

10. Approximate Methods

10.1 Classical Cluster Expansion

Let's say we have the following many-body Hamiltonian:

$$\mathcal{H} = \underbrace{\sum_{i=1}^N \frac{\vec{p}_i^2}{2m}}_{\text{"usual" non-relativistic kinetic energy}} + \underbrace{\sum_{i < j}^N v_{ij}}_{\substack{i < j \text{ to avoid double counting}}} \quad N \text{ particles}$$

"usual" non-relativistic kinetic energy

\vec{p}_i : generalized momentum of i^{th} particle

pairwise two-body interactions

$$v_{ij} = v(|\vec{r}_i - \vec{r}_j|)$$

note: this is quite a restrictive assumption!

In general:

$$v_{ij} = v_{ij}(\vec{r}_i - \vec{r}_j),$$

assuming no spin, isospin, etc.

We want to treat the system classically!

↳ gas of He, H₂, Ar, ...

(we will discuss validity regime later)

Canonical partition function:

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta \sum_i \vec{p}_i^2 / 2m} e^{-\beta \sum_{i,j} v_{ij}} d^{3N} \vec{p} d^3 \vec{q}$$

$$= \frac{1}{d^{3N} N!} \int e^{-\beta \sum_i v_{ij}} d^{3N} \vec{q}$$

the integration
over the momen-
ta can be done
straightforwardly
(we have done it
many times by now)

↑
still need to deal
with integration
over spatial coordinates,

i.e., evaluate config-
ration integral

$$\lambda = \sqrt{\frac{2\pi \hbar^2}{m k T}}$$

de Broglie wave length

performing the integral

does require knowing $v_{ij} \neq 0$

If we have $Q_N(V, T)$, we can write down

$$Q(z, V, T) = \sum_{N=0}^{\infty} z^N Q_N(V, T)$$

$$= \sum_{N=0}^{\infty} \left(\frac{2}{\lambda^3} \right)^N \frac{1}{N!} \int e^{-\beta \sum_{i < j} v_{ij}} d^{3N} \vec{q}$$

(210)

$$I_N(V, T)$$

→ note, the text uses λ_N^2 but this is a bit dangerous since many of you use "2" to denote the partition function

$$J_N(V, T)$$

$$= \int \exp(-\beta \sum_{i < j} v_{ij}) d^{3N} \vec{q}$$

$$Q_N(V, T) = \frac{1}{d^{3N} N!} J_N(V, T)$$

How are we going to evaluate $I_N(V, T)$?

Let's define a new quantity f_{ij} through

$$e^{-\beta v_{ij}} = (1 + f_{ij})$$

f_{ij} is dimensionless

$$\Rightarrow I_N(V, T) = \int \prod_{i < j} (1 + f_{ij}) d^3 \vec{r}_1 \dots d^3 \vec{r}_N$$



this is a fact.
of r_{ij}

$\underbrace{\quad}_{\text{we have } N(N-1)/2 \text{ "if combinations"}}$ pairs

\Rightarrow we have $N(N-1)/2$ factors
 $(1 + f_{ij})$

Of course, we haven't accomplished anything yet... we just rewrote our integral, shifting the "problem" from v_{ij} to f_{ij} .

have exponential

Now, we can multiply out the big integrand...

$$\begin{aligned}
 I_N(V, T) = & \int \left[1 + \underbrace{(f_{12} + f_{13} + \dots + f_{N-1,N})}_{\text{have exponential}} \right. \\
 & + \underbrace{(f_{12} f_{13} + f_{12} f_{14} + \dots)}_{\text{don't have exponential}} \\
 & + \underbrace{(f_{12} f_{13} f_{14} + \dots)}_{\text{don't have exponential}} \\
 & \left. + \dots \right] d^3 \vec{r}_1 d^3 \vec{r}_2 \dots d^3 \vec{r}_N
 \end{aligned}$$

Our hope is now that it is justified, in certain regimes, to cut the sum of terms off and still get a reasonably reliable result.

If we expand I_N further, we see

$$I_N(V, T) = \int \underline{1} d^3 \vec{r}_1 d^3 \vec{r}_2 \dots d^3 \vec{r}_N \longrightarrow V^N$$

the integration over $d^3 \vec{r}_3 \dots d^3 \vec{r}_N$ is already taken care off

$$+ V^{N-2} \int \underline{f_{12}} d^3 \vec{r}_1 d^3 \vec{r}_2$$

+ ...

$$+ V^{N-2} \int \underline{f_{N-1, N}} d^3 \vec{r}_{N-1} d^3 \vec{r}_N$$

$$\frac{N(N-1)}{2}$$

identical integrals
(6-dimensional)

$$+ V^{N-3} \int \underline{f_{12} f_{13}} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3$$

+

...

...

$$\int f_{12} d^3 \vec{r}_1 d^3 \vec{r}_2 \rightsquigarrow [1 - 2]$$

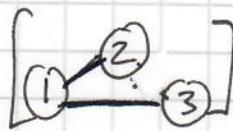
$$\int f_{12} f_{13} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 \rightsquigarrow [1 - 2] \cdot [3]$$

$$\begin{aligned} & \int f_{12} f_{34} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 d^3 \vec{r}_4 \rightsquigarrow [1 - 2] \cdot [3 - 4] \\ &= \int f_{12} d^3 \vec{r}_1 d^3 \vec{r}_2 \int f_{34} d^3 \vec{r}_3 d^3 \vec{r}_4 \end{aligned}$$

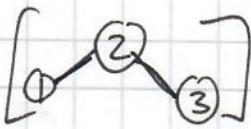
disconnected

Let's look at 3-cluster:

$$f_{12} f_{13}$$



$$f_{12} f_{23}$$



$$f_{13} f_{23}$$



these 3-clusters, i.e., the associated integrals, yield the same results

$$f_{12} f_{23} f_{13}$$



this three-cluster is distinctly different (the value of the integral is, in general, different from the other class of 3-clusters)

Define : $b_l (V, T) = \frac{1}{l! \pi^{3(l-1)} V} \times (\text{sum of all possible } l\text{-clusters})$

dimension less cluster integral

For example : $b_1 = \frac{1}{V} [①] = \frac{1}{V} \int d^3 \vec{r}_1 = 1$

$$\underline{\underline{b_2}} = \frac{1}{2\lambda^3 V} [① - ②]$$

$$= \frac{1}{2\lambda^3 V} \iint f_{12} d^3 \vec{r}_1 d^3 \vec{r}_2$$

{

$$f_{12} = f_{12}(|\vec{r}_1 - \vec{r}_2|)$$

change integration:

$$\iint \dots d^3 \vec{r}_1 d^3 \vec{r}_2 = \iint \dots d^3 \vec{r}_{12} d^3 \vec{R}_{12}$$

relative CM
 $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$

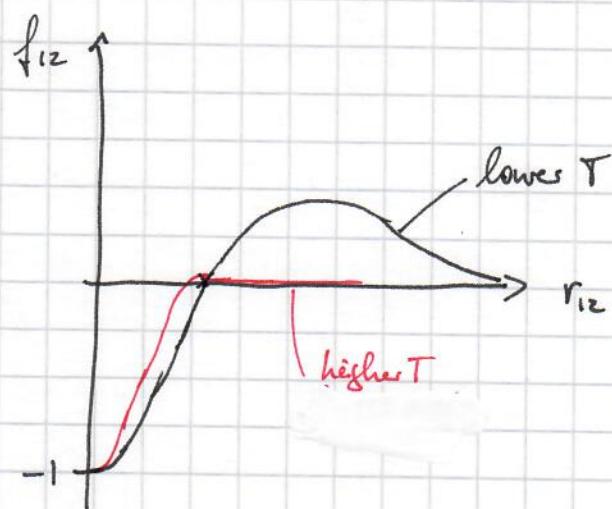
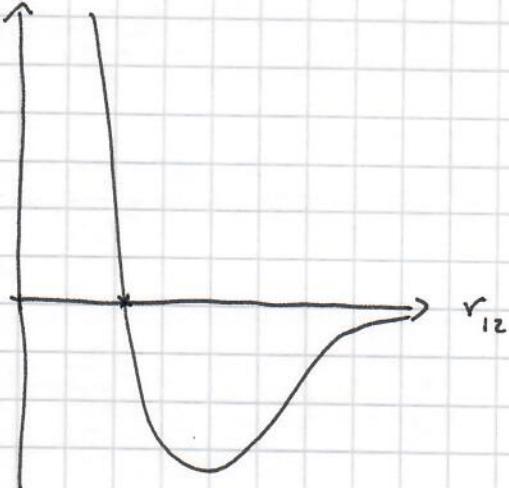
performing the integration in CM coordinates $\rightarrow = \frac{1}{2\lambda^3} \int f_{12} d^3 \vec{r}_{12}$

switching to spherical coordinates $\rightarrow = \frac{4\pi}{2\lambda^3} \int_0^\infty f_{12} r_{12}^2 dr_{12}$

$$= \frac{2\pi}{\lambda^3} \int_0^\infty (e^{-\beta U_{12}} - 1) r_{12}^2 dr_{12}$$

non-trivial integral (at least in general)

Typically : $V_{12} \uparrow$



the higher the temperature, the smaller
the integral under the curve

- In the high temperature regime,
we expect that the two-body
cluster is more important than
the three-body cluster, ...
- high T, low density approximation

Last example : $\underline{b_3} = \frac{1}{6\lambda^6 V} \times (\text{sum of three-body clusters})$

$$= \frac{1}{6\lambda^6 V} \times \left([\begin{array}{c} 2 \\ 1 \\ 3 \end{array}] + [\begin{array}{c} 3 \\ 1 \\ 2 \end{array}] + [\begin{array}{c} 1 \\ 2 \\ 3 \end{array}] + [\begin{array}{c} 2 \\ 3 \\ 1 \end{array}] \right)$$

$$= \frac{1}{6\lambda^6 V} \left[3 \iiint f_{12} f_{23} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 \right.$$

$$\left. + \iiint f_{12} f_{23} f_{13} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 \right]$$

$$\xrightarrow{\quad} \approx 2 b_2^2 + \frac{1}{6\lambda^6 V} \iiint f_{12} f_{23} f_{13} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3$$

integrate over
three-body CM
and switch to
 $d^3 \vec{r}_{12} d^3 \vec{r}_{23}$

It is clear that the integral $I_N(V, T)$ can be expressed in terms of the cluster integrals b_e .

Note: in general, $b_e = b_e(V, T)$!

It turns out that the grand partition function takes a simple form in terms of the b_e :

$$\Omega(z, V, T) = \exp \left(\sum_{\ell=1}^{\infty} b_e z^\ell \frac{V}{\lambda^3} \right)$$

$$\Rightarrow \boxed{\frac{1}{V} \log \Omega(z, V, T) = \frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} b_e z^\ell} \quad (*)$$

using $\frac{PV}{kT} = \log \Omega$

$$\Rightarrow \frac{P}{kT} = \frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} b_e z^\ell \quad (1)$$

as before:
 $N = \text{average}$
of atoms;
 $z \frac{\partial \log \Omega}{\partial z} = N$

$$\frac{N}{V} = \frac{1}{V} = \frac{z}{V} \frac{\partial \log \Omega}{\partial z} = \frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} \ell b_e z^\ell \quad (2)$$

using (*)

$$\text{here: } b_e = b_e(V, T)$$

If $V \rightarrow \infty$ (dilute limit), we write:

$$\frac{P}{kT} = \frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} b_e z^\ell$$

$$\frac{1}{V} = \frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} \ell b_e z^\ell$$

where $b_e(T)$

$$= \lim_{V \rightarrow \infty} b_e(V, T)$$

grand canonical partition function:

$$\Omega(\mu, T, V) = \sum_{N=0}^{\infty} z^N \mathcal{Q}_N(T, V)$$

using def. of $\mathcal{J}_N(T, V)$
from p. 210

$$\rightarrow = \sum_{N=0}^{\infty} z^N \frac{1}{\lambda^{3N} N!} \mathcal{J}_N(T, V)$$

$$\begin{aligned}
 &= \sum_{N=0}^{\infty} \left(\frac{z}{\lambda^3} \right)^N \frac{1}{N!} \left\{ V^{N-1} \textcircled{[①]}^{V b_1} \right. \\
 &\quad + V^{N-2} \frac{N(N-1)}{2} \textcircled{[①-②]}^{2\lambda^3 V b_2} \\
 &\quad + V^{N-3} \frac{N(N-1)(N-2)}{6} \left\{ \textcircled{[①③]} + \right. \\
 &\quad \quad \quad \textcircled{[①②]} + \\
 &\quad \quad \quad \textcircled{[②③]} + \\
 &\quad \quad \quad \left. \textcircled{[①②③]} \right\} \textcircled{[①②③]}^{6\lambda^6 V b_3} \\
 &\quad \left. + \dots \right\}
 \end{aligned}$$

Note: b_3 has contributions from integrals such as

$$\underbrace{\int f_{12} f_{23} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3}_{\text{"2 f's"}} \quad \text{and} \quad \underbrace{\int f_{12} f_{23} f_{13} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3}_{\text{"3 f's"}}$$

On the other hand, the terms with a product of 2 f's contribute to b_3 and b_4 :

$$[(\textcircled{1} \textcircled{2}) \cdot (\textcircled{3})] = \int f_{12} f_{23} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 \rightarrow b_3$$

$$\begin{aligned} [(\textcircled{1} \textcircled{2}) \cdot (\textcircled{3} \textcircled{4})] &= \int f_{12} f_{34} d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 d^3 \vec{r}_4 \\ &= \int f_{12} d^3 \vec{r}_1 d^3 \vec{r}_2 \int f_{34} d^3 \vec{r}_3 d^3 \vec{r}_4 \\ &\rightarrow b_4 \end{aligned}$$

Typically, the virial equation of state is written as

$$\frac{Pv}{kT} = \sum_{\ell=1}^{\infty} a_{\ell}(T) \left(\frac{1}{v} \right)^{\ell-1}$$

Connection between $a_{\ell}(T)$ and $b_{\ell}(T)$?

l.h.s.: $\frac{1}{v} \sum_{\ell=1}^{\infty} b_{\ell} z^{\ell}$

(using ① and ② from p. 217)

r.h.s.: $\sum_{\ell=1}^{\infty} a_{\ell}(T) \left(\frac{1}{v} \right)^{\ell-1} \sum_{\ell'=1}^{\infty} \ell' b_{\ell'} z^{\ell'}$

Setting l.h.s. and r.h.s. equal and comparing powers of z (s.th. like this will be on HW 9):

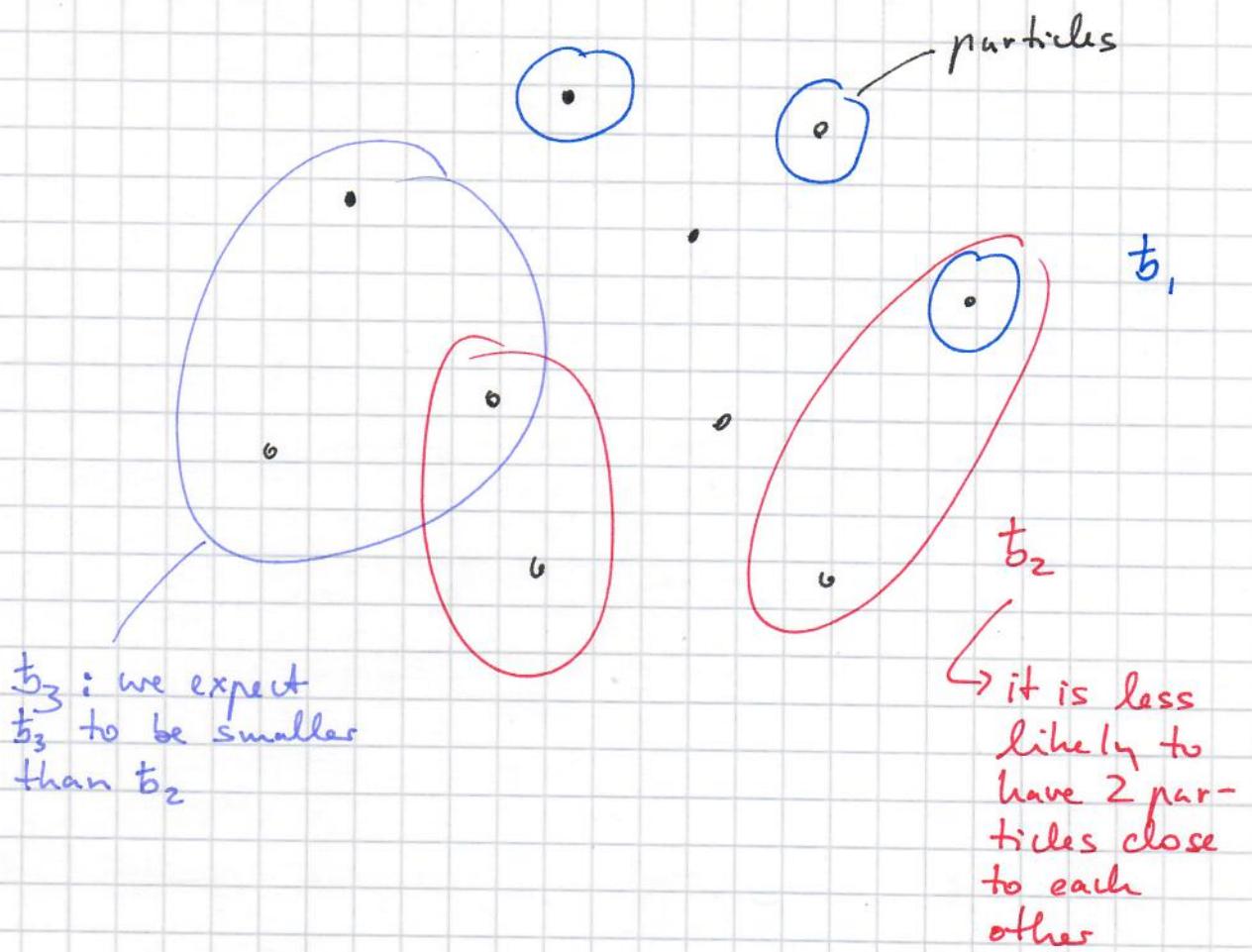
$$a_1 = b_1 = 1$$

$$a_2 = -b_2$$

$$a_3 = 4b_2^2 - 2b_3$$

$$a_4 = -20b_2^3 + 18b_2 b_3 - 3b_4$$

Picture:

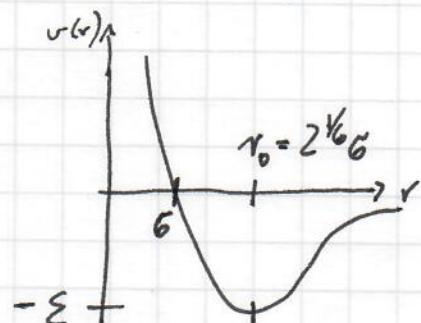


Note: we can argue in terms of
cluster integrals t_k or in
terms of virial coefficients a_k .

Concrete example:

Look at gas w/ two-body Lenard-Jones potential

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$



Make things simpler: $v(r) = \begin{cases} \infty & \text{for } r < r_0 \\ -v_0 \left(\frac{r_0}{r}\right)^6 & \text{for } r > r_0 \end{cases}$

$$a_2 = -b_2 = \frac{2\pi}{\lambda^3} \int_0^\infty (1 - e^{-\beta v(r)}) r^2 dr$$

$$= \frac{2\pi}{\lambda^3} \left[\underbrace{\int_0^{r_0} r^2 dr}_{\frac{1}{3} r_0^3} + \underbrace{\int_{r_0}^\infty (1 - e^{-\frac{v_0}{kT} \left(\frac{r_0}{r}\right)^6}) r^2 dr}_{\approx -\frac{v_0}{kT} \left(\frac{r_0}{r}\right)^6} \right]$$

$$\frac{1}{3} r_0^3$$

$$\frac{v_0}{kT} \ll 1 \quad \approx -\frac{v_0}{kT} \left(\frac{r_0}{r}\right)^6$$

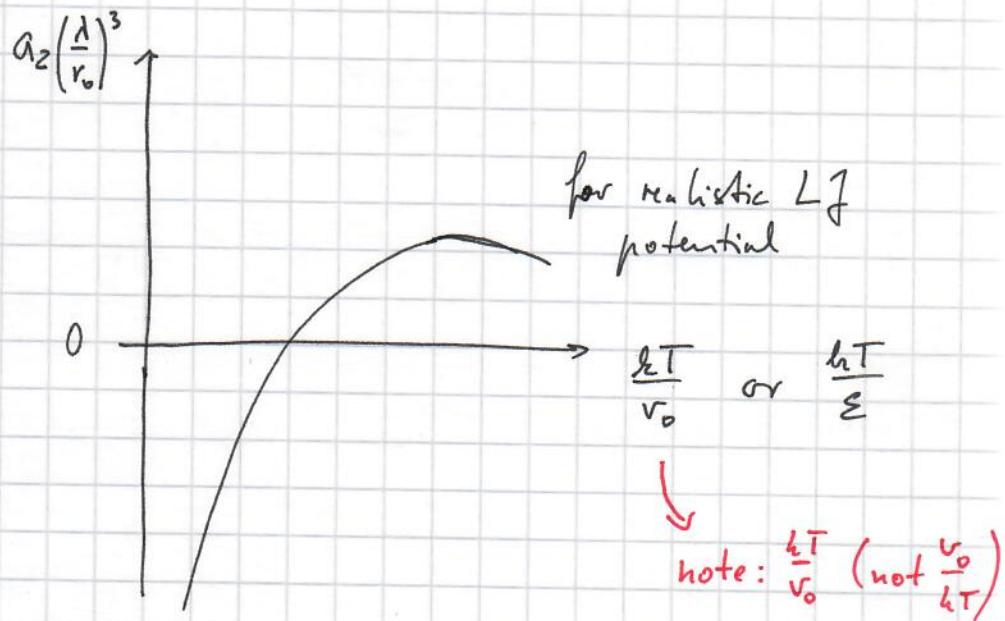
high T
approximation

$$+ \frac{v_0}{kT} r_0^6 \frac{1}{r_0^3} \left(-\frac{1}{3}\right)$$

L22

$$\Rightarrow a_2 \approx \frac{2\pi}{3} \left(\frac{r_0}{\lambda} \right)^3 \left(1 - \frac{v_0}{kT} \right)$$

or $a_2 \left(\frac{\lambda}{r_0} \right)^3 = \frac{2\pi}{3} \left(1 - \frac{v_0}{kT} \right)$



Use this in virial equation of state:

$$\frac{Pv}{kT} \approx a_1 + a_2 \frac{1^3}{v}$$

$$= 1 + \frac{2\pi}{3} \frac{r_0^3}{v} \left(1 - \frac{v_0}{kT} \right)$$

$$\text{or } P + \frac{2\pi r_0^3 v_0}{3} \frac{1}{v^2} = \underbrace{\frac{kT}{v} \left(1 + \frac{2\pi r_0^3}{3v} \right)}_{\approx \left(1 - \frac{2\pi r_0^3}{3v} \right)^{-1}}$$

low density approximation

}

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

define $\bar{v} = \frac{2\pi r_0^3}{3}$ excluded volume

$$\bar{a} = \frac{2\pi r_0^3 v_0}{3}$$

\rightsquigarrow we already used $v_0 \Rightarrow$
I'm using a "bar"

$$\Rightarrow \left[\left(P + \frac{\bar{a}}{v^2} \right) (v - \bar{v}) = kT \right]$$

We obtained the van der Waals equation of state !!!

Moreover, we got some expressions for \bar{a} and \bar{v} !!!



If we use LJ potential instead of simplified potential, we get some reasonable estimates!

10.2 Quantum Cluster Expansion

Note: I take a slightly different approach than that discussed in the text.

$$\text{Start with: } VP = + \delta T \log Q$$

$$= \delta T \log \left(\sum_{N=0}^{\infty} z^N Q_N(V, T) \right)$$

$$\approx kT \left[z Q_1 + \left(Q_2 - \frac{Q_1^2}{2} \right) z^2 + \left(Q_3 - Q_1 Q_2 + \frac{Q_1^3}{3} \right) z^3 + \dots \right] (*)$$

Diagram illustrating the expansion of $\log(1+x)$ around small x . The expansion is given by $x - \frac{x^2}{2} + \frac{x^3}{3}$.

assume
 z is small

$$\Rightarrow \frac{P}{kT} = \frac{1}{V} \sum_{l=1}^{\infty} b_l z^l \quad (\text{same way of defining } b_l \text{ as before})$$

from $(*)$:

$$\frac{P}{kT} = \frac{1}{V} \left[z Q_1 + \left(Q_2 - \frac{Q_1^2}{2} \right) z^2 + \dots \right]$$

→ see Eq. (10.27) of text

$$\text{where } b_1 = \frac{d^3}{V} Q_1$$

$$b_2 = - \frac{d^3}{V} \left(\frac{Q_1^2}{2} - Q_2 \right)$$

$$b_3 = \frac{d^3}{V} \left(\frac{Q_1^3}{3} - Q_1 Q_2 + Q_3 \right)$$

as before: can take $V \rightarrow \infty$ limit $\Rightarrow b_\ell \rightarrow t_\ell$

$$a_1 = t_1 .$$

$$a_2 = -t_2$$

$$a_3 = 4t_2^2 - 2t_3$$

$$a_4 = -20t_2^3 + 18t_2t_3 - 3t_4$$

Actually: the discussion on page 223 never made use of the fact that we're dealing with a quantum system!

→ However: Q_1, Q_2, Q_3, \dots need to be calculated following quantum rules (if our goal is to have a quantum description!)

So, we need to calculate Q_1, Q_2, \dots

$$Q_1(V, T) = V \left(\frac{m k T}{2 \pi \hbar^2} \right)^{3/2}$$

$$= \frac{V}{\lambda^3}$$



we had done this before
 → Since we are looking at
 a single particle, it does
 not matter whether we are
 treating bosons or fermions

$$a_1 = \frac{1}{2},$$

$$= \frac{\lambda^3}{\sqrt{V}} Q_1$$

$$= 1$$

Next, we want to calculate $Q_2(V, T)$.

This is a bit more tricky since we need

to make sure that our quantum mechanical

states have the correct exchange symmetry.

These are
 two-particle states

We want to calculate

$$q_2 = -t_2 \quad \Rightarrow \quad t_2 = -\frac{J^3}{V} \left(\frac{Q_1^2}{2} - Q_2 \right)$$

$\neq 0$ if we are dealing
with identical bosons
or identical fermions even
in the case that we
don't have interactions!

Why?

Single-particle plane wave states:

$$\frac{1}{\sqrt{V}} e^{i \vec{k}_f \cdot \vec{r}_f}$$

for the j^{th} particle

with energy $\frac{\hbar^2 \vec{E}_j^2}{2m}$; $\vec{E}_j = (E_{jx}, E_{jy}, E_{jz})$

can only take

particular values

Let's construct two-particle wave fct. (use \vec{r}_1 and \vec{r}_2):

$$\frac{1}{V} e^{i(\vec{k}_1 \cdot \vec{r}_1 + \vec{k}_2 \cdot \vec{r}_2)}$$

} for now : no interactions!

As written, we do not "see" any features related to exchange symmetry. Let's rewrite the expression:

$$\frac{1}{\sqrt{v}} e^{i(\vec{k}_1 \cdot \vec{r}_1 + \vec{k}_2 \cdot \vec{r}_2)} = \frac{1}{\sqrt{v}} \exp \left[i \left(\frac{\vec{k}_1 - \vec{k}_2}{2} \right) \cdot (\vec{r}_1 - \vec{r}_2) \right] \times$$

Simple manipulation

$$\exp \left[i (\vec{k}_1 + \vec{k}_2) \cdot \frac{(\vec{r}_1 + \vec{r}_2)}{2} \right]$$

We recognize: $\vec{r}_1 - \vec{r}_2 = \vec{r}_{\text{rel}} \hat{=} \text{relative distance vector}$

$$\frac{\vec{r}_1 + \vec{r}_2}{2} = \vec{R}_{\text{cm}} \hat{=} \text{center-of-mass vector}$$

$$\frac{\vec{k}_1 - \vec{k}_2}{2} = \vec{k}_{\text{rel}} \hat{=} \text{wave vector associated with relative degrees of freedom}$$

$$\vec{k}_1 + \vec{k}_2 = \vec{K}_{\text{cm}} \hat{=} \text{wave vector associated with center-of-mass degrees of freedom}$$

(to $\vec{R}_{\text{cm}} \hat{=} \text{total momentum}$)

Two-particle fct. becomes:

$$\frac{1}{\sqrt{v}} e^{i(\vec{k}_{\text{rel}} \cdot \vec{r}_{\text{rel}} + \vec{K}_{\text{cm}} \cdot \vec{R}_{\text{cm}})} = \frac{1}{\sqrt{v}} e^{i \vec{k}_{\text{rel}} \cdot \vec{r}_{\text{rel}}} e^{i \vec{K}_{\text{cm}} \cdot \vec{R}_{\text{cm}}}$$

unchanged under exchange of particles 1 and 2

Look at $e^{i\vec{k}_{nl} \cdot \vec{r}_{nl}}$:

$$e^{i\vec{k}_{nl} \cdot \vec{r}_{nl}} = \cos(\vec{k}_{nl} \cdot \vec{r}_{nl}) + i \sin(\vec{k}_{nl} \cdot \vec{r}_{nl})$$

even under exchange
of 1 and 2
odd under exchange
of 1 and 2

\Rightarrow not all products of single-particle states fulfill the proper exchange symmetry

So: We need to construct fcts. with the proper symmetry \rightarrow solve SE for relative Hamiltonian.

Alternatively, apply $\mathcal{S} = \frac{1}{\sqrt{2}} (1 \pm P_{12})$ onto unsymmetrized two-particle wave fct.

bosons

fermions

P_{12} : exchanges particles 1 and 2

\mathcal{S} : symmetrizer (+) or anti-symmetrizer (-)

$\frac{1}{\sqrt{2}}$: Needed for normalization purposes

If we do have interactions, things are more complicated! Need to solve two-particle SE to determine eigenenergies corresponding to properly symmetrized / anti-symmetrized two-particle states:

$$\hat{\mathcal{H}} \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2)$$

$$\left(-\frac{\hbar^2}{2m} \nabla_{\vec{r}_1}^2 - \frac{\hbar^2}{2m} \nabla_{\vec{r}_2}^2 + V(|\vec{r}_1 - \vec{r}_2|) \right) \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2)$$

$$\left(-\frac{\hbar^2}{2\mu} \vec{\nabla}_{\vec{r}_{\text{rel}}}^2 + V(r_{\text{rel}}) - \frac{\hbar^2}{2M} \vec{\nabla}_{\vec{R}_{\text{cm}}}^2 \right) \psi(\vec{r}_{\text{rel}}, \vec{R}_{\text{cm}}) =$$

$$\mu = \frac{m}{2}$$

$$M = 2m$$

$$\Rightarrow \text{rel. coordinate: } \left(-\frac{\hbar^2}{2\mu} \vec{\nabla}_{\vec{r}_{\text{rel}}}^2 + V(r_{\text{rel}}) \right) \phi_{\text{rel}}(\vec{r}_{\text{rel}})$$

$$= E_{\text{rel}} \phi_{\text{rel}}(\vec{r}_{\text{rel}})$$

$$-\frac{\hbar^2}{2M} \vec{\nabla}_{\vec{R}_{\text{cm}}}^2 \Phi_{\text{cm}}(\vec{R}_{\text{cm}}) = E_{\text{cm}} \Phi_{\text{cm}}(\vec{R}_{\text{cm}})$$

non-trivial

plane waves

for relative part: use spherical coordinates and
solve radial SE for each l

$$\left(-\frac{t^2}{2\mu} \frac{\partial^2}{\partial r_{nl}^2} + \frac{t^2 l(l+1)}{2\mu r_{nl}^2} + V(r_{nl}) \right) u_e(r_{nl})$$

$$= E_{nl} u_e(r_{nl})$$

$$\text{where } \phi_{nl}(r_{nl}) = \frac{u_e(r_{nl})}{r} Y_{lm}(\hat{r}_{nl})$$

l even: symmetric $\phi_{nl}(\vec{r}_{nl})$

l odd: anti-symmetric $\phi_{nl}(\vec{r}_{nl})$

See Sec. 10.3 of text for a "classic"

example! \rightarrow I will not work through the math in class.

\hookrightarrow it's a very nice quantum HW problem

Clearly, virial equation of state is approximate!

To get l 'th order virial coefficient, need to solve l -body problem.

→ gets challenging quickly, except in some special cases ...

So: is it useful? i.e., does anybody use this today?

→ Yes!

For example: Two-component Fermi gas with infinitely strong interactions.

${}^6\text{Li} \rightsquigarrow$ two hyperfine states serve as effective spin- $\frac{1}{2}$ system

Feshbach resonance tuned such that s-wave scattering length (effective interaction strength) is infinitely large.

→ very challenging problem since we don't have a small parameter coming from interaction
but: in "high" temperature regime,

$n\lambda^3$ serves as a small parameter.

Virial equation of state has been used as a thermometry tool!

Third- and fourth-order virial coefficients have been extracted from experimental data by Zwierlein's and Salomon's groups.

→ theory for fourth-order virial coefficient is hard (a student of mine developed a path integral Monte Carlo approach for this purpose a few years ago — one of the most challenging research problems I've tackled...)