

Property Relations including the Virial Equation of State

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Dense Gas Property Relations

- In the Canonical representation

$$dS[1/T] = -Ud(1/T) + \frac{P}{T}dV - \frac{\mu}{T}dN$$

- Thus

$$\frac{P}{T} = \left. \frac{\partial S[1/T]}{\partial V} \right)_{1/T, N}$$

- Since

$$S[1/T] = k \ln Q$$

- We have

$$P = kT \left. \frac{\partial \ln Q}{\partial V} \right)_{1/T, N}$$

- The only term in $\ln Q$ that contains V is $\ln Z_\phi$,
so

$$P = kT \left. \frac{\partial \ln Z_\phi}{\partial V} \right)_{1/T, N}$$

- Now, $\ln Z_\phi$ is in the form of $\ln(1+x)$ where x is small, and

$$\ln(1+x) \simeq x - \frac{x^2}{2} + \dots$$



- Using this fact, we can write P as

$$P = \frac{NkT}{V} + \frac{N^2kTB(T)}{V^2} + \dots$$

- or

$$P = \frac{kT}{v} + \frac{kTB(T)}{v^2} + \dots$$

- where $v = \frac{V}{N}$

In molar units $R = N_A k$, where N_A is Avogadro's Number.

$$P = \frac{RT}{v} + \frac{RTN_A B(T)}{v^2} + \dots \quad v = \frac{VN_A}{N}$$

Virial Equation of State

- An expansion in $1/v^n$ is known as a virial expansion, hence virial equation of state
- For example:

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \dots$$

- This type of relation often forms the basis of empirical equations of state.

Internal Energy

- Recall

$$\begin{aligned}\frac{S[1/T]}{k} &= -\frac{A}{kT} = \ln Q \\ &= N \left[\ln q_{\text{int}} - (\ln N - 1) + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) \right] + \ln Z_{\phi}\end{aligned}$$

- and

$$dS[1/T] = -Ud(1/T) + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$U = - \left(\frac{\partial S[1/T]}{\partial [1/T]} \right)_{V,N}$$

Internal Energy

- Thus energy becomes

$$\begin{aligned} U &= \frac{3}{2} N k_B T + k_B T^2 \left(\frac{\partial \ln Z_\phi}{\partial T} \right)_{N,V} \\ &= \frac{3}{2} N k_B T + \bar{U} \end{aligned}$$

- where

$$\bar{U} = \frac{\int \cdots \int \phi e^{-\phi/k_B T} dr_1 dr_2 \cdots dr_N}{Z_\phi}$$

- It remains to evaluate $B(T)$ which we will address in the next video..