Van der Waals equation of state

2nd virial coefficient

\[ B_2(T) = -\frac{1}{2} \hat{b}_2 = -\frac{1}{2} \int d^3q \left( e^{\frac{\beta u_0}{r}} - 1 \right) \]

Model potential

\[ B_2(T) = \frac{1}{2} \left( \int_{lq<\rho_0} d^3q - \int_{lq>\rho_0} d^3q \left( e^{\frac{\beta u_0}{r}} - 1 \right) \right) \]

\approx \beta u_0 \left( \frac{\rho_0}{r} \right)^6 \text{ at large } r, \]

and use this as a model

\[ = \frac{1}{2} \left( \frac{4\pi}{3} \rho_0^3 - \int_{\rho_0}^{\infty} 4\pi r^2 dr \beta u_0 \left( \frac{\rho_0}{r} \right)^6 \right) \]

\[ = \frac{1}{2} \left( \frac{4\pi}{3} \rho_0^3 - \beta u_0 \left[ \frac{4\pi r^6}{6} \right]_{\rho_0}^{\infty} \right) = \beta u_0 \frac{4\pi \rho_0^3}{3} \]

\[ = \frac{1}{2} \cdot \frac{4\pi}{3} \rho_0^3 \left( 1 - \beta u_0 \right) = \frac{1}{2} \rho \left( 1 - \beta u_0 \right) \]

\[ \frac{P}{k_B T} \approx n + B_2(T) n^2 = n \left( 1 + \frac{1}{2} \rho u_0 \right) - n^2 \frac{1}{2} \rho \beta u_0 \]
\[ p + \frac{1}{2} k_B n^2 = n k_B T \left( 1 + \frac{1}{2} \ln n \right) \]

\[ n k_B T = \frac{(p + \frac{1}{2} k_B n^2)}{1 + \frac{1}{2} \ln n} \approx (p + \frac{1}{2} k_B n^2) \left( 1 + \frac{1}{2} \ln n \right) \]

\[ N k_B T = \left( p + \frac{1}{2} k_B \left( \frac{N}{V} \right)^2 \right) \left( V - \frac{1}{2} \pi n \right) \]

\[ N k_B T = \left( p + a \left( \frac{N}{V} \right)^2 \right) (V - Nb) \]

- **vander Waals equation of state**

**Physical ingredients:**

* \( b = \frac{1}{2} \pi \) — "effective volume reduction per particle" because of mutual exclusion of hard cores

* \( a = \frac{1}{2} k_B u_0 \) — writing \( p = \frac{N k_B T}{V - Nb} - a \left( \frac{N}{V} \right)^2 \), \( a \left( \frac{N}{V} \right)^2 \) is effective reduction in the pressure exerted on the outside walls because of long-range van der Waals attraction between molecules

**Remark**

Van der Waals equation can be viewed as approximate phenomenological equation of state. We motivated it from more microscopic treatment by truncating series, which is accurate at low density/high pressure.
With additional physical fixing (Maxwell construction), van der Waals equation can be also used to discuss liquid-gas transition (liquid-dense phase formed because of attractive forces between molecules).

**Isotherms of the van der Waals gas**

\[
P = \frac{Nk_B T}{V-Nb} - a\left(\frac{N}{V}\right)^2 = \frac{k_B T}{V-b} - \frac{a}{V^2}
\]

\[
V = \frac{V}{N} \quad \text{- volume per particle; assuming } V > b
\]

\[
\frac{dp}{dv} = \frac{-k_B T}{(V-b)^2} + \frac{2a}{v^3} = -\frac{v^3 k_B T - 2a(v-b)^2}{v^3(V-b)^2} = -\frac{1}{v^3}\left(\frac{v k_B T}{(v-b)}\right)^2 - 2a
\]

At high enough \( T \), e.g., \( b k_B T > 2a \), clearly \( \frac{dp}{dv} < 0 \) for all \( v > b \).
Critical point is given by:

\[
\frac{\partial p}{\partial u} = -\frac{k_B T}{(u-b)^2} + \frac{2a}{u^3} = 0 \quad \text{when is it possible to satisfy this eq. ?}
\]

Consider

\[
\bar{s}(u) = \frac{2a}{u^3} - \frac{k_B T}{(u-b)^2}
\]

Maximize \( \bar{s}(u) \):

\[
\bar{s}'(u) = -\frac{6a}{u^4} + \frac{2k_B T}{(u-b)^3} = 0
\]

\[
\Rightarrow \frac{u^4}{(u-b)^3} = \frac{3a}{k_B T} \Rightarrow u = u(T)
\]

If \( s(u(T)) < 0 \), then \( \frac{\partial p}{\partial u} < 0 \) for all \( u \).

Critical \( T_c \) is when

\[
\bar{s}'(u_c, T_c) = 0
\]

\[
\frac{k_B T_c}{(u_c-b)^3} - \frac{3a}{u_c^4} = 0
\]

\[
-\frac{k_B T_c}{(u_c-b)^2} + \frac{2a}{u_c^3} = 0
\]

\[
\Rightarrow u_c-b = \frac{2}{3} u_c, \quad u_c = 3b
\]

\[
\frac{k_B T_c}{(u_c-b)^3} = \frac{3a}{u_c^4}
\]

\[
\frac{k_B T_c}{(u_c-b)^2} = \frac{2a}{u_c^3}
\]

\[
\Rightarrow u_c-b = \frac{2}{3} u_c, \quad u_c = 3b
\]

\[
k_B T_c = \frac{8a}{27b}
\]

\[
p_c = \frac{8a}{27b} - \frac{a}{9b^2} = \frac{a}{27b^2}
\]
Remarks (non-universal)

\[ \frac{p_c T_c}{k_B T_c} = \frac{3}{8} = 0.375 \]

- "universal number" (in the sense that all system-dependent parameters dropped out)

Experimentally, \( \frac{p_c T_c}{k_B T_c} \) varies between 0.23 (H2O) and 0.31 (He)

Measure \( p, \bar{v}, \bar{T} \) in units of \( p_c, v_c, T_c \):

\[ \bar{p} = \frac{p}{p_c}, \quad \bar{v} = \frac{v}{v_c}, \quad \bar{T} = \frac{T}{T_c} \]

- "reduced variables"

\[ \bar{p} \cdot a = \frac{8a}{27b^2} \left( \frac{1}{\bar{v}^3} - \frac{a}{3b^2} \right) \]

\[ \bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2} \]

\[ \left( \bar{p} + \frac{3}{\bar{v}^2} \right) \left( \bar{v} - \frac{1}{3} \right) = \frac{8}{3} \bar{T} \]

All material parameters dropped out

Van der Waals equation implies "law" of corresponding states" - "universal equation of state".

This is special to the van der Waals equation and does not hold in general (e.g., equation of state of a gas depends on the details of the interatomic potential). Still, it is roughly satisfied and is useful for crude comparisons.

(Later will discuss different "true universality" in the vicinity of Tc)
Liquid-gas transition in the van der Waals model

\[ T > T_c \Rightarrow \text{van der Waals equation is physically sensible} \]

(any general thermodynamic laws and in principle there can be gases obeying precisely this equation of state)

\[ T < T_c \]

\[ \frac{\partial P}{\partial V} > 0 \Rightarrow \text{Compressibility } \alpha_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T < 0 \]

Negative compressibility is thermodynamically unstable — from general arguments of stability in thermodynamics.

\[ F = U - TS \]

\[ dF = -SdT - pdV \]

\[ P = -\left( \frac{\partial F}{\partial V} \right)_T \]

\[ \left( \frac{\partial P}{\partial V} \right)_T = -\left( \frac{\partial^2 F}{\partial V^2} \right)_T \leq 0 \]

\[ \text{will argue for this physically below} \]

\[ \text{not sure how to prove, but this is correct} \]

\[ \text{(e.g. Landau's hint)} \]

must be in thermodynamics
The breakdown of the van der Waals equation is not the problem of statistical mechanics. If we could calculate the partition sum exactly, the derived thermodynamics satisfies the stability conditions automatically. For example:

\[
\langle N \rangle = \frac{1}{\beta^3} \left( \frac{\partial \ln Z}{\partial \mu} \right)_{T,V} = \frac{1}{\beta^2} \left( \frac{\partial}{\partial \mu} \left( \frac{\beta V}{k_B T} \right) \right)_{T,V} = +V \left( \frac{\partial \mu}{\partial \mu} \right)_{T,V}
\]

\[
\langle N^2 \rangle = \frac{1}{\beta^2} \left( \frac{\partial^2 \ln Z}{\partial \mu^2} \right)
\]

\[
\langle N \rangle = \frac{1}{\beta^2} \left( \frac{\partial^2 \ln Z}{\partial \mu^2} \right)
\]

\[
\langle N \rangle - \langle N^2 \rangle = \frac{1}{\beta^2} \left( \frac{1}{3} \frac{\partial^2 \ln Z}{\partial \mu^2} - \left( \frac{1}{3} \frac{\partial \ln Z}{\partial \mu} \right)^2 \right) = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \mu^2} = + \frac{1}{\beta^2} \left( \frac{\partial}{\partial \mu} \langle N \rangle \right)_{T,V}
\]

\[

\text{positive!}
\]

\[
\left\{ \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{k_B T}{V} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{k_B T}{V} \left( \frac{\partial p}{\partial \mu} \right)_{T,V} \right. \Rightarrow
\]

Mathematics:

\[p = p(N,T,V)\]

keep \(T\) fixed: \(p = p(N,V)\)

from extensivity \(n \Rightarrow\)

chain rule \(\frac{\partial p}{\partial N} \frac{\partial N}{\partial v} \frac{\partial v}{\partial p} \frac{\partial p}{\partial N} = -1\)

\[\Rightarrow k_B T \frac{\partial N}{\partial v} \left( -\frac{1}{V} \frac{\partial v}{\partial p} \right)_{N,T} = k_B T \cdot n \cdot \vec{e}_T \Rightarrow \vec{e}_T \text{ must be} \text{+ve.} \]
Exact: \[ n k_B T \cdot \Delta T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} > 0 \]

van der Waals equation is not an exact eq. of state — we made approximations and in the process we violated the above condition of thermodynamic stability. We will try to first fix six things "by hand" appealing to thermodynamic arguments. Then we will motivate this "fix" also differently doing microscopic calculation smartly differently approximations in the "mean field calculation"