B(T) \approx \frac{2\pi r_0^3}{3} + 2\pi \int_{r_0}^\infty r^2\, \beta u(r)\, dr.$$

The factor of $\beta = 1/kT$ can be pulled outside the integral, so this expression has the form

$$B(T) = b - \frac{a}{kT},$$

where

$$b = \frac{2\pi r_0^3}{3} \quad \text{and} \quad a = -2\pi \int_{r_0}^\infty r^2 u(r)\, dr.$$

This result agrees with the prediction of the van der Waals model, Problem 1.17(c), although here we see that this form for $B(T)$ should be accurate only at relatively high temperatures, and only if the molecules have an impenetrable "hard core" where $u = \infty$. The prediction for b is of the order of the volume of a molecule as expected. The prediction for a is of order $u_0 r_0^3$, assuming that $u(r)$ becomes negligible beyond a distance of order r_0; this is what we would expect from the discussion on page 180.

Problem 8.13. The average energy of an interacting gas can be computed from the formula derived in Problem 6.16:

$$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \ln Z_{\text{ideal}} - \frac{\partial}{\partial \beta} \ln Z_c.$$

The first term is the same as for an ideal gas, so it evaluates to $\frac{3}{2} NkT$ as in Section 6.7. The correction term can be written in terms of diagrams using equation 8.23:

$$\Delta U = -\frac{\partial}{\partial \beta} \left(\text{◦┊◦} + \text{△} + \text{▢} + \cdots \right).$$

If we keep only the first diagram, and evaluate it explicitly as in equation 8.31, then

$$\Delta U = -\frac{\partial}{\partial \beta} \left(\frac{1}{2} \frac{N^2}{V} \int d^3 r\, f(r) \right) = -\frac{1}{2} \frac{N^2}{V} (4\pi) \int_0^\infty r^2 \frac{\partial}{\partial \beta} (e^{-\beta u(r)} - 1)\, dr$$

$$= 2\pi \frac{N^2}{V} \int_0^\infty r^2 u(r) e^{-\beta u(r)}\, dr.$$