fugacity expansion for classical gases

$z = e^{\beta\mu}$

$$\mathcal{Z} = \sum_{0}^{\infty}{}_N\, z^N Z_N = 1 + z Z_1 + z^2 Z_2 + \mathcal{O}(z^3)$$

$$\ln \mathcal{Z} = z Z_1 + z^2 Z_2 - \frac{z^2}{2} Z_1^2 = \cancel{z Z_1 + \frac{z^2}{2} Z_2}$$

$$\Omega = -PV = -\frac{\left(z - \frac{z^2}{2} Z_1\right) Z_1 + z^2 Z_2}{\beta}$$

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = -\frac{\partial \Omega}{\partial z}\frac{\partial z}{\partial \mu} = +\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial z}\right)\beta z = z \frac{\partial \ln \mathcal{Z}}{\partial z}$$

$$\langle N \rangle = z\left(Z_1 + 2 z Z_2 - z Z_1^2\right)$$

$$\frac{\beta P}{\rho} = \frac{\left(z - \frac{z^2}{2} Z_1\right) Z_1 + z^2 Z_2}{z Z_1 + 2 z^2 Z_2 - z^2 Z_1^2} = \frac{Z_1 + z\left(Z_2 - \frac{1}{2} Z_1^2\right)}{Z_1 + 2z\left(Z_2 - \frac{1}{2} Z_1^2\right)} = \frac{1 + z\varepsilon}{1 + 2z\varepsilon}$$

$$\varepsilon = \left(Z_2 - \frac{1}{2} Z_1^2\right) / Z_1$$

$$\frac{\beta P}{\rho} \cong (1 + z\varepsilon)(1 - 2z\varepsilon) = 1 + z\varepsilon - 2z\varepsilon = 1 - z\varepsilon$$

$$\frac{\beta P}{\rho} = 1 - z\,\frac{Z_2 - \frac{1}{2} Z_1^2}{Z_1} = 1 + z Z_1\left[\frac{1}{2} - \frac{Z_2}{Z_1^2}\right]$$

we can eliminate z from this equation leading to the equation of state

$$z = \frac{\langle N \rangle}{Z_1}$$

assuming z calculated to first order one get

$$\ln \mathcal{Z} = z Z_1$$

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \mathcal{Z} = z Z_1$$

$$\frac{\beta P}{\rho} = 1 + \langle N \rangle \left[\frac{1}{2} - \frac{Z_2}{Z_1^2} \right]$$

therefore the ~~first~~ second virial coefficient is

$$\frac{\beta P}{\rho} = 1 + \rho \underbrace{V \left[\frac{1}{2} - \frac{Z_2}{Z_1^2} \right]}_{B_2}$$

Better Use

$$Z_2 - \frac{1}{2} Z_1^2$$

$$B_2 = V \frac{Z_1^2 - 2Z_2}{2 Z_1^2} = -\frac{V}{Z_1} \frac{Z_2 - \frac{1}{2} Z_1^2}{Z_1} = -\frac{V}{Z_1} \varepsilon$$

$$\mathcal{Z}_1 = \int \frac{d^3q\, d^3p}{h^3\, 1!}\, e^{-\beta \frac{p_1^2}{2m}} = \frac{V}{\lambda^3}$$ no ext fields

$$\mathcal{Z}_2 = \frac{1}{2!}\int \frac{d^3q_1}{\lambda^3}\frac{d^3q_2}{\lambda^3}\, e^{-\beta V(q_1-q_2)}$$

$$\mathcal{Z}_2 - \frac{1}{2}\mathcal{Z}_1^2 = \frac{1}{2}\int \frac{d^3q_1\, d^3q_2}{\lambda^3\lambda^3} - \frac{1}{2}\int \frac{d^3q_1}{\lambda^3}\frac{d^3q_2}{\lambda^3}$$

$$= \frac{1}{2}\int \frac{d^3q_1\, d^3q_2}{\lambda^6}\left(e^{-\beta V(q_1-q_2)} - 1\right) = \frac{V}{2\lambda^6}\int d^3r\left(e^{-\beta V(r)} - 1\right)$$

$$\frac{\mathcal{Z}_2 - \frac{1}{2}\mathcal{Z}_1^2}{\mathcal{Z}_1} = \frac{1}{2\lambda^3}\int d^3r\left[e^{-\beta v(r)} - 1\right] = \varepsilon$$

eliminate $z = e^{+\beta\mu}$ to get the equation of state to first order

$$\ln \mathcal{Z} = z\mathcal{Z}_1$$

$$\langle N\rangle = z\frac{\partial}{\partial z}\ln\mathcal{Z} = z\mathcal{Z}_1$$

$$\Rightarrow z = \frac{\langle N\rangle}{\mathcal{Z}_1}$$ therefore

$$\frac{\beta P}{\rho} = 1 - \frac{\langle N\rangle}{\mathcal{Z}_1}\varepsilon = 1 - \frac{\langle N\rangle}{V}\lambda^3\frac{1}{2\lambda^3}\int d^3r\left(e^{-\beta v(r)} - 1\right)$$

$$\frac{\beta P}{\rho} = 1 - \frac{\rho}{2}\int d^3r \left(e^{-\beta v(r)} - 1\right)$$

at low density

$$B_2 = -\frac{1}{2}\int d^3r \left[e^{-\beta v(r)} - 1\right]$$

Mayer function

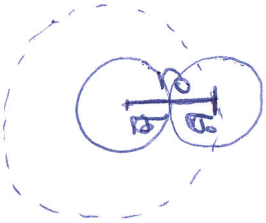
for hard spheres

$$v(r) = \begin{cases} = \infty & |r| < r_0 \\ = 0 & \text{otherwise} \end{cases}$$

$$B_2 = +\frac{1}{2} 4\pi \int_0^{r_0} dr\, r^2 = +\frac{1}{2}\left(\frac{4}{3}\pi r_0^3\right)$$

~~excluded volume~~
~~volume of the hard sphere~~

$$\frac{\beta P}{\rho} = 1 + \frac{\rho}{2} v_{excl}$$



the ~~volume~~ radius of the sphere is σ therefore $r_0 = 2\sigma$

$$B_2 = \frac{1}{\cancel{2}}\,\frac{4}{3}\pi \cancel{8}^{\,4} \sigma^3 = 4\, v_{sphere}$$

The virial coefficients of the hard sphere fluids do not depend on temperature

$$\frac{\beta P}{\rho} = 1 + \rho \underbrace{V\left[-\frac{Z_2 - \frac{1}{2}Z_1^2}{Z_1^2}\right]}_{B_2} + B_3\rho^2 + B_4\rho^3 + \cdots$$

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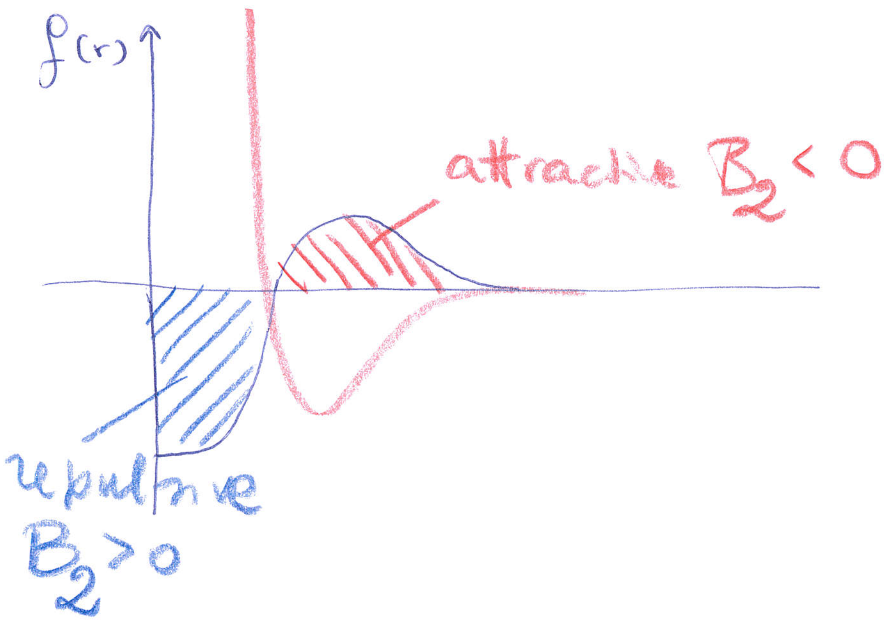
$$Z_1 = \frac{V}{\lambda^3}$$

$$Z_2 = \frac{1}{2!}\int \frac{d^3q_1\, d^3q_2\, e^{-\beta U}}{\lambda^6} = \frac{V}{2\lambda^6}\int d^3r\, e^{-\beta U}$$

$$Z_2 - \frac{1}{2}Z_1^2 = \frac{V}{2\lambda^6}\int dr\, e^{-\beta U(r)} - \frac{V^2}{2\lambda^6} = \frac{V}{2\lambda^6}\int dr\left(e^{-\beta U(r)} - 1\right)$$

$$V\,\frac{Z_2 - \frac{1}{2}Z_1^2}{Z_1^2} = \frac{\frac{\cancel{V}^2}{2\cancel{\lambda^6}}\int d^3r\left(e^{-\beta U(r)} - 1\right)}{\cancel{V^2/\lambda^6}} = \frac{1}{2}\int d^3r$$

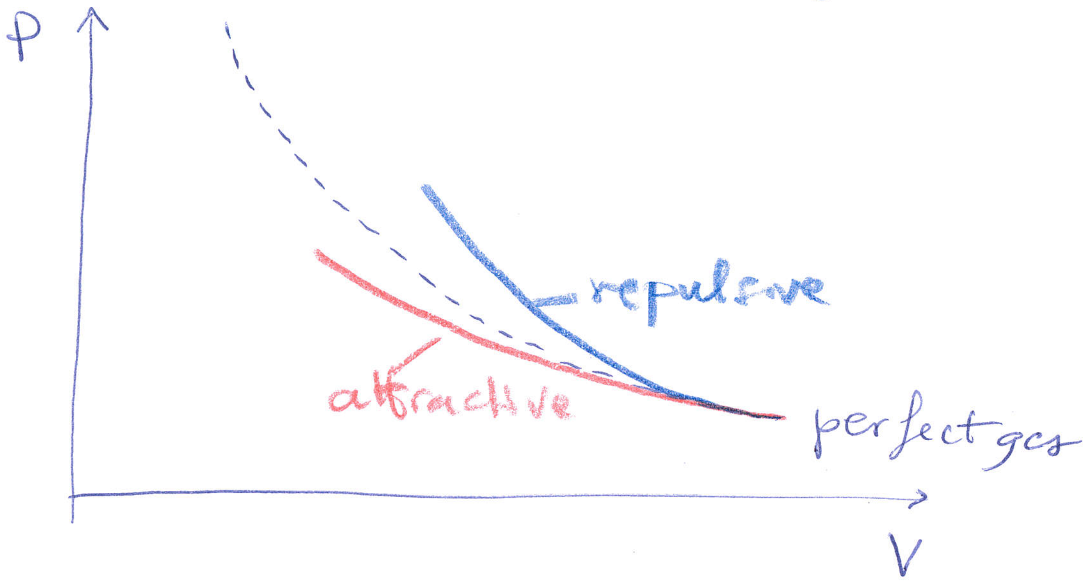
$$B_2 = -\frac{1}{2}\int d^3r\,\underbrace{\left(e^{-\beta U(r)} - 1\right)}_{f(r)}$$

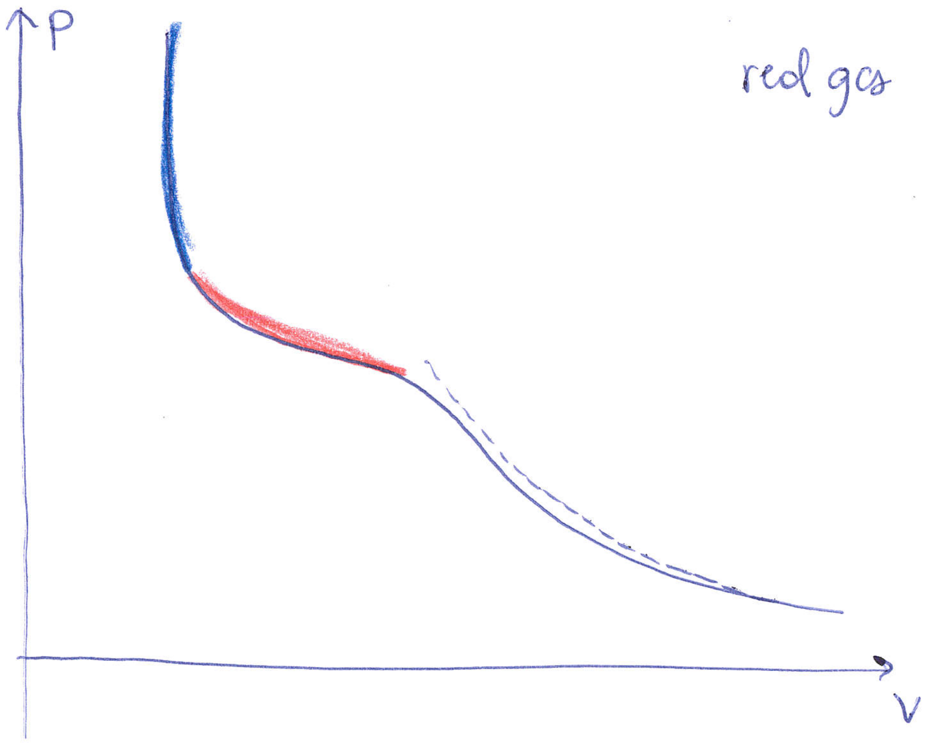


$$\frac{PV}{Nk_BT} = 1 + \rho B_2$$

$T = const$
$B_2 \simeq const$

⑥





classical phase transition → competition b/w attractive repulsive interaction