Monotonic gas with interactions

$$Q = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \underset{\sim}{Z}_N$$

$$\underset{\sim}{Z}_N = \int \cdot\cdot \int e^{-\beta U_N(r_1,\ldots r_N)} dr_1 \ldots dr_N$$

configurational partition function

if $U_N = 0 \rightarrow Z_N = V^N$ and $Q = \frac{q^N}{N!}$

How do we go from *Q* to the virial eq.:

$$\frac{p}{kT} = \rho + \underbrace{B_2(T)}_{\text{two-body}}\rho^2 + \underbrace{B_3(T)}_{\text{three-body}}\rho^3 + \ldots$$

The goal is to derive expressions for B_2 and B_3

In the grand canonical ensemble

$$\Xi(V,T,\mu)=\sum_{N=0}^{\infty}Q(N,V,T)\lambda^{n}, \quad \lambda=e^{\beta\mu}$$

$$N=0 \quad \Rightarrow E=0, \text{ one state with } \quad Q(0,V,T)=1$$

(a) $\Xi=1+\sum_{N=1}^{\infty}Q_N(V,T)\lambda^N$

(b) $pV=kT\ell n\Xi$

(c) $N=kT\left(\frac{\partial \ell n\Xi}{\partial\mu}\right)_{V,T}=\lambda\left(\frac{\partial \ell n\Xi}{\partial\lambda}\right)_{V,T}$

Shown when we first considered the GCE

$$pV=kT\left[\left(Q_1\lambda+Q_2\lambda^2\right)-\frac{Q_1^2\lambda^2}{2}+\ldots\right]$$

$$N=\lambda\left[Q_1+2\lambda Q_2-Q_1^2\lambda+\ldots\right]$$

substitute (a) into (b) and (c) and use Taylor Series

as $\lambda\to 0$

$$N=\lambda Q_1$$

and $\quad \rho=\frac{\lambda Q_1}{V}$: set this equal to *z*

$$\Xi = 1 + \sum_{N=1} \frac{Q_N V^N}{Q_1^N} z^N = 1 + \sum \frac{Z_N z^n}{N!}$$

where $Z_N = N!\left(\frac{V}{Q_1}\right)^N Q_N$

Now assume $p = kT\sum_{j=1}^{\infty} b_j z^j$ (a)

$\Xi = e^{pV/kT}$ (b)

$$b_1 = \frac{Z_1}{(1!V)} = 1$$

$$b_2 = \frac{Z_2 - Z_1^2}{2!V}$$

$$b_3 = \frac{Z_3 - 3Z_2 Z_1 + 2Z_1^2}{3!V}$$

substitute (a) into (b) and expand

compare with expansion of Ξ in terms of Z_n defined on the previous slide

Would prefer an expansion in ρ

$$\rho = \frac{N}{V} = \frac{\lambda}{V}\left(\frac{\partial \ell n \Xi}{\partial \lambda}\right)_{V,T} = \frac{z}{V}\left(\frac{\partial \ell n \Xi}{\partial z}\right)_{V,T} = \frac{z}{kT}\left(\frac{\partial p}{\partial z}\right)_{V,T}$$

Thus, $\rho = \sum_{j=1} j b_j z^j$

now write $z = a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots$

Same strategy as used in our treatment of quantum statistics

$$\rho = b_1 z + 2b_2 z^2 + 3b_3 z^3 + \ldots$$

$$= b_1\left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right)$$

$$+ 2b_2\left(a_1\rho + a_2\rho^2 + \ldots\right)^2 + 3b_3\left(a_1\rho + \ldots\right)^3$$

$$\Longrightarrow \begin{cases} a_1 = 1 \\ a_2 = 2b_2 \\ a_3 = -3b_3 + 8b_2^2 \end{cases}$$

Now return to the expansion for *p*.

$$\frac{p}{kT} = b_1 z + b_2 z^2 + b_3 z^3 + \ldots$$

$$= \left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right)$$

$$+ b_2\left(a_1\rho + a_2\rho^2 + \ldots\right)^2 + b_3\left(a_1\rho + \ldots\right)^3$$

$$\frac{p}{kT} = \rho - 2b_2\rho^2 + \left(-3b_3 + 8b_2^2\right)\rho^3$$

$$+ b_2\left(\rho + \left(-2b_2\right)\rho^2 + \ldots\right)^2 + b_3\rho^3 + \ldots$$

$$= \rho - b_2\rho^2 + \left(4b_2^2 - 2b_3\right)\rho^3 + \ldots$$

$$= \rho - \frac{Z_2 - Z_1^2}{2V}\rho_1^2 + \left(\frac{V\left(Z_3 - 3Z_2Z_1 + 2Z_z^3\right) - 3\left(Z_2 - Z_1^2\right)^2}{3V^2}\right)\rho^3$$

$$= \rho - \left[\frac{2V^2}{2Q_1^2}\frac{Q_2}{V} - \frac{V^2}{2V}\right]\rho^2 + \ldots$$

$$= \rho - V\left[\frac{Q_2}{Q_1^2} - \frac{1}{2}\right]\rho^2 + \ldots$$

Using our earlier result giving the b_j in terms of the Z_i

b_js appear to be simply intermediate variables, but in canonical ensemble b_j is related to a cluster of *j* molecules (atoms)

$$Q_1 = V / \Lambda^3$$

$$Q_2 = \frac{Z_2}{2\Lambda^6} \qquad Z_2 = \int e^{-U_2/kT} dr_1 dr_2$$

$$Q_3 = \frac{Z_3}{6\Lambda^9} \qquad Z_3 = \int e^{-U_3/kT} dr_1 dr_2 dr_3$$

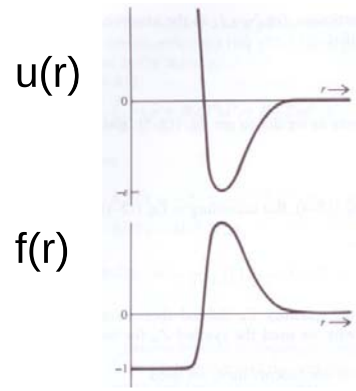
$$\begin{aligned}
B_2 &= -\frac{1}{2V}\left[Z_2 - Z_1^2\right] \\
&= -\frac{1}{2V}\int\int\left[e^{-\beta\mu(r_{12})} - 1\right] d\vec{r}_1 d\vec{r}_2 \\
&= -\frac{1}{2V}\int d\vec{r}_1 \int\left[e^{-\beta\mu(r_{12})} - 1\right] d\vec{r}_{12} \\
&= -\frac{1}{2}\int_0^{\pi}\sin\theta d\theta \int_0^{2\pi} d\phi \int_0^{\infty}\left[e^{-\beta\mu(r)} - 1\right] r^2 dr \\
&= -2\pi\int_0^{\infty}\left[e^{-\beta\mu(r)} - 1\right] r^2 dr
\end{aligned}$$

Integration over $d\vec{r}_1$ gives a factor of V

Mayer *f* function

$$f\left(r_{ij}\right)=e^{-u\left(r_{ij}\right)kT}-1$$

Now consider B_3



From McQuarrie

$$B_3 = 4b_2^2 - 2b_3$$

The b_3 term involves U_3

$$U_3\left(r_1,r_2,r_3\right)\approx u\left(r_{12}\right)+u\left(r_{13}\right)+u\left(r_{23}\right)+\Delta\left(r_1,r_2,r_3\right)$$

where Δ is the 3-body correction

If we assume the potential is pair-wise additive,
we can ignore Δ when evaluating b_3.

$$6Vb_3 = Z_3 - 3Z_2Z_1 + 2Z_1^2$$

Shown previously

$$Z_3 = \int\int\int (1+f_{12})(1+f_{13})(1+f_{23})\, d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$= \int\int\int \left[f_{12} f_{13} f_{23} + f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{23} + f_{12} + f_{13} + f_{23} + 1 \right] d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$Z_1 Z_2 = V \int\int (f_{12} + 1)\, d\vec{r}_1 d\vec{r}_2 = \int\int\int (f_{12} + 1)\, d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

Recall $Z_1 = V$

$$6Vb_3 = \int\int\int \left[f_{12} f_{13} f_{23} + f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} \right] d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$B_3 = 4b_2^2 - 2b_3$$

$$= \frac{1}{3V}\left(6Vb_3 - 12Vb_2^2\right)$$

$$b_2 = \frac{1}{2}\int f_{12}\, d\vec{r}_{12}$$

$$4Vb_2^2 = \int d\vec{r}_1 \int f_{12}\, d\vec{r}_{12} \int f_{13}\, d\vec{r}_{13} = \int\int\int f_{12} f_{13}\, d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$B_3(T) = -\frac{1}{3V}\int\int\int f_{12} f_{13} f_{23}\, d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

0 unless all three particles are close

We now evaluate B_2 for some simple potentials

Hard-core potential

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

$$B_2(T)=\frac{1}{2}\int_0^{\sigma}4\pi r^2 dr=\frac{2\pi\sigma^3}{3}=b_0$$

Square-well potential

$$u(r)=\begin{cases}\infty & r<\sigma \\ -\varepsilon & \sigma<r<\lambda\sigma \\ 0 & r>\lambda\sigma\end{cases}$$

$$B_2(T)=b_0\left\{1-\left(\lambda^3-1\right)\left(e^{\beta\varepsilon}-1\right)\right\}$$

Lennard-Jones potential

$$u(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

$$B_2(T) == \frac{1}{2}\int_0^\infty \left[\exp\left\{-\frac{4\varepsilon}{kT}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right\} - 1\right] 4\pi r^2 dr$$

$$B_2^*(T*) = -3\int_0^\infty \left[\exp\left\{-\frac{4}{T*}\left(x^{-12} - x^{-6}\right)\right\} - 1\right] x^2 dx$$

Switching to reduced temperature

$$T* = kT/\varepsilon$$

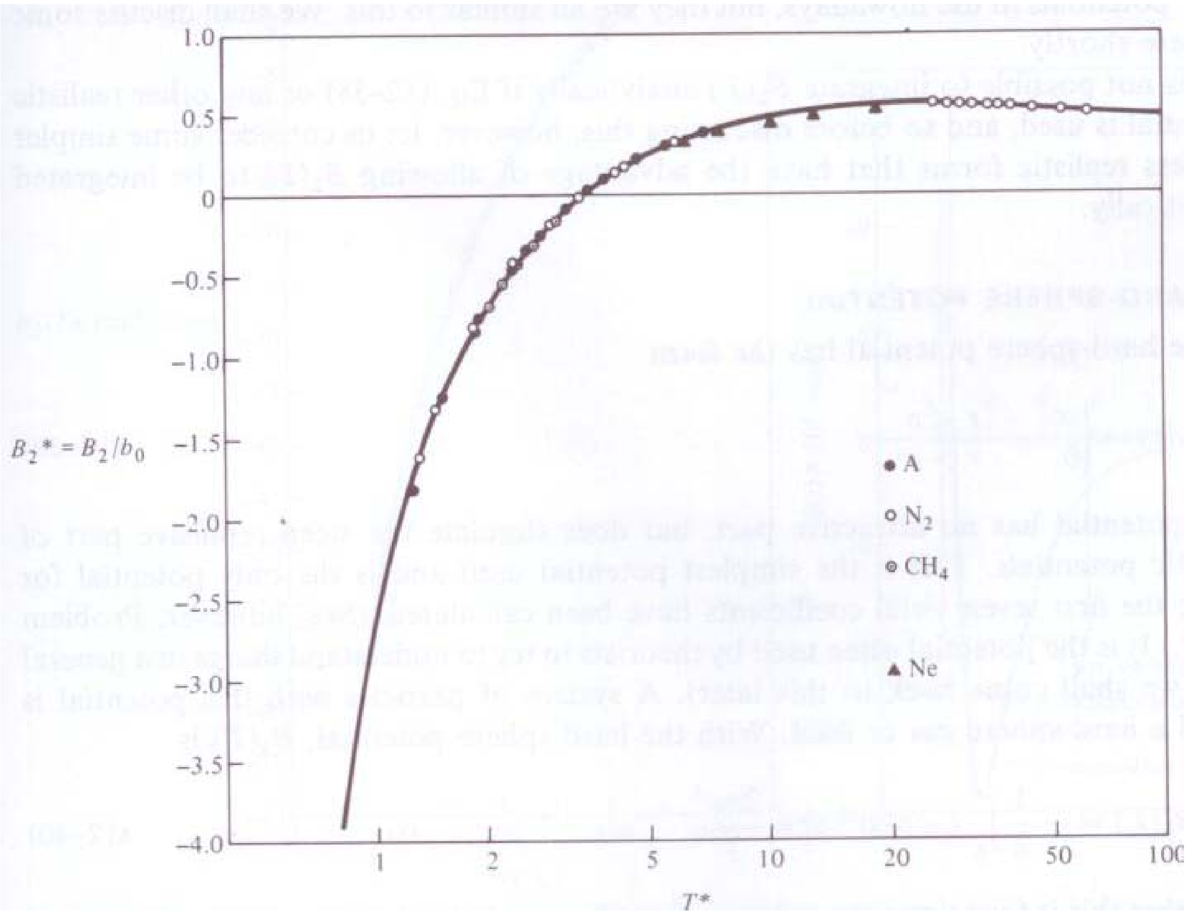
$$B_2^* = B_2/b_0$$

$$x = r/\sigma$$

Can generalize to include more terms in the long-range expansion of the potential, e.g.

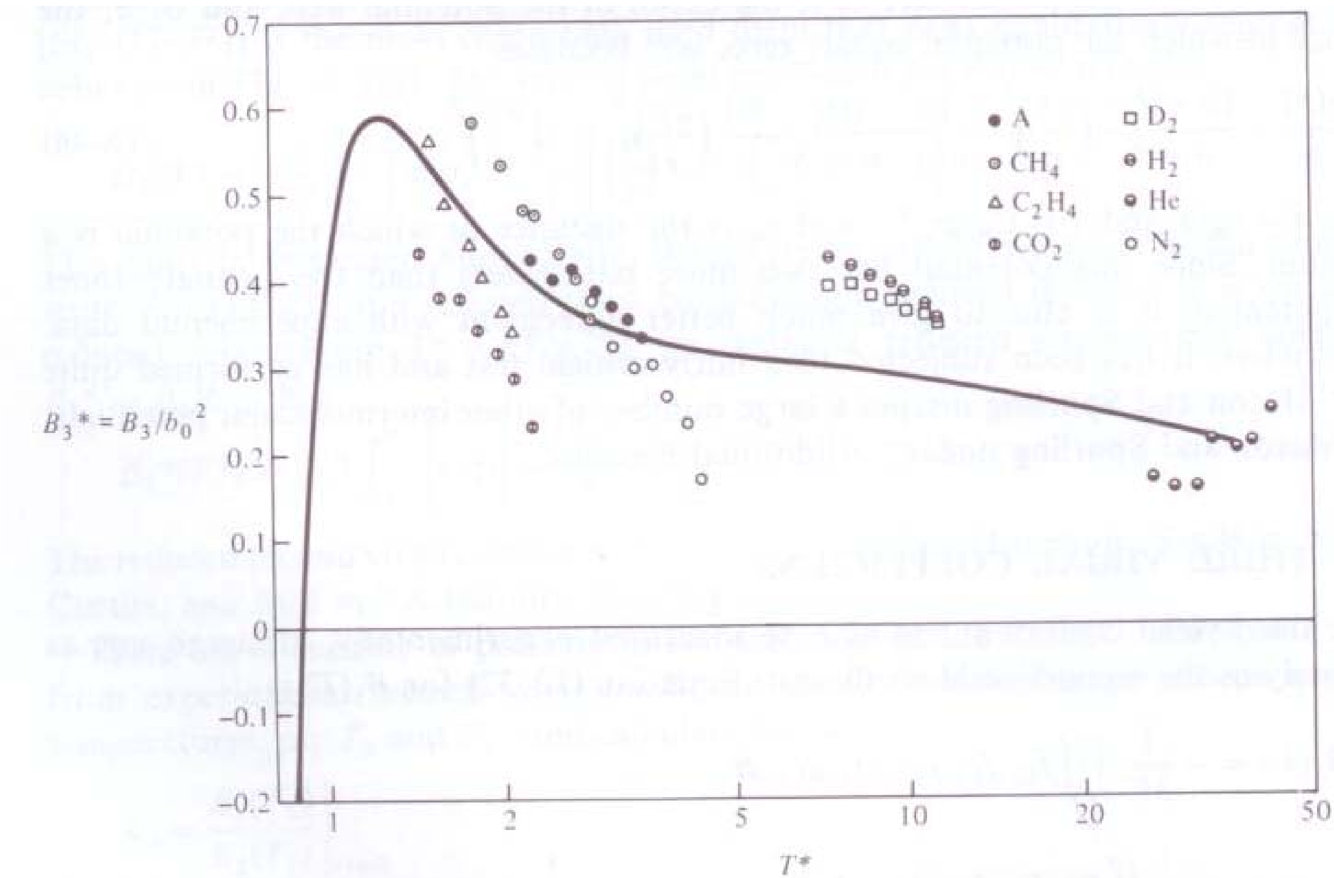
$$u(r) = \frac{A}{r^n} - \frac{C_6}{r^6} - \frac{C_8}{r^8}$$

2nd virial coefficients calculated for a LJ potential vs. experiment



$$B_3(T) = -\frac{1}{3V}\iiint_{v} f_{12}\, f_{13}\, f_{23}\, dr_1 dr_2 dr_3$$

$$= -\frac{1}{3}\iint f_{12}\, f_{13}\, f_{23}\, dr_{12} dr_{23}$$



Third virial coefficients for LJ potential and experiment

Deviations largely due to 3-body interactions