Gases and the Virial Expansion

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- First task is to examine what ensemble theory tells us about simple systems via the thermodynamic connection
  - Calculate thermodynamic quantities: average energy, pressure, etc..
  - Expressions can be evaluated if partition function can be calculated.
- Consider a system of N identical point particles with mass m occupying a volume V. General Hamiltonian

$$H(\mathbf{x}^{(N)}) = \frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m} + U(\mathbf{r}^{(N)}).$$

- The canonical partition function is:

$$\begin{aligned} Q_N(T,V) &= \frac{1}{N!h^{3N}}\int d\mathbf{x}^{(N)}\, e^{-\beta H(\mathbf{x}^{(N)})} = \frac{1}{N!h^{3N}}\int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)}\, e^{-\beta\left(\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m}+U(\mathbf{r}^{(N)})\right)} \\ &= \frac{1}{N!h^{3N}}\int d\mathbf{p}^{(N)}\, e^{-\beta\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m}}\int d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})} \end{aligned}$$

- Integral over the momenta can be done explicitly:

$$\int d\mathbf{p}^{(N)}\, e^{-\beta\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m}} = \left[\int dp\, e^{-\beta\frac{p^2}{2m}}\right]^{3N} = \left(\frac{2m\pi}{\beta}\right)^{3N/2} = (2\pi mkT)^{3N/2}.$$

- Defining the configurational part of the partition function as

$$Z_n = \int d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})},$$

  we have

$$Q_N = \frac{1}{N!h^{3N}}\left(\frac{2m\pi}{\beta}\right)^{3N/2} Z_N = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} Z_N.$$

Ideal Gas System: $U(\mathbf{r}^{(N)}) = 0$

- Simplest possible system: particles do not interact but are confined to volume.

  $$Z_N = \int_V d\mathbf{r}^{(N)}\; e^{-\beta u(\mathbf{r}^{(N)})} = \int_V d\mathbf{r}^{(N)} = V^N$$

  so

  $$Q_N = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N = \frac{q^N}{N!} \qquad q \equiv \left(\frac{2\pi mkT}{h^2}\right)^{3/2}.$$

  - Note that $q = Q_1$ is the partition function for a 1-particles system.

- Recall that:

  $$\overline{E} = -\frac{\partial \ln Q_N}{\partial \beta} \qquad \text{and} \qquad P = kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T.$$

  Now for the ideal gas system,

  $$\begin{aligned} \ln Q_N &= N\ln q - \ln N! \approx N\ln q - N\ln N + N - \ln(2\pi N)^{1/2} \approx N\ln\left(\frac{qe}{N}\right) \\ &= N\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] = N\ln\left[\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}\frac{Ve}{N}\right] \\ &= N\ln V - \frac{3}{2}N\ln\beta + N\ln f(m,N) \end{aligned}$$

  1. The pressure is therefore:

     $$P \;=\; kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T = kTN\frac{\partial \ln V}{\partial V} = \frac{nkT}{V} \qquad \text{Ideal gas equation of state}$$

  2. The energy and heat capacity at constant volume are

     $$\begin{aligned} \overline{E} &= -\frac{\partial \ln Q_N}{\partial \beta} = \frac{3}{2}N\frac{\partial \ln\beta}{\partial\beta} = \frac{3}{2}nkT. \\ C_v &= \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \frac{3}{2}Nk. \end{aligned}$$

- Note that $\overline{E}$ and C_v scale with N as assumed earlier.

Non-ideal gas

- Must evaluate Z_N for each model.
- 1-particle system: external potential (such as gravitational): $U(\mathbf{r}^{(N)}) = \phi(\mathbf{r}_1)$ leads to a non-uniform system where properties depend on location in volume (ex. barometric pressure formula).
- 2-particle system in absence of external potential: particles interact via a pair potential:

$$U(\mathbf{r}_1, \mathbf{r}_2) = U(|\mathbf{r}_2 - \mathbf{r}_1|) = U(r_{12}).$$

  - Example: Lennard-Jones potential: $U(r_{12}) = Ar_{12}^{-12} + Br_{12}^{-6}$.
- 3-particle system in absence of external potential:

$$\begin{aligned} U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= U(r_{12}) + U(r_{13}) + U(r_{23}) + \omega(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ \omega(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \text{“3” body interaction potential} \end{aligned}$$

  - Typically, $\omega(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is usually small and neglected hence the interactions are considered to be *pairwise-additive*:

$$U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \approx \sum_{i=1}^{3} \sum_{\substack{j=1 \\ j>i}}^{3} U(r_{ij}) = \frac{1}{2} \sum_{i=1}^{3} \sum_{\substack{j=1 \\ j\neq i}}^{3} U(r_{ij})$$

- For an N-particle system, with pairwise additive potential:

$$U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \approx \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} U(r_{ij}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} U(r_{ij}) \equiv \sum_{i<j}^{N} U(r_{ij}).$$

- For non-electrostatic potentials, pair interactions $U(r_{ij})$ are usually *short-ranged* so that $U(r_{ij}) \to 0$ if $r_{ij} \gg \xi$, where typically $\xi \sim 10^{-8}$ m.
  - Particles separated by long distances do not interact.
  - Define the “Ursell-Mayer” function $f(r) = \exp\{-\beta U(r)\} - 1$ so that $f(r) \to 0$ for $r \gg \xi$.
- In terms of the Mayer function, Z_N is:

$$Z_N = \int d\mathbf{r}^{(N)}\; e^{-\beta \sum_{i<j} U(r_{ij})} = \int d\mathbf{r}^{(N)} \prod_{i<j}^{N} \left(e^{-\beta \sum_{i<j} U(r_{ij})} - 1 + 1 \right) = \int d\mathbf{r}^{(N)} \prod_{i<j}^{N} \left(f_{ij} + 1 \right),$$

where the short hand notation $f_{ij} = f(r_{ij})$ has been used.

The Virial Expansion

- For systems of very low density, the ideal gas equation of state is approximately correct.
  - On average, particles are far apart an non-interacting.
- What about correcting this approximation by expanding the partition function in powers of the density $\rho = N/V$?
- Can we correct the ideal gas equation of state in this fashion?

$$\begin{aligned} PV &= NkT\left[1+\rho B_2(T)+\rho^2 B_3(T)+\cdots\right] \\ \frac{P}{kT} &= \rho+\rho^2 B_2(T)+\rho^3 B_3(T)+\cdots \end{aligned}$$

- Can relate $B_i(T)$ to integrals of Ursell-Mayer functions
- It is rather difficult to obtain these results in the canonical ensemble.
- Is it simpler to use other ensembles?

Virial expansion using the grand canonical ensemble

- Goal: write pressure P in a series in density $\rho = \langle N\rangle/V$.

$$P = kT\rho\left[1+\sum_{j=1}^{\infty}\rho^j B_{j+1}(T)\right]$$

- Recall that the grand canonical partition function is:

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

and

$$PV = kT\ln\Xi = kT\ln\left(1+\sum_{N=1}^{\infty}Q_N\lambda^N\right).$$

- Also recall that

$$Q_N=\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}Z_N \qquad Z_N=\int d\mathbf{r}_1\cdots d\mathbf{r}_N\ e^{-\beta U(\mathbf{r}^{(N)})}.$$

- Note that in the absence of an external potential,

$$Q_1=\left(\frac{2\pi mkT}{h^2}\right)^{3/2}V \qquad \text{so} \qquad Q_N=\frac{1}{N!}\left(\frac{Q_1}{V}\right)^N Z_N.$$

- The pressure can now be written as:

$$PV = kT\ln\Xi = kT\ln\left(1+\sum_{N=1}^{\infty} Z_N z^N\right) \qquad \text{where} \qquad z = \lambda\frac{Q_1}{V} = \lambda a.$$

- Formally, we can expand this to get a series expression for P in terms of z (homework problem):

$$P = kT\sum_{j=1}^{\infty} b_j z^j \qquad \text{with} \qquad \begin{array}{l} b_1 = \frac{Z_1}{V} = 1 \\ b_2 = \frac{1}{2!V}\left(Z_2 - Z_1^2\right) \\ b_3 = \frac{1}{3!V}\left(Z_3 - 3Z_2Z_1 + 2Z_1^3\right) \end{array}$$

  and so on.

- Strategy is to express this series in terms of the density by expressing the density in a power series of z and inverting.

- The density is given by

$$\rho = \frac{\langle N\rangle}{V} = \frac{1}{V}\left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)_{V,T}$$

- Since $\lambda = \exp\{\beta\mu\}$,

$$\frac{\partial}{\partial\beta\mu} = \frac{\partial\lambda}{\partial\beta\mu}\frac{\partial}{\partial\lambda} = \lambda\frac{\partial}{\partial\lambda},$$

  and since $PV = kT\ln\Xi$,

$$\rho = \frac{\lambda}{V}\left(\frac{\partial\ln\Xi}{\partial\lambda}\right)_{V,T} = \frac{\lambda}{V}\frac{V}{kT}\frac{\partial P}{\partial\lambda} = \frac{\lambda}{kT}\frac{\partial P}{\partial\lambda}.$$

- Recall that $z = a\lambda$, where $a = Q_1/V$, so

$$\begin{aligned} \rho &= \frac{\lambda}{kT}a\frac{\partial P}{\partial z} = z\frac{\partial P/kT}{\partial z} \\ &= z\sum_{j=1}^{\infty} jb_j z^{j-1} = \sum_{j=1}^{\infty} jb_j z^j. \end{aligned}$$

- We wish to invert this relationship to write z in terms of ρ. The procedure is to solve for the coefficients a_i where:

$$\begin{aligned} \rho &= b_1z + 2b_2z^2 + 3b_3z^3 + \cdots \\ z &= a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots . \end{aligned}$$

- Inserting expression for z into the expansion of ρ and collecting like powers of ρ:

$$\rho = \rho(b_1 a_1) + \rho^2 \left(b_1 a_2 + 2b_2 a_1^2\right) + \rho^3 \left(b_1 a_3 + 4b_2 a_1 a_2 + 3b_3 a_1^3\right) + \cdots$$

so

$$\begin{aligned}
b_1 a_1 &= 1 \quad \rightarrow \quad a_1 = 1/b_1 = 1 \\
b_1 a_2 &= -2b_2 a_1^2 \quad \rightarrow \quad a_2 = -2b_2 \qquad b_2 = -a_2/2 \\
b_1 a_3 &= -4b_2 a_1 a_2 - 3b_3 a_1^3 \quad \rightarrow \quad a_3 = 8b_2^2 - 3b_3 \qquad b_3 = \frac{1}{3}\left(2a_2^2 - a_3\right)
\end{aligned}$$

- Thus the density expansion for z is:

$$z = \rho - 2b_2\rho^2 + \left(8b_2^2 - 3b_3\right)\rho^3 + \ldots$$

- Inserting this expression of z is the expansion of P/kT,

$$\begin{aligned}
\frac{P}{kT} &= b_1 z + b_2 z^2 + b_3 z^3 + \cdots = z - \frac{1}{2}a_2 z^2 + \frac{1}{3}\left(2a_2^2 - a_3\right) z^3 + \ldots \\
&= \left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right) - \frac{a_2}{2}\left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right)^2 + \frac{1}{3}(2a_2^2 - a_3)\left(a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots\right) \\
&= a_1\rho + \rho^2\left(a_2 - \frac{a_1 a_2}{2}\right) + \rho^3\left(a_3 - a_1 a_2^2 + \frac{1}{3}(2a_2^2 - a_3)a_1^3\right) + \ldots \\
&= \rho + \rho^2(-b_2) + \rho^3\left(\frac{2(8b_2^2 - 3b_3) - 4b_2^2}{3}\right) + \ldots \\
&= \rho + \rho^2(-b_2) + \rho^3\left(4b_2^2 - 2b_3\right) +
\end{aligned}$$

- Comparing this with the virial expansion, we have:

$$\begin{aligned}
B_2(T) &= -b_2 = -\frac{1}{2V}\left(Z_2 - Z_1^2\right) \\
B_3(T) &= 4b_2^2 - 2b_3 = \frac{1}{V^2}\left(Z_2 - Z_1^2\right) - \frac{1}{3V}\left(Z_3 - 3Z_2 Z_1 + 2Z_1^3\right)
\end{aligned}$$

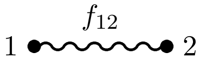
- We must now show that these results are equivalent to the Mayer expansion results obtained in the canonical ensemble.

Evaluation of Virial Coefficients

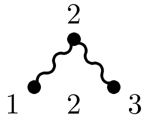
- Must express configurational partion functions Z_i in terms of Mayer functions.
- If no external potenial, $U = \sum_{j<i} U(r_{ij})$.
- Now:

$$\begin{aligned}
Z_1 &= \int_V d\mathbf{r}_1 = V \\
Z_2 &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 \, e^{-\beta U(r_{12})} = \int_V d\mathbf{r}_1 d\mathbf{r}_2 \, (1 + f_{12}) = V^2 + \int_V d\mathbf{r}_1 d\mathbf{r}_2 f_{12}
\end{aligned}$$

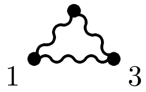
- We introduce the (new) graphical notation:
  - Each graph has a factor of $1/V$.
  - Each line  represents a factor of f connecting the vertices.
  - Each darkened dot indicates the argument is integrated over.
- For example:



$$= \frac{1}{V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 f_{12}$$



$$= \frac{1}{V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ f_{12} f_{23}$$



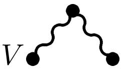
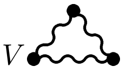
$$= \frac{1}{V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ f_{12} f_{23} f_{13}$$

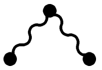
- Thus:

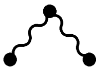
$$Z_2 = V^2 + V$$ 

- Now Z_3 is given by:

$$\begin{aligned} Z_3 &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ (1+f_{12})(1+f_{13})(1+f_{23}) \\ &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ [1 + (f_{12}+f_{13}+f_{23}) + (f_{12}f_{13}+f_{12}f_{23}+f_{13}f_{23}) + f_{12}f_{23}f_{13}] \end{aligned}$$

$= V^3 + 3V^2$  $+\ 3V$  $+\,V$ 

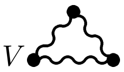
- The diagram  is *reducible* since

V 

$$\begin{aligned} &= \int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ f_{12} f_{23} = \int_V d\mathbf{r}_{12} d\mathbf{r}_2 d\mathbf{r}_{23}\ f_{12} f_{23} \\ &= V\left(\int_V d\mathbf{r}_{12}\ f_{12}\right)\left(\int_V d\mathbf{r}_{23} f_{23}\right) \end{aligned}$$

$= V\ ($  $)^2.$

- Thus

$Z_3 = V^3 + 3V^2$  $+\ 3V($  $)^2\ +V$ 

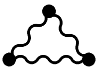
- The virial coefficients are therefore:

$B_2(T) = -\frac{1}{2V}(Z_2 - Z_1^2) = -\frac{1}{2}\Big(V^2 + V$  $- V^2\Big) = -\frac{1}{2}$ 

$$= -\frac{1}{2V}\int_V d\mathbf{r}_1 d\mathbf{r}_2\, f(r_{12}) = -\frac{1}{2}\int_V d\mathbf{r}_{12}\left(e^{-\beta U(r_{12})} - 1\right).$$

and

$$B_3(T) = 4B_2(T)^2 - \frac{1}{3V}\left(Z_3 + 3Z_2Z_1 + 2Z_1^3\right)$$

$= ($  $)^2 - \frac{1}{3V}\Big(V^3 + 3V^2$  $+ 3V($  $)^2 + V$ 

$-3V^2 - 3V^2$  $+ 2V^3\Big)$

$$= -\frac{1}{3V}\int_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\, f(r_{12})f(r_{23})f(|\mathbf{r}_{12} + \mathbf{r}_{23}|).$$

as obtained with the Mayer expansion method.

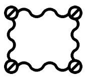
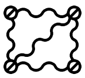
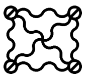
- In general, $B_n(T)$ are expressed in terms of doubly connected (irreducible) graphs:

$$B_{n+1}(T) = -\frac{n}{n+1}\gamma_{n+1}$$

$$\gamma_{n+1} = \frac{1}{n!V}\int_V d\mathbf{r}_1 \cdots d\mathbf{r}_{n+1} S_{1,2,\ldots,n+1}$$

$S_{1,2,\ldots,n+1}$ = Sum of all topologically distinct doubly-connected graphs with $n+1$ vertices.

- For example:

$S_{1,2,3,4} = 3$  $+ 6$  $+$ 

  - Coefficients are number of topologically distinct ways of permuting indices on graph.

- Can generalize this to multi-component systems (homework?).

Limits of validity of virial expansion

1. Large systems (i.e. $N \gg 1$), rigorous in *thermodynamic limit* $N \to \infty$, $V \to \infty$ with fixed $\rho = \langle N \rangle / V$.

2. Short-ranged potentials with at least $U(r) \sim r^{-(3+\epsilon)}$ for large r.

$$B_2(T) = -\frac{1}{2}\int_V d\mathbf{r}\ \left(e^{-\beta U(r)} - 1\right) = -2\pi\int_0^\infty dr\, r^2\left(e^{-\beta U(r)} - 1\right).$$

For large r, $\beta U(r) \ll 1$ so $\exp\{-\beta U(r)\} - 1 \approx -\beta U(r)$. Now the integral for $B_2(T)$ will converge at upper limit in thermodynamic limit only if

$$\int_a^\infty dr\, r^2 U(r) \sim \int_a^\infty dr\, \frac{r^2}{r^{3+\epsilon}}$$

converges (i.e. $\epsilon > 0$).

3. Convergence of power series in ρ requires ρ not too big: Not valid for condensed systems (liquids).

Evaluation of virial coefficients

- Obviously model dependent since depends on interaction potential $U(r)$.
- We will look at specific cases:
  1. Hard spheres: No attractive interaction but short-ranged repulsion.

$$U(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

$$\begin{aligned} B_2(T) &= \frac{1}{2}\int_V d\mathbf{r}\, \left(1 - e^{-\beta U(r)}\right) = 2\pi \int_0^\infty dr\, r^2 \left(1 - e^{-\beta U(r)}\right) \\ &= 2\pi \int_0^\sigma dr\, r^2 = \frac{2\pi}{3}\sigma^3 \end{aligned}$$

    - This gives:

$$\frac{PV}{NkT} = 1 + \rho\frac{2\pi}{3}\sigma^3.$$

    - Note that no temperature dependence of $B_j(T)$: All isotherms of plot of P versus ρ (or V) are identical.
    - No condensation or other phase transition for such a system.

  2. Square well potential

$$U(r) = \begin{cases} \infty & r \leq \sigma_1 \\ -\epsilon & \sigma_1 < r < \sigma_2 \\ 0 & r \geq \sigma_2 \end{cases}$$

$$\begin{aligned} B_2(T) &= 2\pi \int_0^\infty dr\, r^2(\left(1 - e^{-\beta U(r)}\right) = 2\pi \left[\int_0^{\sigma_1} dr r^2 + \int_{\sigma_1}^{\sigma_2} dr\, r^2 \left(1 - e^{\beta\epsilon}\right)\right] \\ &= \frac{2\pi}{3}\left[\sigma_1^3 + \left(1 - e^{\beta\epsilon}\right)(\sigma_2^3 - \sigma_1^3)\right]. \end{aligned}$$

    - Isotherms of P vs. V now differ and condensation possible.

Perturbation Theory and the Van-der-Waals Equation

- Recall that the configurational partition function is:

$$Z_N = \int d\mathbf{r}_1 \cdot d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

- Suppose that the potential can be written as the sum of two components:

$$U(\mathbf{r}^{(N)}) = U_0(\mathbf{r}^{(N)}) + U_1(\mathbf{r}^{(N)})$$

  where U_1 is small in some sense compared to U_0.

- Let

$$\begin{aligned} Z_N^0 &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ n^0(\mathbf{r}^{(N)}) &= \frac{e^{-\beta U_0(\mathbf{r}^{(N)})}}{Z_N^0} \end{aligned}$$

  - Note that $n^0(\mathbf{r}^{(N)})$ is the configurational part of the probability density for a system with potential $U_0(\mathbf{r}^{(N)})$.
  - Ideally, one would like to be able to evaluate Z_N^0 analytically.

- We may express Z_N as:

$$\begin{aligned} Z_N &= \frac{Z_N^0}{Z_N^0} \int d\mathbf{r}^{(N)} \, e^{-\beta U_0(\mathbf{r}^{(N)})} \, e^{-\beta U_1(\mathbf{r}^{(N)})} \\ &= Z_N^0 \int d\mathbf{r}^{(N)} \, n^0(\mathbf{r}^{(N)}) e^{-\beta U_1(\mathbf{r}^{(N)})} = Z_N^0 \left\langle e^{-\beta U_1(\mathbf{r}^{(N)})} \right\rangle_0 . \end{aligned}$$

- Notation $\langle \cdots \rangle_0$ means average with respect to probability density for the *unperturbed* system.

- Implications: the contribution of the configurational part of the partition function to the Helmholtz free energy is

$$\begin{aligned} A(N,V,T) &= -\frac{1}{\beta} \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3N/2} \frac{Z_N}{N!} \right] \\ &= -\frac{1}{\beta} \ln \left[\left(\frac{2\pi m k T}{h^2} \right)^{3N/2} \frac{Z_N^0}{N!} \right] - \frac{1}{\beta} \ln \left\langle e^{-\beta U_1(\mathbf{r}^{(N)})} \right\rangle_0 \\ &= A_0 + A_1 = A_0 - \frac{1}{\beta} \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j \end{aligned}$$

  - The coefficients C_j are called *cumulants* and are defined by

$$\begin{aligned} \exp\left\{ \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j \right\} &= \left\langle e^{-\beta X} \right\rangle \\ \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \left\langle X^k \right\rangle &= \exp\left\{ \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j \right\} = 1 + \sum_{j=1}^{\infty} \frac{(-\beta)^j}{j!} C_j + \frac{1}{2} \left(\frac{(-\beta)^j}{j!} C_j \right)^2 + \ldots \end{aligned}$$

  where $\langle X \rangle$ denotes the average of variable X with respect to a probability density $f(X)$.

  - Solving for C_j (homework) gives:

$$\begin{aligned} C_1 &= \langle X \rangle \\ C_2 &= \langle X^2 \rangle - \langle X \rangle^2 \\ C_3 &= \langle X^3 \rangle - 3\langle X \rangle \langle X^2 \rangle + 2\langle X \rangle^3 \\ &\vdots \end{aligned}$$

- General properties of cumulants:
  1. Typically, if the property $X \sim N$, then $C_j \sim N$. This makes them much more useful in expansions than moment expansions.
  2. Quite often, $C_j > C_{j+1}$ so truncations of the expansions are possible.
- In terms of the cumulants, we have the perturbation expansion of the Helmholtz free energy

$$\begin{aligned} A &= A_0 + C_1(\beta) - \frac{\beta}{2!} C_2(\beta) + \frac{\beta^2}{3!} C_3(\beta) + \cdots \\ &= A_0 + \langle U_1 \rangle_0 - \frac{\beta}{2!} \left(\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2 \right) + \frac{\beta^2}{3!} \left(\langle U_1^3 \rangle_0 - 3\langle U_1 \rangle_0 \langle U_1^2 \rangle_0 + 2\langle U_1^3 \rangle_0 \right) + \cdots \end{aligned}$$

Derivation of the Van der Waals Equation

- We define the pairwise additive reference potential to be

$$U_0(\mathbf{r}^{(N)}) = \frac{1}{2} \sum_{i \neq j} u_0(r_{ij})$$

  with

$$u_0(r) = \begin{cases} 0 & \text{if } r > \sigma \\ \infty & \text{if } r \leq \sigma \end{cases}$$

  where σ is the diameter of the spherical particles. The form of the attractive potential U_1 is not particularly important

- According to the perturbation scheme above,

$$A(N,T,V) = A_0(N,T,V) + \langle U_1 \rangle_0 + \ldots$$

- We define the Van der Waals parameter a so that

$$\begin{aligned} a &= -\frac{\langle U_1 \rangle_0}{N\rho} \\ A(N,V,T) &= A_0(N,V,T) - \frac{aN^2}{V} + \cdot \end{aligned}$$

  - Evaluation of a can be done once the form of U_1 is specified.
- If we take $\sigma = 0$, then $Z_N^0 = V^N$ is the ideal gas result.

- Due to hard core repulsions, particles *cannot* overlap, so volume is restricted. Excluded volume per pair of particles is $4\pi/3\sigma^3$, and hence excluded volume per particle is $2\pi/3\sigma^3 \equiv b$. The configurational partition function is therefore

$$Z_N^0 = (V - Nb)^N$$

  - Nb is the excluded volume for each particle, $V - Nb$ is the total free volume for each particle.

- The Helmholtz free energy is therefore:

$$\begin{aligned} A(N,T,V) &\approx -\frac{1}{\beta}\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\frac{(V-Nb)^N}{N!}\right] - \frac{aN^2}{V} \\ &= -kT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\frac{1}{N!}\right] - kT\ln(V-Nb)^N - \frac{aN^2}{V} \end{aligned}$$

- From the thermodynamic relations, the energy and pressure are therefore

$$\begin{aligned} E &= -\frac{\partial \ln Q_N}{\partial \beta} = \frac{3}{2}kT + aN\rho \\ P &= -\left(\frac{\partial A}{\partial V}\right)_{N,T} = kT\left(\frac{N}{V-Nb}\right) - \frac{aN^2}{V^2} \\ &= \frac{kT\rho}{1-\rho b} - a\rho^2 \end{aligned}$$

  - This is the *Van der Waals* equation of state.
  - In the low density limit, $\rho b << 1$ so

$$\frac{1}{1-\rho b} \approx 1 + \rho b$$

    and hence

$$\frac{P}{kT} \approx \rho + \rho^2\left(b - \frac{a}{kT}\right)$$

  - The second virial coefficient is therefore approximately $B_2(T) \approx b - a/kT$.

- Plot of P-V isotherms of Van der Waals gas show interesting behavior:
  - At high temperatures, we have $\partial P/\partial V < 0$ as expected of a gas: decreasing the volume increases the pressure.
  - At a particular (called *critical temperature* T_c), there is a region in the curve (at a *critical volume* V_c) where $\partial P/\partial V = 0$ and there is no curvature, $\partial^2 P/\partial V^2 = 0$.
  - For all isotherms below T_c, there are unphysical regions where $\partial P/\partial V > 0$.
  - For these regions, see a volume discontinuity as pressure is lowered: liquid-gas transition.

  - Correct isotherm curves determined by the *equal areas* approach that follows from the equality of chemical potentials of the liquid and gase phases.

- What are these critical points? Determined by the conditions

$$\frac{\partial P}{\partial V} = 0 \qquad \frac{\partial^2 P}{\partial V^2} = 0$$

- Evaluation of these conditions gives:

$$V_c = 3Nb \qquad kT_c = \frac{8a}{27b} \qquad P_c = \frac{a}{27b^2}$$

- Near the critical point, we can expand the pressure around the critical temperature and density and find that:

$$\begin{aligned}
\frac{P}{kT} &= \frac{P_c}{kT_c} + \frac{1}{kT_c}\frac{\partial P}{\partial \rho}\bigg|_{\rho=\rho_c} (\rho-\rho_c) + \frac{1}{2kT_c}\frac{\partial^2 P}{\partial \rho^2}\bigg|_{\rho=\rho_c} (\rho-\rho_c)^2 + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial \rho^3}\bigg|_{\rho=\rho_c} (\rho-\rho_c)^3 + \cdots \\
&= \frac{P_c}{kT_c} + \frac{1}{kT_c}\frac{\partial P}{\partial V}\frac{\partial V}{\partial \rho}\bigg|_{\rho=\rho_c} (\rho-\rho_c) + \frac{1}{2kT_c}\left[\frac{\partial^2 P}{\partial V^2}\left(\frac{\partial V}{\partial \rho}\right)^2 + \frac{\partial P}{\partial V}\frac{\partial^2 V}{\partial \rho^2}\right]_{\rho=\rho_c} (\rho-\rho_c)^2 \\
&\quad + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial \rho^3}\bigg|_{\rho=\rho_c} (\rho-\rho_c)^3 + \cdots \\
&= \frac{P_c}{kT_c} + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial \rho^3}\bigg|_{\rho=\rho_c} (\rho-\rho_c)^3 + \cdots = \frac{1}{8b} + \frac{81}{16}b^2(\rho-\rho_c)^3 + \cdots
\end{aligned}$$

- Thus, we expect that near the critical point,

$$\frac{P}{kT} \sim \text{constant} + C(\rho-\rho_c)^\delta$$

  with the *critical exponent* $\delta = 3$.

- Experimentally, it is found that $\delta \sim 4.2$.

- Improvements: higher order in perturbation theory or better zeroth order potential