Origin of the a/V_m^2 term

Assume n_moles moles of gas in volume V. The number of nearest neighbours is proportional to n_moles/V, and so attractive intermolecular interactions lower the total potential energy by an amount proportional the number of atoms multiplied by the number of nearest neighbours, i.e. we can write the energy change as

$$\frac{an_\mathrm{moles}^2}{V}, \tag{26.3}$$

where a is a constant. Hence, if you change V, the energy changes by an amount

$$-\frac{an_\mathrm{moles}^2\mathrm{d}V}{V^2}, \tag{26.4}$$

but this energy change can be thought of as being due to an effective pressure p_eff, so that the energy change would be $-p_\mathrm{eff}\,\mathrm{d}V$. Hence

$$p_\mathrm{eff} = -a\frac{n_\mathrm{moles}^2}{V^2} = -\frac{a}{V_\mathrm{m}^2}. \tag{26.5}$$

The pressure p that you measure is the sum of the pressure p_ideal neglecting intermolecular interactions and p_eff. Therefore

$$p_\mathrm{ideal} = p - p_\mathrm{eff} = p + \frac{a}{V_\mathrm{m}^2} \tag{26.6}$$

is the pressure which you have to enter into the formula for the ideal gas,

$$p_\mathrm{ideal}V_\mathrm{m} = RT, \tag{26.7}$$

making the correction $V_\mathrm{m} \to V_\mathrm{m} - b$ to take account of the excluded volume. This yields

$$\left(p + \frac{a}{V_\mathrm{m}^2}\right)(V_\mathrm{m} - b) = RT, \tag{26.8}$$

in agreement with eqn 26.10. This equation of state can also be justified from statistical mechanics as follows: taking the expression for the partition function of N molecules in a gas, $Z_N = (1/N!)(V/\lambda_\mathrm{th}^3)^N$, we replace the volume V by $V - n_\mathrm{moles}b$, the volume actually available for molecules to move around in; we also include a Boltzmann factor $\mathrm{e}^{-\beta(-an_\mathrm{moles}^2/V)}$ to give

$$Z_N = \frac{1}{N!}\left(\frac{V - n_\mathrm{moles}b}{\lambda_\mathrm{th}^3}\right)^N \mathrm{e}^{\beta an_\mathrm{moles}^2/V}, \tag{26.9}$$

which after using $F = -k_\mathrm{B}T\ln Z_N$ and $p = -(\partial F/\partial V)_T$ yields the van der Waals equation of state.