

Real gases

- Lit: Greiner Ch. 16
Srednicki 5.2
Schubel Ch. 5.

So for non-interacting gases.

Consider the Hamiltonian

$$H = \sum_i \frac{\vec{p}_i^2}{2m} + \sum_{i < j} U_{ij}(|\vec{r}_i - \vec{r}_j|).$$

2-particle potential.

Calculate canonical partition function:

$$Z(T, V, N) = \frac{1}{N! h^{3N}} \int d^{3N} p \exp\left(-\frac{\beta}{2m} \sum \vec{p}_i^2\right) \int d^{3N} r \exp\left(-\beta \sum_{i < j} U_{ij}\right)$$

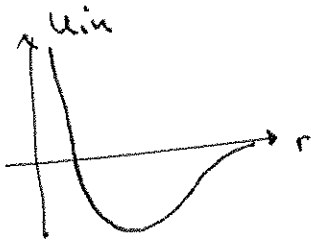
$$= \frac{1}{N!} \left(\frac{2\pi m kT}{h^2}\right)^{3N/2} Q_N(V, T).$$

where $Q_N(V, T) = \int d^{3N} r \prod_{i < j} \exp(-\beta U_{ij})$.

Note. for an ideal gas $U_{ij} = 0 \Rightarrow Q_N = V^N$

Approximate solution for $U_{ij} \neq 0$:

typical interaction potentials



- strongly repulsive for small distances "hard core"
- attractive for large distances
- vanishes for $r \rightarrow \infty$.

expand to around the limiting case of the ideal gas.

$$\beta U_{ij} \ll 1 \Rightarrow \exp(-\beta U_{ij}) \approx 1$$

we $f_{ij} = \exp(-\beta U_{ij}) - 1$ as an expansion parameter ($f_{ij} \rightarrow 0$ for $r \rightarrow \infty$ (low density) or $T \rightarrow \infty$)

How to calculate

$$\prod_{i < j} (1 + f_{ij}) = 1 + \sum_{i < j} f_{ij} + \sum_{i < j < k} f_{ij} f_{jk} + \dots$$

Consider only the first two terms
 ↳ Systematic expansion: Mayer's cluster expansion
 → Potlauer, ~~Gruber~~ Gruber

$$\Rightarrow Q_N(V, T) = \int d^3N r \left(1 + \sum_{i < j} f_{ij} + \dots \right)$$

$$\approx V^N + V^{N-2} \sum_{i < j} \int d^3 r_i \int d^3 r_j (\exp(-\beta U_{ij}) - 1)$$

Center-of-mass coord. $\vec{R} = \frac{1}{2}(\vec{r}_i + \vec{r}_j)$ and rel. coord. $\vec{r} = \vec{r}_i - \vec{r}_j$.

$$Q_N(V, T) \approx V^N + V^{N-1} \underbrace{\frac{N(N-1)}{2}}_{\text{pairs}} \int d^3 r (\exp(-\beta U(r)) - 1) \underbrace{a(T)}_{}$$

$$a(T) = 4\pi \int r^2 dr [\exp(-\beta U(r)) - 1]$$

$$\Rightarrow \frac{N(N-1)}{2} \approx \frac{N^2}{2}$$

$$d = \left(\frac{h^2}{2\pi m k T} \right)^{3/2}$$

$$Z(T, V, N) = \frac{1}{N!} \left(\frac{2\pi m k T}{h^2} \right)^{3N/2} \left[V^N + V^{N-1} \frac{N^2}{2} a(T) + \dots \right]$$

$$Z(T, V, N) = \frac{1}{N!} \frac{V^N}{\lambda^{3N}} \left[1 + \frac{N^2 a(T)}{2V} + \dots \right]$$

Thermal e.o.s.: i.e. pressure

$$p(T, V, N) = - \frac{\partial F}{\partial V} \Big|_{T, N} = \frac{\partial}{\partial V} (kT \ln Z)$$

$$= \frac{NkT}{V} - kT \frac{\frac{a}{2} \frac{N^2}{V^2}}{1 + \frac{a}{2} \frac{N^2}{V}}$$

$$\approx \frac{NkT}{V} \left(1 - \frac{a}{2} \frac{N}{V} \right)$$

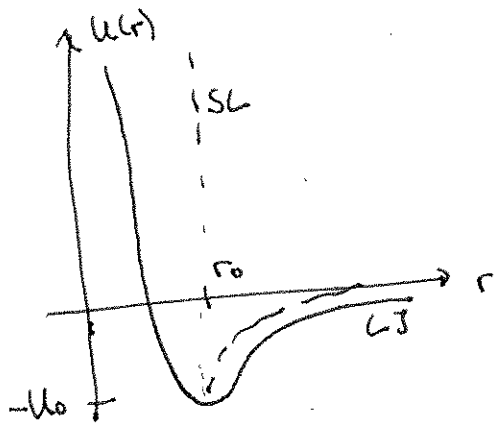
To proceed we need $u(r)$ i.e. the interaction potential $U(r)$:

e.g. Lennard-Jones

$$U(r) = U_0 \left(\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right).$$

minimum at $(r_0, -U_0)$.

c.f. Schrodler.



here: simpler potential for which $u(r)$ can be calculated analytically

Sutherland

$$U(r) = \begin{cases} \infty & r < r_0 \\ -U_0 \left(\frac{r_0}{r} \right)^6 & r > r_0 \end{cases}$$

solid sphere with radius $r = r_0/2$.

$$\Rightarrow a(T) = 4\pi \int_0^{r_0} r^2 dr (-1) + 4\pi \int_{r_0}^{\infty} dr r^2 \left[\exp(\beta U_0 (r_0/r)^6) - 1 \right]$$

$$\approx -\frac{4\pi}{3} r_0^3 + 4\pi \beta U_0 \int_{r_0}^{\infty} r^2 dr \left(\frac{r_0}{r} \right)^6$$

$$= -\frac{4\pi}{3} r_0^3 (1 - \beta U_0)$$

Pressure:

$$p = \frac{kT}{v} \left(1 + \frac{2\pi r_0^3}{3v} \left(1 - \frac{U_0}{kT} \right) \right)$$

where $v = \frac{V}{N}$ volume per particle

$$\left(p + \frac{2\pi r_0^3 U_0}{3v^2} \right) = \frac{kT}{v} \left(1 + \frac{2\pi r_0^3}{3v} \right)^{-1}$$

$\frac{4\pi r_0^3}{3} \ll v$
proper vol.

$$\left(p + \frac{a}{V^2}\right)(V - b) = kT$$

with

$$a = \frac{2\pi}{3} r_0^3 U_0$$

measure strength of the attractive force

$$b = \frac{4\pi}{3} r_0^3$$

volume related to volume of the particles

but $\frac{4\pi}{3} \left(\frac{r_0}{2}\right)^3 = \frac{1}{4} \frac{2\pi}{3} r_0^3$ from the repulsive part of the potential.

c.f. Schrodler for a derivation from the L.-J. potential.

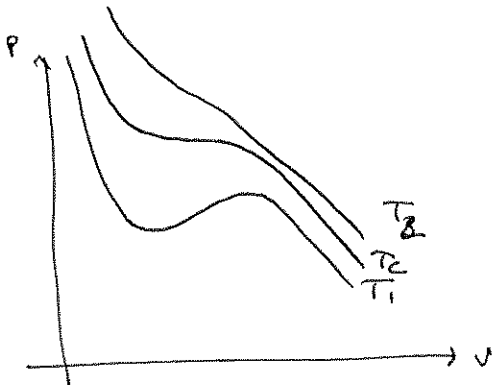
van der Waals isotherms & Maxwell construction

c.f. Schrodler ch. 5
Potlitz ch. 11.

free energy concave $\Rightarrow p = -\frac{\partial F}{\partial V}$

$\frac{\partial p}{\partial V} < 0$ everywhere

violated by v.d.W. no Kelvin



c.f. Fig 5.1. in the lecture notes

a) for $T > T_c$ no Kelvin nonhomogen

b) at T_c $\frac{\partial p}{\partial V} = \frac{\partial^2 p}{\partial V^2} = 0.$

T_c : critical temperature

$$V_c = 3b \quad kT_c = \frac{8}{27} \frac{a}{b} \quad p_c = \frac{a}{27b^2}$$

dim'less ratio $\frac{kT_c}{p_c V_c} = \frac{8}{3}.$

rewrite e.o.s. using

$$p^* = \frac{p}{p_c} \quad V^* = \frac{V}{V_c} \quad T^* = \frac{T}{T_c}$$

$$p^* = \frac{8T^*}{3V^{*2} - 1} - \frac{3}{V^*}$$

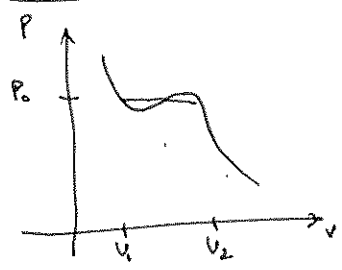
\rightarrow same for all substances: law of corresp. states

c) $T < T_c$: regions where $(\frac{\partial P}{\partial V})_T > 0$.
 Unstable have to be corrected

reason for the appearance of unphysical region

- o approximate evaluation of the partition function assumed uniform density throughout the system
- o exact evaluation must include configurations destabilized by coexisting phases with different densities

Maxwell construction c.f. p. 46



$$P_0 = P(v_1) = P(v_2)$$

$$\int_{v_1}^{v_2} (P_0 - P(v)) dv = 0$$

van der Waals e.o.s corrected by Maxwell construction gives qualitatively accurate description of liquid-gas phase transition

Critical phenomena c.f. Potlina

going back to reduced e.o.s.

$$(p^* + \frac{3}{v^{*2}})(3v^* - 1) = 8T^* \quad (*)$$

investigate the system close to the critical point.

Therefore write

$$p^* = 1 + \pi \quad v^* = 1 + \eta \quad T^* = 1 + \epsilon$$

$$\Rightarrow 3\pi^2 - 8\epsilon(1+\eta)^2 + \pi(1+\eta)^2(2+3\eta) = 0 \quad (**)$$

~~3\pi^2 - 8\epsilon(1+\eta)^2 + \pi(1+\eta)^2(2+3\eta) = 0~~

1. critical exponents $t=0$, close to crit pt. $|\pi|, |\eta| \ll 1$
 $\Rightarrow \pi \approx -\frac{3}{2}\eta^3$ from $\pi \approx 4\epsilon - 6\epsilon\eta + 9\epsilon\eta^2 - \frac{3}{2}(1+\eta)\eta^3$ (up to η^3).
2. Consider dependence of η on t : ($t < 0$)

~~3\pi^2 - 8\epsilon(1+\eta)^2 + \pi(1+\eta)^2(2+3\eta) = 0~~

~~3\pi^2 - 8\epsilon(1+\eta)^2 + \pi(1+\eta)^2(2+3\eta) = 0~~

and insert $\pi \approx 4\epsilon$ yields

$$\eta \rightarrow \frac{2(\sqrt{|t|} - 2t)}{1+4t} \approx \sqrt{2} |t|^{1/2}$$

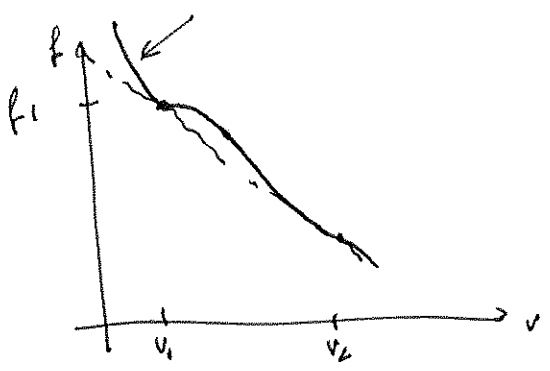
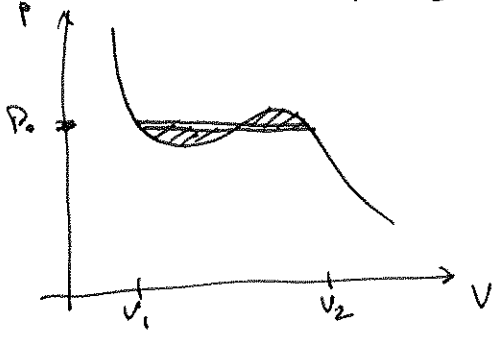
in the liquid/gas phase.

$$P = - \left(\frac{\partial f}{\partial v} \right)_T$$

$$f(T, v) = f(T, v_2) - \int_{v_2}^v P(T, v') dv'$$

specific free energy

$T < T_c$



$$f_{1,2} = f(T, v_{1,2})$$

--- dashed line
 $f_1 - P_0(v - v_1)$
 (assuming constant pressure P_0).

at v_2 the two curves meet again.

f derived from v.d.W. e.o.S. is not concave. ($P > P_0$ f.v. v_1 , $P < P_0$ f.v. v_2).

+ dashed line with slope P_0 is precisely the double tangent to $f(T, v)$
 \Rightarrow violates thermodynamic inequality.

Compare!

2-phase heterogeneous system

$$c_1 = \frac{v_2 - v}{v_2 - v_1} \quad \text{in state } (v_1, T)$$

$$c_2 = \frac{v - v_1}{v_2 - v_1} \quad \text{in state } (v_2, T)$$

same pressure and temperature

\Rightarrow free energy $c_1 f_1 + c_2 f_2 \Rightarrow$ lies on the dashed curve.
 i.e. lower free energy than that of v.d.W. May.

between $[v_1, v_2]$ (two-phase region) substance divides into two phases:
 • liquid phase (T, v_1) pressure P_0
 • gas phase (T, v_2)

Maxwell construction

3. $\frac{1}{k_T} = -V \left(\frac{\partial P}{\partial V} \right)_T = -P_c (1+\gamma) \left(\frac{\partial \pi}{\partial \eta} \right)_t$
 For $\eta=0$: $k_T = \frac{1}{6 P_c t}$

- power law behaviour of the system in the vicinity of the critical point
- universal (independent of the microscopic details of the interaction)

Critical exponents

		<u>vdw</u>
e.g. 1. $\pi \propto \eta^\delta$	for $t=0$ as $\pi \rightarrow 0$ and $\eta \rightarrow 0$	$\delta = 3$
2. $\eta \propto t ^\beta$	for $t < 0, t \rightarrow 0$ $\pi = \pi_0(t)$ vapour pressure	$\beta = \frac{1}{2}$
3. $k_T \propto t ^{-\gamma}$	for $t \rightarrow 0, \eta = 0$	$\gamma = 1$

Scaling relations

$\alpha = \alpha'$
 $\gamma = \gamma'$
 $\nu = \nu'$

$vd = 2 - \alpha$
 $= 2\beta + \gamma$
 $= \beta(\delta + 1)$
 $= \delta \frac{\delta + 1}{\delta - 1}$

$2 - \gamma = \frac{\delta}{\nu} = d \frac{\delta - 1}{\delta + 1}$

only two independent critical exponents.

here $2 - \gamma = 2 = \beta(\delta + 1) = \delta \frac{\delta + 1}{\delta - 1}$

$t > 0$ disordered

$C \propto t^{-\alpha}$
 $\chi \propto t^{-\gamma}$
 $\nu \propto \frac{1}{\delta} t^{-\nu}$

$t < 0$: ordered

$C \propto (-t)^{-\alpha'}$
 $\eta \propto (-t)^\beta$
 $\chi \propto (-t)^{-\gamma'}$
 $\xi \propto (-t)^{-\nu'}$

$t = 0$:

$J \propto \eta^\delta$
 ~~χ~~
 $C \chi(0) \eta(t) \propto \tau^{-d+2-\gamma}$