(1) For 2 identical Bosons, out of $j=2,1,0$, one can consider only $j=2,0$; $j=2$ must be present to get $m=2,-2$ — Now we have 5 states & need one more — this comes from $j=0$. So $j=1$ is excluded. Rotational invariance tells us that whole subspaces should be present or absent. || Also, $j=2,0$ gives sym. wavefns.

Problem set 2 **Date due: April 7, 2006**

1. Consider a system with N independent sites and $2N$ identical spin 1 bosonic particles distributed equally among the sites so that each site contains two particles. The whole system is kept in a uniform magnetic field so that the Hamiltonian of the system is given by $-\mu\vec{B} \cdot \sum_i \vec{S}_i$, with the sum over i running over all the $2N$ bosons.

   a) Calculate the canonical partition function and specific heat of this system.

   Suppose $j=0,1,2,3$ top one is always sym.

   b) Repeat the calculation if each site contained two spin 3/2 fermionic particles instead of two spin 1 bosonic particles.

   → $j=0,1,2,3$; $j=0,2$ gives anti sym. wave function

2. Consider a system of N spin half electrons. A fraction 1/2 of them are polarized along the z direction, a fraction 1/4 are polarized along the x direction and another fraction 1/4 are polarized along the $-z$ direction. Calculate the density matrix of the system in a basis of S_z eigenstates.

3. Consider a set of non-interacting particles moving in a harmonic oscillator potential. The parameters of the potential are such that the angular frequency is ω.

   a) Find the expression for the grand partition function of the system in quantum statistical mechanics. Consider both cases, when the particles are fermionic and the particles are bosonic.

   b) Consider the high temperature limit at a fixed value of the total number of particles, and show that the result agrees with that of classical statistical mechanics. (For this comparison you need to calculate the grand partition function of a system of classical particles moving in a harmonic oscillator potential.) Find the specific heat of the system in this limit.

4. a) Find an expression for the grand partition function Q of two dimensional ideal Bose gas, and express $V^{-1} \ln Q$ as a function of the fugacity z and temperature T in the thermodynamic limit.

   c Check

   b) Find the average number of particles per unit area in the thermodynamic limit as a function of z and T.

   c) Show that there is no Bose-Einstein condensation for a two dimensional ideal Bose gas.

d) Calculate various other thermodynamic quantities like entropy per unit volume, total energy per unit volume and specific heat at constant volume, as a function of T and N at low temperature for fixed density.

5. Consider an ideal gas of spin 1 bosons in three dimensions. The system is placed in a uniform magnetic field $\vec{B}$, and in this field the total Hamiltonian of the system acquires an additional term (besides the knetic energy) of the form $-\mu\vec{B}\cdot\sum_i \vec{S}_i$ where $\vec{S}_i$ denotes the spin operator of the i-th particle. This corresponds to bosons carrying magnetic moment μ.

   a) For a given temperature find an expression for the critical density of particles at which Bose-Einstein condensation takes place.

   b) Find an expression for the total magnetization (which is defined as the ensemble average of $\mu\sum_i \vec{S}_i$) of the system both below and above the critical density.

   c) Calculate the magnetization in the $B \to 0$ limit both below and above the critical density.

6. Consider an ideal gas of spin 1/2 massless fermions. In this case we need to use relativistic relation between energy and momentum i.e. $e(\vec{p}) = c|\vec{p}|$.

   a) Find the expression for the grand partition function and the number of particles in the system in terms of T, V, z.

   $\bar{N}_1 - \bar{N}_2 = \frac{1}{\beta}\frac{\partial \ln Q}{\partial \mu}$

   b) Show that in the high temperature limit the equation of state reduces to the classical result. (For this comparison you first need to find the equation of state for an ideal gas of relativistic massless particles obeying Boltzmann statistics.) Also find the lowest order correction to the equation of state.

   $N_1 + N_2 = ?$

   c) More realistically, if we have massless fermions, then fermion - antifermion pairs may be produced without violating any conservation laws. (Antifermions have similar properties as the fermions but are distinguishable from the fermions.) Thus the conserved quantity for a given system is the difference between the total number of fermions and antifermions but not the number of fermions and antifermions individually. Repeat parts a) and b) for such a system.

$$\psi^i(x_1, x_2, x_3) = \sum_{k_1, k_2, k_3} e^{2\pi i\left(x_1 k_1/N_1 + x_2 k_2/N_2 + x_3 k_3/N_3\right)} \phi^i_{k_1, k_2, k_3}$$

a lattice point

(y^1, y^2, y^3)

22/2/06

Imperfect gas (Classical) ~~case~~

$$\mathcal{H} = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m + V(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$$

$$V = \sum_{i<j} v(\vec{x}_i - \vec{x}_j)$$

↳ two body interaction

$$v(\vec{x}_i - \vec{x}_j) = v(\vec{x}_j - \vec{x}_i)$$

V has $\frac{N(N-1)}{2}$ terms $\sim N^2$ terms whereas $\sum_{i=1}^{N} \vec{p}_i^{\,2}/2m \sim N$ terms

Reason that we'll be able to do pert. expansion with $V(\ldots)$ is that it is short-ranged

Also a very small fraction of N^2 terms contribute bcos most are far apart

$[\hat{n} \cdot (\vec{x}_i - \vec{x}_j)]^2$ is inv. under the interchange $i \leftrightarrow j$, but is not a fn. of $|\vec{x}_i - \vec{x}_j|$

Canonical partition function:

$$Z_N(V, T) = \frac{1}{N!\,h^{3N}} \int d^{3N}p \, d^{3N}x \, e^{-\beta \mathcal{H}}$$

$$\mathcal{Q}(V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N!\,h^{3N}} \int d^{3N}p \, d^{3N}x \, e^{-\beta \mathcal{H}}$$

$$\boxed{e^{\beta\mu} = z}$$

$$\mathcal{Q} = \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} \int d^{3N}p \, e^{-\sum_{i=1}^{N} \beta \vec{p}_i^{\,2}/2m} \int d^{3N}x \, e^{-\sum_{i<j} \beta v(\vec{x}_i - \vec{x}_j)}$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} (2\pi m k T)^{\frac{3N}{2}} \int d^{3N}x \, e^{-\beta \sum_{i<j} v(\vec{x}_i - \vec{x}_j)}$$

$$\Rightarrow \mathcal{G} = \sum_{N=0}^{\infty} \frac{y^N}{N!} \int d^{3N}x\, e^{-\beta \sum_{i<j} v(\vec{r}_i - \vec{r}_j)}$$

$$\boxed{y = \frac{z}{h^3}(2\pi m kT)^{3/2}}$$

Define:- $f(\vec{r}) = e^{-\beta v(\vec{r})} - 1$

$f_{ij} = f(\vec{r}_i - \vec{r}_j)$

$f(\vec{r}) \to 0$ as $\vec{r} \to \infty$ since $v(\vec{r}) \to 0$ as $\vec{r} \to \infty$

$$e^{-\beta v(\vec{r}_i - \vec{r}_j)} = (1 + f_{ij})$$

$$\Rightarrow \mathcal{G} = \sum_{N=0}^{\infty} \frac{y^N}{N!} \int d^{3N}x \prod_{i<j} (1 + f_{ij})$$

$$\prod_{i<j}(1+f_{ij}) = 1 + \sum_{i<j} f_{ij} + \frac{1}{2}\sum_{i<j}\sum_{\substack{k<l \\ (ij)\neq(kl)}} f_{ij} f_{kl} + \cdots$$

$(1+f_{12})(1+f_{23})(1+f_{13})$

$= 1 + f_{12} + f_{23} + f_{13}$

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

Each such term has a diagrammatic representation.

o o o o ---------- o

1 2 3 4 N

On the other hand,

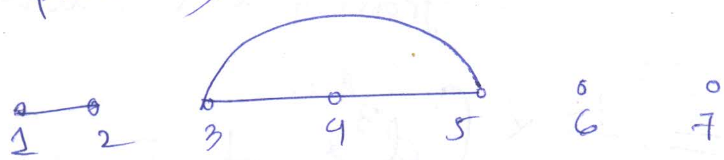
$\sum_{i<j}\sum_{k<l} f_{ij} f_{kl}$

$= (f_{12} + f_{13} + f_{23})$

$\cdot (f_{12} + f_{13} + f_{23})$

For N particles, draw N circles

(7 particles):-



$$\int d^3x_1 \cdots d^3x_N \, f_{12} \, f_{34} \, f_{45} \, f_{35}$$

represents $\underline{1}$

Each term in the sum corresponds to a diagram

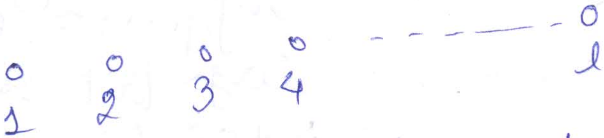
You have to sum over the diagrams

Not allowed

bcos $f_{12}{}^2$ not allowed

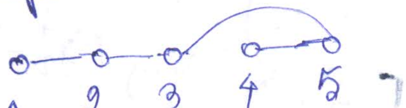
Diagram also represents the integral

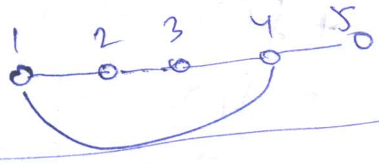
Suppose we have l particles



Definition :- An l-particle diagram is part of an l-cluster if each particle is attached to every other particle either directly or indirectly. l-cluster is the sum of all these diagrams.

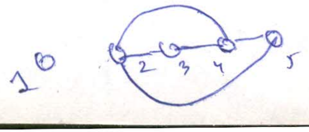
Examples of 5-clusters :-





All the things must be continuously joined by the line segments

Not a 5-cluster (bcos 2 & 3 not joined directly or indirectly)



" " 5-cluster (bcs 1 isn't joined to anything else)

Define: $B_l(V,T) = \frac{1}{V} \times$ ~~[illegible]~~ contributions from the l cluster

e.g. ① $B_1(V,T) = \frac{1}{V} \times \int d^3x \; 1 = 1$

② $B_2(V,T) = \frac{1}{V} \times \int d^3x_1 \, d^3x_2 \; \cancel{f(\vec{x}_1 - \vec{x}_2)} \; f(\vec{x}_1 - \vec{x}_2)$

$\boxed{\vec{x} = (x^{(1)}, x^{(2)}, x^{(3)})}$

$= \frac{1}{V} \int d^3x_1 \int d^3\vec{x} \; f(\vec{x})$

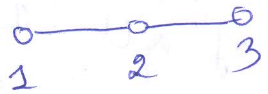
$= \int d^3x \; f(\vec{x}) \rightarrow$ assume that $f(\vec{x})$ falls off sufficiently fast for large $|\vec{x}|$ so that this integral is finite

It should be finite in the thermodyn. limit

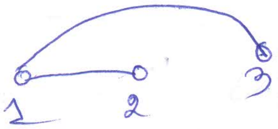
$\frac{1}{V}$ was introduced by hand to kill off the $\int d^3x_1$ term

t [illegible] → 23C

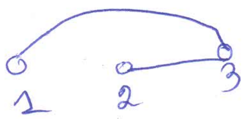
③ 3 cluster



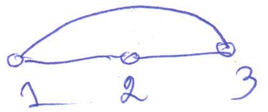
$\cancel{B_3 = \frac{1}{V} \int d^3x_1 \int d^3x_2 \int d^3x_3}$



$$B_3 = \frac{1}{V} \int d^3x_1 \, d^3x_2 \, d^3x_3$$



$$\Big[f(\vec{x}_1 - \vec{x}_2) f(\vec{x}_2 - \vec{x}_3) + f(\vec{x}_1 - \vec{x}_2) f(\vec{x}_1 - \vec{x}_3) + f(\vec{x}_1 - \vec{x}_3) f(\vec{x}_2 - \vec{x}_3) + f(\vec{x}_1 - \vec{x}_2) f(\vec{x}_1 - \vec{x}_3) f(\vec{x}_2 - \vec{x}_3) \Big]$$



Use $\vec{r}_1$, $\vec{\rho}_2 = \vec{r}_1 - \vec{r}_2$, $\vec{\rho}_3 = \vec{r}_1 - \vec{r}_3$ as independent variables.

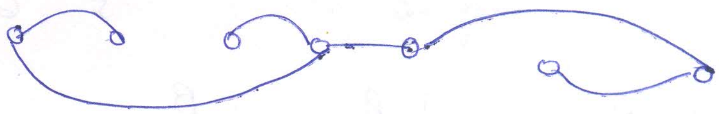
$$B_3 = \underbrace{\frac{1}{V}\int d^3x_1}_{=1} \int d^3\rho_2\, d^3\rho_3 \Big[f(\vec{\rho}_2)\, f(\vec{\rho}_3 - \vec{\rho}_2) + f(\vec{\rho}_3)\, f(\vec{\rho}_3 - \vec{\rho}_2) + f(\vec{\rho}_2) f(\vec{\rho}_3) f(\vec{\rho}_3 - \vec{\rho}_2) \Big]$$

One you take differences integrals become finite

$\Rightarrow$ has finite thermodynamic limit.

$\vec{\rho}_2$ is finite – integral is restricted to finite volume so once you assume f falls off fast & int. converges.

if $\vec{\rho}_2$ is finite, $\vec{\rho}_3 - \vec{\rho}_2$ is finite



All B_l's have finite thermodynamic limit.

(this is not true if the diag. isn't an n-cluster)

$\vec{x}_1 - \vec{x}_2 = \vec{\rho}_1$

$\vec{x}_4 - \vec{x}_3 = \vec{\rho}_2$

$$\int d^3x_1\, d^3x_2\, d^3x_3\, d^3x_4\, f_{12}\, f_{34}$$

$$= \int d^3x_1\, d^3\rho_1\, f(\vec{\rho}_1)\, d^3x_3\, d^3\rho_2\, f(\vec{\rho}_2)$$

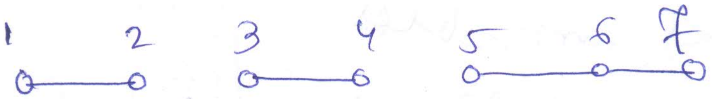
$$= V^2 \int d^3\rho_1\, f(\vec{\rho}_1) \int d^3\rho_2\, f(\vec{\rho}_2)$$

these 2 are finite integrals

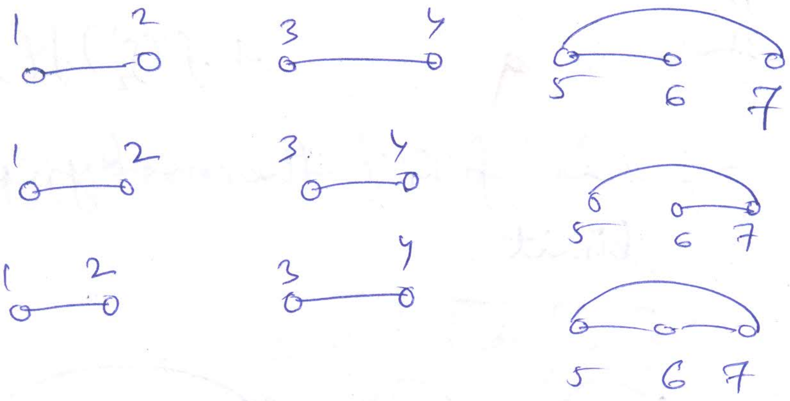
disconnected pts ~~segment~~ will give $V^{\#}$ factor

You can approx. f by a Θ fn. & say f is zero for $|\vec{r}_1 - \vec{r}_2| > a$ --- then the range of int. of $|\vec{\rho}_2|$ is restricted to a ~~length~~ ~~volume~~ length a --- so we get a finite integral.

Consider a general graph



(Add to this the following diagrams:)



$= V B_2 \quad V B_2 \quad V B_3$

Any given graph in a N-particle system is part of a term

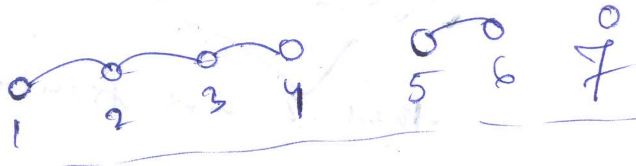
$$\prod_{l=1}^{\infty} (B_l V)^{m_l}$$

m_l = no. of l- clusters

e.g.:- Take an N-particle graph ($N=7$)

$(B_1 V)^7$

This diag. by itself isn't $(B_4 V)(B_2 V)(B_1 V)$



This diag. constitutes one of the terms of the above expression

is part of $(B_4 V)(B_2 V)(B_1 V)$

$$\sum_{l=1}^{\infty} l m_l = N$$

$$\mathcal{Q} = \sum_{N=0}^{\infty} \frac{y^N}{N!} \sum_{m_1, m_2, m_3 \ldots = 0}^{\infty} \prod_{l=1}^{\infty} (B_l V)^{m_l}$$

(subject to the condn.) $\sum_{l=0}^{\infty} l\, m_l = N$

→ is not completely correct (haven't taken permutations)

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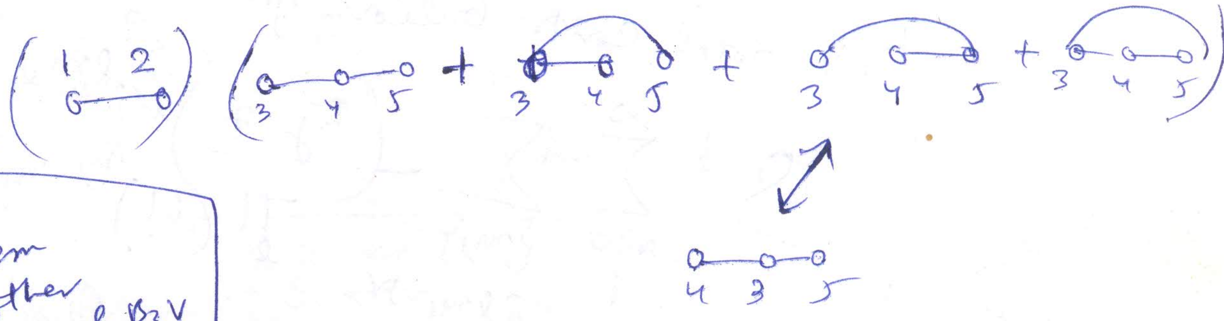
e.g. $N=5$ $\quad (B_2 V)(B_3 V)$



But a 5 particle system will have other permut. of $B_2 V$ & $B_3 V$

$$\mathcal{Q} = \sum_{N=0}^{\infty} \frac{y^N}{N!} \sum_{m_1, m_2, m_3, \ldots = 0} \prod_{l=1}^{\infty} (B_l V)^{m_l} \times \frac{N!}{\prod_l (l!)^{m_l} \prod_l (m_l!)}$$

compensates for permutation inside a clusters

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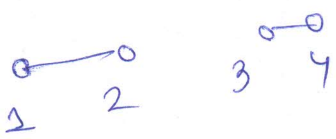
e.g. $N=4$



You can exchange 1, 2 & 3, 4.

$\longrightarrow \frac{1}{\prod_l m_l!}$ should be there

① There are m_l l-clusters & a permutation of these m_l things doesn't lead to a new graph.
② in the sum over all l-clusters, a perm. of the l particles within it doesn't lead to a new graph.

22/2/06

$$Q = \sum_{N=0}^{\infty} \frac{\tilde{y}^N}{N!} z^N \sum_{\substack{\{m_l\} \\ \sum_{l=1}^{\infty} l m_l = N}} \frac{N!}{\prod_l \left((l!)^{m_l} m_l!\right)} \prod_l (B_l V)^{m_l}$$

$$\tilde{y} = \frac{1}{h^3} \left(2 m \pi k T\right)^{3/2}$$

$B_l V$ = total contribution from l-cluster.

$$Q = \sum_{N=0}^{\infty} \sum_{\substack{\{m_l\} \\ \sum l m_l = N}} \frac{(\tilde{y} z)^{\sum_{l=1}^{\infty} l m_l} \prod_l (B_l V)^{m_l}}{\prod_l (l!)^{m_l} m_l!}$$

We'll reorganise it otherwise in the thermodyn. limit it may seem it grows very large

No N explicitly anywhere so you can remove the constraint

$$= \sum_{m_1, m_2, \ldots} \prod_{l=1}^{\infty} \left\{ \frac{(\tilde{y}^l z^l)^{m_l}}{(l!)^{m_l} m_l!} (B_l V)^{m_l} \right\}$$

$$= \prod_{l=1}^{\infty} \sum_{m_l = 0}^{\infty} \left(\frac{\tilde{y}^l z^l}{l!}\right)^{m_l} (B_l V)^{m_l} \frac{1}{m_l!}$$

$$\sum_{m_1, m_2, \ldots} \prod_{l=1}^{\infty} \frac{A_l^{m_l}}{m_l!} \qquad \text{where } A_l = \frac{\tilde{y}^l z^l (B_l V)}{l!}$$

$$\Downarrow$$

$$\sum_{m_1, m_2, \ldots} \frac{A_1^{m_1}}{m_1!} \frac{A_2^{m_2}}{m_2!} \cdots$$

$$= \left(\sum_{m_1} \frac{A_1^{m_1}}{m_1!}\right) \left(\sum_{m_2} \frac{A_2^{m_2}}{m_2!}\right) \cdots$$

$\rightarrow$ (we have factorised it; it was a sum of prodts., we have written it as a prdt. of sums)

$$= \prod_l \sum_{m_l} \frac{A_l^{m_l}}{m_l!}$$

we have used $\left(\sum_i x_i\right)\left(\sum_\alpha y_\alpha\right) = \sum_{i,\alpha} x_i y_\alpha$

$$\Rightarrow \mathcal{Q} = \prod_{l=1}^{\infty} \exp\left(\frac{\tilde{y}^l z^l}{l!} B_l V\right)$$

$$\Rightarrow \ln \mathcal{Q} = \sum_l \frac{\tilde{y}^l z^l}{l!} B_l V$$

$$= V\left(\sum_{l=1}^{\infty} \frac{\tilde{y}^l z^l}{l!} B_l\right)$$

Define $b_l = \frac{B_l}{l!} \tilde{y}^{l-1}$

where $\tilde{y} = \frac{1}{h^3}(2\pi m k T)^{3/2}$

$$\boxed{\ln \mathcal{Q} = V \tilde{y} \sum_{l=1}^{\infty} b_l z^l}$$

$b_1 = B_1 = 1$ (so this expansion starts with 1)

$$\ln \mathcal{Q} = V/h^3 (2m\pi k)^{3/2} z\left(1 + b_2 z + b_3 z^2 + \cdots\right)$$

Compare with quantum statistics:

$$\ln \mathcal{Q} = \frac{V}{h^3}(2m\pi k T)^{3/2} f_1(z)$$

$$f_1(z) = z + k_2 z^2 + k_3 z^3 + \cdots$$

(for small z)

$\longrightarrow$ same structure as a classical gas with interaction.

Effectively, the effect of Q. statistics can be reinterpreted that there is some additional force give rise to these terms in classical picture

An ideal quantum gas behaves as a classical gas with some interactions

Fermi gas $\to$ classical gas with some repulsive interactions

Bose gas $\to$ --- attractive int.

$$\bar{N} = z \frac{\partial}{\partial z} \ln \mathcal{Q} \Big|_{T,V}$$

$$= \frac{V}{h^3}(2m\pi k T)^{3/2} z\left(1 + 2b_2 z + 3b_3 z^2 + \cdots\right)$$

$$\frac{P}{kT} = \frac{\partial}{\partial V} \ln Q \Big|_{z,T} = \frac{1}{h^3}\left(2m\pi kT\right)^{3/2} z\left(1 + b_2 z + b_3 z^2 + \cdots\right)$$

$$\boxed{\frac{PV}{NkT} = \frac{1 + b_2 z + b_3 z^2 + \cdots}{1 + 2b_2 z + 3b_3 z^2 + \cdots}}$$

z isn't an indep. variable & is to be det. from the eqn. $\bar{N} = \frac{V}{h^3}(\cdots)^{3/2} z(\cdots)$

The coefficients $b_2, b_3, b_4, \ldots$ are calculable.

b_l involves calculating l-cluster.

becomes more & more complicated for large l

In practice we can calculate a few terms, though in principle it is calculable to all orders

$\xRightarrow{\text{so}}$ cluster expansion is useful for small z.

$$z\left(1 + 2b_2 z + 3b_3 z^2 + \cdots\right) = \frac{N}{V}\left(\frac{h^2}{2m\pi kT}\right)^{3/2} = \eta$$

z is small if η is small

$\xRightarrow[\text{in turn means}]{\text{which}}$ low density or high temperature

why low density? → this exp. is the powers of int. Here we talking about avg. int. Low density means most times particles are far away. If it's a highly packed system like a liquid, then cluster exp. isn't useful

K.E. is dominant over P.E. even if density is moderate, but temp. is high

$$z = \eta\left(1 + \sum_{n=1}^{\infty} c_n \eta^n\right)$$

calculable in terms of b_n

$$z = \eta - 2b_2 z^2 - 3b_3 z^3 - \cdots$$

Using this we get

$$\frac{PV}{NkT} = 1 + \sum_{n=2}^{\infty} a_n \eta^{n-1}$$

calculable in terms of b_n

Calculation of a_2

$$\frac{PV}{NkT} = 1 - b_2 z + O(z^2)$$

$$= 1 - b_2 n + O(n^2)$$

[$\because$ $z = n$ to leading order]

$$\Rightarrow a_2 = -b_2$$

$$b_l = \frac{B_l}{l!} \tilde{y}^{\,l-1}$$

$$= \frac{1}{2} \tilde{y} B_2$$

$$= \frac{1}{2} \tilde{y} \frac{1}{V} \int d^3r_1 \, d^3r_2 \, f(\vec{r}_1 - \vec{r}_2)$$

$$= \frac{1}{2} \tilde{y} \int d^3r \, f(\vec{r})$$

$$f(\vec{r}) = e^{-\beta v(\vec{r})} - 1$$

We have taken the origin in such a way that As $r \to \infty$, v is zero

$$v(\vec{r}) > 0 \Rightarrow f(\vec{r}) < 0$$ (force is repulsive)

$$\Rightarrow b_2 < 0$$

(Pressure is more that what you'll get for an ideal gas — particle will tend to go away from each other for rep. force & more pressure)

$$\boxed{a_n\text{'s} \xrightarrow{\text{called}} \text{Virial Coefficients}}$$

For dilute gas, this method of cluster exp gives a method to calculate the virial coeff.

Classical ideal gas has zero virial coeffs.

classical interacting gas has non-zero virial coefficients.

quantum ideal gas also has non-zero virial coefficients $\longrightarrow$ $b_l = (\mp 1)^{l-1} \frac{1}{l^{5/2}}$ — for fermions, + for bosons

Q) How to calculate the virial coefficients of interacting quantum gas?

Quantum cluster expansion

In the $\hbar \to 0$ limit, virial coeff. of ~~classical~~ quantum ideal gas will be zero — we'll get classical ideal gas

N particle system with

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} v(\vec{r}_i - \vec{r}_j)$$

$$\Psi_\alpha(\vec{r}_1, \ldots, \vec{r}_N) \quad \alpha = 1, 2, \ldots, \infty$$

$\longrightarrow$ a complete set of basis states

they may or may not be energy e. states

Canonical partition function

$$Z_N(V, T) = \sum_\alpha \langle \Psi_\alpha | e^{-\beta \mathcal{H}} | \Psi_\alpha \rangle$$

$$= \sum_\alpha \int d^3 r_1 \cdots d^3 r_N \, \Psi_\alpha^*(\vec{r}_1, \ldots, \vec{r}_N) \, e^{-\beta \hat{\mathcal{H}}} \Psi_\alpha(\vec{r}_1, \ldots, \vec{r}_N)$$

Define $W_N(\vec{r}_1, \ldots, \vec{r}_N) = N! \underbrace{\frac{h^{3N}}{(2m\pi kT)^{3N/2}}}_{\frac{1}{\tilde{y}^N}} \sum_\alpha \Psi_\alpha^*(\vec{r}_1, \ldots, \vec{r}_N) \, e^{-\beta \hat{\mathcal{H}}} \Psi_\alpha(\vec{r}_1, \ldots, \vec{r}_N)$

$$Z_N = \frac{1}{N!} \tilde{y}^N \int d^3 r_1 \cdots d^3 r_N \, W_N(\vec{r}_1, \ldots, \vec{r}_N)$$

Only difference is how we calculate the B_l's is different from the classical case

Compare with the classical case:

$$Z_N(V, T) = \frac{1}{N!} \tilde{y}^N \int d^3 r_1 \cdots d^3 r_N \, e^{-\beta \sum_{i<j} v(\vec{r}_i - \vec{r}_j)}$$

$$\underbrace{e^{-\beta \sum_{i<j} v(\vec{r}_i - \vec{r}_j)}}_{\prod_{i<j}(1 + f_{ij})} \xrightarrow[\text{quantum theory}]{\text{gets replaced by — in}} W(\vec{r}_1, \ldots, \vec{r}_N)$$

W, off-hand doesn't have a cluster exp. ∵ it doesn't have the str. $e^{-\beta\Sigma\cdots}$

Define new quantities ~~U_1~~

$$U_1(\vec{r}_1),\ U_2(\vec{r}_1, \vec{r}_2),\ U_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$

etc. through the eqns:

$$W_1(\vec{r}_1) = U_1(\vec{r}_1) \longrightarrow \text{defines } U_1$$

$$W_2(\vec{r}_1, \vec{r}_2) = U_1(\vec{r}_1)U_1(\vec{r}_2) + U_2(\vec{r}_1, \vec{r}_2)$$

$$\longrightarrow \text{defines } U_2$$

For single particle, there is no int. — it's just the ideal gas — involves one-particle Ham.

There is no native cluster exp. — but a natural way to split W — we are doing it by hand to make it look like a cluster expansion

$$W_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$
$$= U_1(\vec{r}_1)U_1(\vec{r}_2)U_1(\vec{r}_3)$$
$$+ U_2(\vec{r}_1, \vec{r}_2)U_1(\vec{r}_3) + U_2(\vec{r}_1, \vec{r}_3)U_1(\vec{r}_1)$$
$$+ U_2(\vec{r}_2, \vec{r}_3)U_1(\vec{r}_1) + U_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$

$$\vdots$$

Define:—

$$B_l = \frac{1}{V}\int d^3r_1\, d^3r_2\, d^3r_3 \cdots d^3r_l\, U_l(\vec{r}_1, \ldots, \vec{r}_l)$$

Claim :—

$$\int d^3r_1 \cdots d^3r_N\, W_N(\vec{r}_1, \ldots, \vec{r}_N)$$
$$= \sum_{\substack{\{m_l\} \\ \sum l m_l = N}} \frac{N!}{\prod_l \{(l!)^{m_l} m_l!\}} \prod_l (B_l V)^{m_l}$$

Examples:

① $\int d^3r_1\, W_1(\vec{r}_1) = \int d^3r_1\, U_1(\vec{r}_1) = B_1 V$

② $\int d^3r_1\, W_2(\vec{r}_1, \vec{r}_2) = \int d^3r_1\, d^3r_2 \left[U_1(\vec{r}_1)U_1(\vec{r}_2) + U_2(\vec{r}_1, \vec{r}_2)\right]$

$$= (B_1 V)^2 + (B_2 V)$$

$\sum l m_l = 2$ can be satisfied in 2 ways: $l=1,\ m_l=2$; $l=2,\ m_l=1$

$l=1,\ m_l=2$: $\frac{2!}{2!}(B_1 V)^2 = (B_1 V)^2 \Big\|\ m_1=2,\ m_2=m_3=\cdots=0$

$l=2,\ m_l=1$ $\quad \frac{2!}{2!}(B_2 V) = B_2 V \Big|\ m_1=0,\ m_2=1,\ m_3=m_4=\cdots=0$

$\therefore$ LHS = RHS

(So it's as if we are doing a classical cluster expn. — adv. in doing this is that once we have gotten it this form, analysis is the same as before in terms ~~terms~~ of the B_l's — of course calculation of the B_l's is different)

In terms of the B_l's the final formula for $\ln Q$ is exactly the same as in the classical case.
The difference lies ~~in~~ the calculation of the B_l's.

\# Q> Do the B_l's have finite $V \to \infty$ limit?

24/2/06

Quantum Cluster Expansion

N-particle system

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} v(\vec{r}_i - \vec{r}_j)$$

$\Psi_\alpha(\vec{r}_1, \cdots, \vec{r}_N)$: $\alpha = 1, 2, \cdots \infty$

representing a basis of N-particle states.

Define: $W_N(\vec{r}_1, \cdots, \vec{r}_N) = N!\, \frac{h^{3N}}{(2m\pi kT)^{3N/2}}$

$$\times \sum_\alpha \Psi_\alpha^*(\vec{r}_1, \cdots, \vec{r}_N)\, e^{-\beta\hat{\mathcal{H}}}\, \Psi_\alpha(\vec{r}_1, \cdots, \vec{r}_N)$$

Define $U_1(\vec{r}_1)$, $U_2(\vec{r}_1, \vec{r}_2)$, ---- through the eqns

$$W_1(\vec{r}_1) = U_1(\vec{r}_1).$$

$$W_2(\vec{r}_1, \vec{r}_2) = U_1(\vec{r}_1) U_1(\vec{r}_2) + U_2(\vec{r}_1, \vec{r}_2)$$

$$W_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = U_1(\vec{r}_1) U_1(\vec{r}_2) U_1(\vec{r}_3) + U_1(\vec{r}_1) U_2(\vec{r}_2, \vec{r}_3) + U_1(\vec{r}_2) U_2(\vec{r}_1, \vec{r}_3) + U_1(\vec{r}_3) U_2(\vec{r}_1, \vec{r}_2) + U_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$

Define:

$$B_\ell V = \int d^3r_1 \cdots d^3r_\ell \, U_\ell(\vec{r}_1, \ldots, \vec{r}_\ell)$$

Grand canonical partition fn. has the same form as the classical grand canonical partition fn when expressed in terms of the B_ℓ's.

Q) Do the B_ℓ's have finite thermodynamic limit?

$$B_1 = \frac{1}{V} \int d^3r \, U_1(\vec{r}) = \frac{1}{V} \int d^3 \, W_1(\vec{r})$$

$$\Downarrow$$

$$(\ldots) \sum_\alpha \psi_\alpha^*(\vec{r}) e^{-\beta \hat{H}} \psi_\alpha(\vec{r})$$

$$= 1 \text{ (to be shown later)}$$

The theory is translation invariant, so $\sum_\alpha$ all states is indep. of $\vec{r}$ — though indiv. states can depend on $\vec{r}$ — actually it is $\mathrm{Tr}(e^{-\beta \hat{H}})$ — so $\vec{r}$-indep. & $\int d^3 W_1(\vec{r})$ will have an overall factor of V

$$B_2 = \frac{1}{V} \int d^3r_1 \, d^3r_2 \, U_2(\vec{r}_1, \vec{r}_2)$$

$$= \frac{1}{V} \int d^3r_1 \, d^3r_2 \left\{ W_2(\vec{r}_1, \vec{r}_2) - W_1(\vec{r}_1) W_1(\vec{r}_2) \right\}$$

$$= \frac{1}{V} \int d^3r_1 \, d^3r_2$$

W_2 should also be translation inv. & so, should be a fn of $\vec{r}_1 - \vec{r}_2$

(we take) $\vec{r}_1$ & $\vec{\rho} = \vec{r}_1 - \vec{r}_2$ as independent variables

Then, $B_2 = \underbrace{\frac{1}{V}\int d^3 r_1}_{=1} \int d^3\rho \left[W_2(\vec{\rho}, 0) - W_1(\vec{\rho}) W_1(0) \right]$

! W_2 is translation inv., we can shift $\vec{r}_2$ to zero

Using $W_2(\vec{r}_1, \vec{r}_2) - W_1(\vec{r}_1) W_1(\vec{r}_2)$
$= W_2(\vec{r}_1 - \vec{r}_2, 0) - W_1(\vec{\rho}) W_1(0)$

$W_2(\vec{\rho}, 0) \to W_1(\vec{\rho}) W_1(0)$ as $\vec{\rho} \to \infty$ sufficiently fast.

$W_2(\vec{r}_1, \vec{r}_2) \to W_1(\vec{r}_1) W_1(\vec{r}_2)$ as $|\vec{r}_1 - \vec{r}_2| \to \infty$ sufficiently fast.

Condition for B_ℓ to be finite :-

$W_\ell(\vec{r}_1, \ldots, \vec{r}_\ell)$

Divide the set $\{\vec{r}_1, \ldots, \vec{r}_\ell\}$ into two arbitrary sets A & B.

A: $\{\vec{y}_1, \ldots, \vec{y}_m\}$ $\quad A \cup B = \{\vec{r}_1, \ldots, \vec{r}_\ell\}$

B: $\{\vec{z}_1, \ldots, \vec{z}_{\ell-m}\}$

In the limit $|\vec{y}_i - \vec{z}_k| \to \infty$ for any $\vec{y}_i \in A$ & any $\vec{z}_k \in B$,

$W_\ell(\vec{r}_1, \ldots, \vec{r}_N) \to W_m(\vec{y}_1, \ldots, \vec{y}_m) W_{\ell-m}(\vec{z}_1, \ldots, \vec{z}_{\ell-m})$ sufficiently fast.

Test this for $\int d^3 r_1\, d^3 r_2\, d^3 r_3\, U_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$

set of 3 can be divided into set of 2 + set of 1

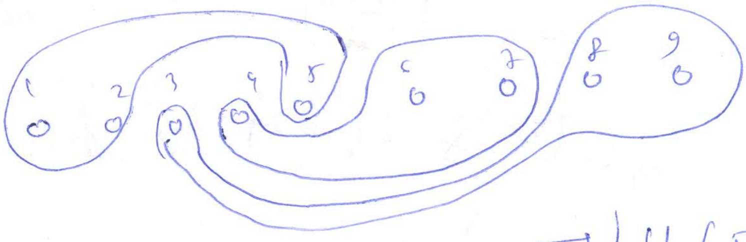
(Diagrammatically)

W_9

(A given term in W_9 can be thought of in the following way!)

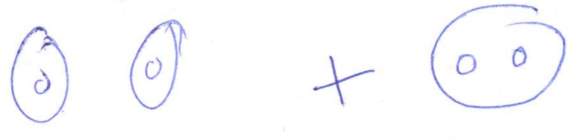
It is a condition on the Ham. in this case — in the classical case, it was the condition on the potential

There is still a notion of cluster, though not like before. U's can be drawn!



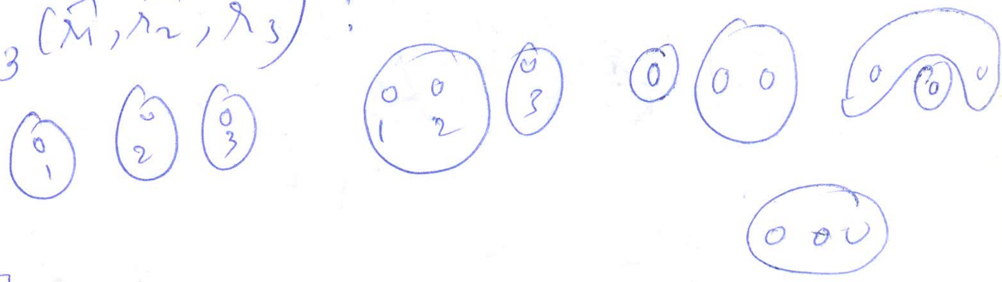
$U_3(\vec{x}_1, \vec{x}_2, \vec{x}_5)\, U_3(\vec{x}_4, \vec{x}_6, \vec{x}_7)\, U_3(\vec{x}_3, \vec{x}_8, \vec{x}_9)$

$W_2(\vec{x}_1, \vec{x}_2) = U_1(\vec{x}_1)\, U_1(\vec{x}_2) + U_2(\vec{x}_1, \vec{x}_2)$



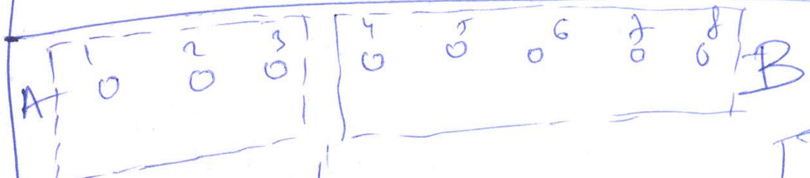
Diag. way of rep. diagrammatically — this is no analog of lines

$W_3(\vec{x}_1, \vec{x}_2, \vec{x}_3)$:

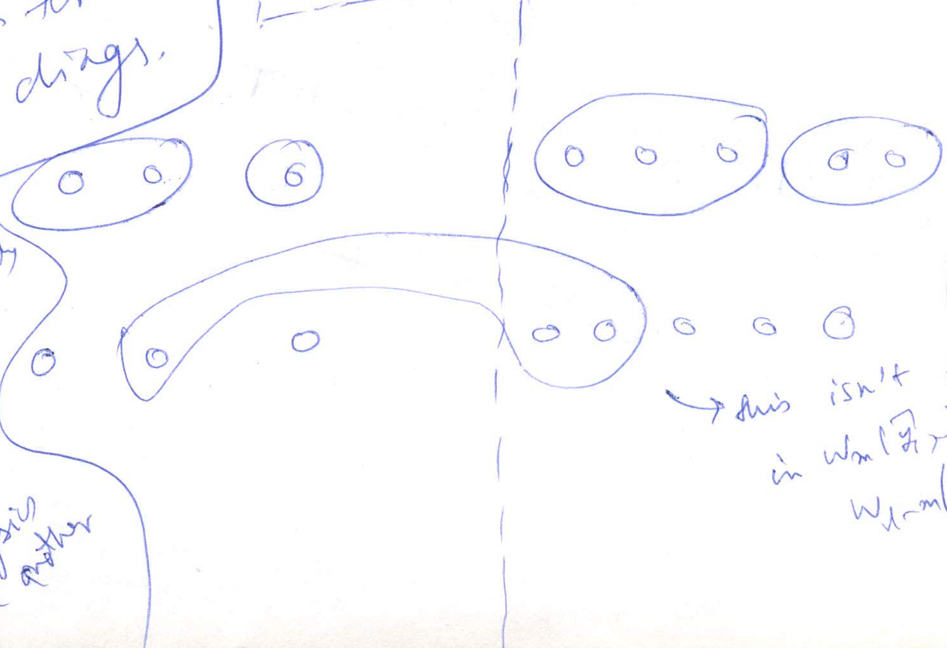


Here cluster is thought as one object defined in terms of W

we're sort of running things in reverse — we define clusters in terms of the given diags.



just my choice of sets of A & B — arbitrary division



Inside a cluster, if 2 elements are widely separated, it goes to zero — physics of one particle isn't dep. on physics on another

→ this isn't included in $W_m(\vec{x}_1, \ldots \vec{x}_m)$ $W_{l-m}(\vec{x}_1, \ldots \vec{x}_{l-m})$

Explicit calculation of $b_\ell = \frac{B_\ell}{\ell!} \tilde{f}^{\ell-1}$

→ much more difficult than the classical case.

We'll illustrate the ~~calc~~ procedure by calculating $b_2 = \frac{B_2}{2!} \tilde{f}$

Need $W_1(\vec{x}_1)$ & $W_2(\vec{x}_1, \vec{x}_2)$

Begin with $W_1(\vec{x}_1)$

$$H = \frac{\vec{p}_1^{\,2}}{2m}$$

$$\psi_{\vec{p}}(\vec{x}) = \frac{1}{\sqrt{V}} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{x}}$$

Use periodic ~~box~~ boundary condition

$$\therefore \vec{p} = \left(\frac{2\pi\hbar n_1}{L_1}, \frac{2\pi\hbar n_2}{L_2}, \frac{2\pi\hbar n_3}{L_3}\right)$$

where $V = L_1 L_2 L_3$

$$W_1(\vec{x}_1) = \sum_\alpha \psi_\alpha(\vec{x}_1)^* e^{-\beta \hat{H}} \psi_\alpha(\vec{x}_1)$$

$$= \frac{V}{h^3} \int d^3p \, \frac{1}{V} e^{-\beta p^2/2m}$$

$$W_1(\vec{x}_1) = \frac{1}{h^3}(2m\pi kT)^{3/2}$$

$$\left(\frac{2m\pi kT}{h^3}\right)^{3/2} W_1(\vec{x}_1) = \frac{1}{h^3}(2m\pi \cancel{k}\cancel{T})^{3/2}$$

$$\Rightarrow W_1(\vec{x}_1) = 1$$

$$W_1(\vec{x}_1)\left(\frac{2m\hbar\pi}{h^3}\right)^{3/2} =$$

Calculation of $W_2(\vec{r}_1, \vec{r}_2)$:-

$$\mathcal{H}^{(2)} = -\frac{\hbar^2}{2m}\left(\vec{\nabla}_1^2 + \vec{\nabla}_2^2\right) + u(\vec{r}_1 - \vec{r}_2)$$

Centre-of-mass coordinates

$$\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}, \quad \vec{r} = \vec{r}_1 - \vec{r}_2$$

$$H^{(2)} = -\frac{\hbar^2}{4m}\vec{\nabla}_R^2 - \frac{\hbar^2}{m}\vec{\nabla}_r^2 + u(\vec{r})$$

$$-\frac{\hbar^2}{4m}\vec{\nabla}_R^2 \frac{1}{\sqrt{V}} e^{i\vec{P}\cdot\vec{R}/\hbar} = \frac{P^2}{4m} e^{i\vec{P}\cdot\vec{R}/\hbar}\frac{1}{\sqrt{V}}$$

Define : $\psi_n(\vec{r})$: eigenstate of $-\frac{\hbar^2}{m}\vec{\nabla}_r^2 + u(\vec{r})$

with eigenvalue e_n

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}_r^2 + u(\vec{r})\right]\psi_n(\vec{r}) = e_n\psi_n(\vec{r})$$

Complete basis :

$$\psi_{\vec{P},n} = \frac{1}{\sqrt{V}} e^{i\vec{P}\cdot\vec{R}/\hbar}\psi_n(\vec{r})$$

$$W_2(\vec{r}_1, \vec{r}_2)$$

$$= 2!\left\{\frac{h^3}{(2m\pi kT)^{3/2}}\right\}^2 \times \sum_\alpha \psi_\alpha^*(\vec{r}_1, \vec{r}_2)\, e^{-\beta\hat{\mathcal{H}}}\,\psi_\alpha(\vec{r}_1, \vec{r}_2)$$

$$\frac{V}{h^3}\int d^3p \sum_n \underbrace{\frac{1}{V} e^{-\beta P^2/4m}}_{\text{from c.m.}}\; \underbrace{e^{-\beta e_n}\psi_n^*(\vec{r})\psi_n(\vec{r})}_{\text{from relative coordinate}}$$

$$\frac{\cancel{V}}{h^3}\int d^3p \sum_n \frac{1}{\cancel{V}} e^{-\beta p^2/4m} \qquad e^{-\beta \epsilon_n}\psi_n^*(\vec{r})\psi_n(\vec{r})$$

$$\Downarrow$$

$$\frac{1}{h^3}(4m\pi kT)^{3/2} \sum_n e^{-\beta \epsilon_n}\psi_n^*(\vec{r})\psi_n(\vec{r})$$

$$\therefore\ W_2(\vec{r}_1,\vec{r}_2) = 2\cdot 2\sqrt{2}\,\frac{h^3}{(2m\pi kT)^{3/2}}\sum_n\left[e^{-\beta\epsilon_n}\psi_n^*(\vec{r})\,\psi_n(\vec{r})\right]$$

For ideal gas:

$$W_2^{(0)}(\vec{r}_1,\vec{r}_2)$$

$$= 4\sqrt{2}\,\frac{h^3}{(2m\pi kT)^{3/2}}\sum_n e^{-\beta\epsilon_n^{(0)}}\psi_n^{(0)*}(\vec{r})\,\psi_n^{(0)}(\vec{r})$$

eigenvalues of a free particle of mass m/2 — eigenstates

$$W_1(\vec{r}) = 1$$

$$W_1^{(0)}(\vec{r}_1) = 1$$

$$U_2(\vec{r}_1,\vec{r}_2) - U_2^{(0)}(\vec{r}_1,\vec{r}_2)$$

$$= W_2(\vec{r}_1,\vec{r}_2) - W_1(\vec{r}_1)\,W_1(\vec{r}_2) + W_1^{(0)}(\vec{r}_1)\,W_1^{(0)}(\vec{r}_2) - W_2^{(0)}(\vec{r}_1,\vec{r}_2)$$

$$= W_2(\vec{r}_1,\vec{r}_2) - W_2^{(0)}(\vec{r}_1,\vec{r}_2)$$

$$(B_2 - B_2^{(0)})V = \int d^3r_1\, d^3r_2 \left\{U_2(\vec{r}_1,\vec{r}_2) - U_2^{(0)}(\vec{r}_1,\vec{r}_2)\right\}$$

$$= \int d^3R\, d^3r \left\{W_2(\vec{r}_1,\vec{r}_2) - W_2^{(0)}(\vec{r}_1,\vec{r}_2)\right\}$$

$$\left(B_2 - B_2^{(0)}\right) = \frac{1}{V}\int d^3R \; 4\sqrt{2} \; \frac{h^3}{(2m\pi kT)^{3/2}}$$

Neither $W_2(\vec{r}_1, \vec{r}_2)$ nor $W_2^{(0)}$ depends on $\vec{R}$ — so it factors out

$$\int d^3r \left(\sum_n e^{-\beta e_n} \psi_n^*(\vec{r}) \psi_n(\vec{r}) - \sum_n e^{-\beta e_n^{(0)}} \psi_n^{(0)*}(\vec{r}) \psi_n^{(0)}(\vec{r}) \right)$$

ψ_n's are normalised — when u take trace, should be normalised

$$\int d^3r \, \psi_n^*(\vec{r}) \psi_n(\vec{r}) = 1 = \int d^3r \, \psi_n^{(0)*}(\vec{r}) \psi_n^{(0)}(\vec{r})$$

$$\Rightarrow B_2 - B_2^{(0)} = 4\sqrt{2} \frac{h^3}{(2m\pi kT)^{3/2}} \left[\sum_n e^{-\beta e_n} - \sum_n e^{-\beta e_n^{(0)}} \right]$$

$$b_2 - b_2^{(0)} = \frac{1}{2}\left(B_2 - B_2^{(0)}\right) \tilde{y}$$

$$\boxed{\tilde{y} = \frac{(2m\pi kT)^{3/2}}{h^3}}$$

$$= 2\sqrt{2}\left(\sum_n e^{-\beta e_n} - \sum_n e^{-\beta e_n^{(0)}} \right)$$

In the thermodyn. limit, e_n's have a continuous spectrum

For finite — e_n is discrete spectrum

27/2/06

Calculation of b_2 for interacting quantum gas

$$b_2 = \frac{1}{2} B_2 \tilde{y}, \quad \tilde{y} = (2m\pi kT)^{3/2}/h^3$$

B_2 given in terms of $W_2(\vec{r_1}, \vec{r_2})$ & $W_1(\vec{r_1})$

$$B_2 - B_2^{(0)} = 4\sqrt{2}\, \frac{h^3}{(2m\pi kT)^3} \left(\sum_n e^{-\beta e_n} - \sum_n e^{-\beta e_n^{(0)}} \right)$$

$B_2^{(0)}$: free quantum gas

e_n: energy e.v.'s of the relative motion of 2-particle system in interaction theory

$e_n^{(0)}$: energy e.v.'s of the free theory

This gives

$$b_2 - b_2^{(0)} = 2\sqrt{2} \underbrace{\left(\sum_n e^{-\beta e_n} - \sum_n e^{-\beta e_n^{(0)}} \right)}$$

$b_2^{(0)}$: already known (bcos grand canonical partition fn. for free particle is already known)

Need to calculate this

Suppose for the free system $g^{(0)}(e)\,de$ denotes the number of states with energy between e & $e+de$.

Then $\sum_n e^{\beta e_n^{(0)}} \xrightarrow[\text{replaced by}]{\text{is to be}} \int_0^\infty de\, \hat{g}^{(0)}(e) \times e^{-\beta e}$

$$\sum_n e^{-\beta e_n} \longrightarrow \sum_\alpha e^{-\beta e_\alpha^B} + \int_0^\infty \hat{g}(e)\, e^{-\beta e}\, de$$

$\sum_\alpha$: bound states of the interacting theory

$\hat{g}(e)\,de$ = # of states betn energy e & $e+de$ in the interacting theory

The rel. coord. also acts as a free particle coord. & shows continuous spectrum for +ve energy $\because V \to 0$ as $r \to \infty$

So the summation doesn't make sense

Typically in a pot. there will be bound states

$$b_2 - b_2^{(0)} = 2\sqrt{2}\left[\sum_\alpha e^{-\beta e_\alpha^B} + \underbrace{\int_0^\infty de\left(\hat{g}(e) - \hat{g}^{(0)}(e)\right) e^{-\beta e}}\right]$$

can be expressed in terms of phase shifts in the scattering problem

We can solve it ~~anaf~~ analytically or not is another matter

Introduce new variable k through the relation: $e = \frac{\hbar^2 k^2}{m}$

mass $= m/2$ because here we are dealing with the relative motion

$g(k)\,dk$ = no. of states in the interacting theory between k & $k + dk$

~~Similarly~~

$= \hat{g}(e)\,de$

Similarly for $g^{(0)}$.

$$g^{(0)}(k)\,dk = g^{(0)}(e)\,de$$

$$b_2 - b_2^{(0)} = 2\sqrt{2}\left[\sum_\alpha e^{-\beta e_\alpha^B} + \int_0^\infty dk\, e^{-\beta \hbar^2 k^2/m}\left(g(k) - g^{(0)}(k)\right)\right]$$

phase shift

We shall show that:-

$$g(k) - g^{(0)}(k) = \frac{1}{\pi}\sum_{l=\text{even}}{}'(2l+1)\frac{\partial \eta_l(k)}{\partial k} \quad \text{for bosons}$$

$$= \frac{1}{\pi}\sum_{l=\text{odd}}(2l+1)\frac{\partial \eta_l(k)}{\partial k} \quad \text{" fermions}$$

Calculation of $g(k) - g^{(0)}(k)$:-

Recall the form of scattering wave fn. in the presence of spherically symmetric potential

$$\psi_{klm}(r, \theta, \phi) = A_{klm}\, Y_{lm}(\theta, \phi)\frac{u_{kl}(r)}{r}$$

A_{klm} → constants

$u_{kl}(r)$ → depends on the choice of potential

$$\psi^{(0)}_{klm}(r,\theta,\phi) = A_{klm}\, Y_{lm}(\theta,\phi)\, \frac{u^{(0)}_{kl}(r)}{r}$$

$$u^{(0)}_{klm}(r) \xrightarrow[r\to\infty]{} \sin\left(kr + l\pi/2\right)$$

$$u_{kl}(r) \xrightarrow[r\to\infty]{} \sin\left(kr + l\pi/2 + \eta_l(k)\right)$$

$$\boxed{\begin{aligned}&\sin(kr - l\pi/2)\\ &= \sin(kr + l\pi/2 - l\pi)\\ &= (-1)^l \sin(kr + l\pi/2)\end{aligned}}$$

We det. $u_{kl}(r)$ by a linear combn of e^{ikr}/r & e^{-ikr}/r demanding soln is regular at origin

For infinite volume system, there are ∞ no. states betn. k & $k+dk$ since k is continuous.

First put the system in a finite box, the calculate $g(k) - g^{(0)}(k)$ & then take box size to ∞ limit.

Take a box of radius R with boundary condition $\psi(r,\theta,\phi)=0$ at $r=R$.

$$\Rightarrow u^{(0)}_{kl}(R) = 0$$

$$\Rightarrow kR + l\pi/2 = n\pi, \quad n = \text{integer (+ve)}$$

Δk = spacing between levels in k-space

$$(k+\Delta k)R + l\pi/2 = (n+1)\pi$$

$$\Rightarrow \Delta k = \pi/R$$

$$\therefore \cancel{g^{(0)}_l(k) = \frac{1}{\Delta k} = \frac{R}{\pi}\sum_l (2l+1)}$$

$g^0_l(k)\,dk$ = no. of states of orbital angular mom. l betn. k & $k+dk$

$$= R/\pi\,(2l+1)$$

Interacting system

$$u_{kl}(R) = 0$$

$$kR + l\pi/2 + \eta_l(k) = n\pi$$

$$(k+\Delta k)R + \frac{l\pi}{2} + \eta_l(k+\Delta k) = (n+1)\pi$$

taking the diff.

(Sub.) $\Delta k \cdot R + \eta_l'(k)\,\Delta k = \pi$

Δk in the thermodyn. limit is very small, because it is multiplied by R

$$\Rightarrow \Delta k = \frac{\pi}{R + \eta_l'(k)}$$

$$\therefore g_l(k) = \frac{R + \eta_l'(k)}{\pi}(2l+1)$$

$$\therefore g_l(k) - g_l^{(0)}(k) = \frac{(2l+1)}{\pi}\eta_l'(k)$$

Now we see that R has dissappeared

Though g_l & $g_l^{(0)}$ itself were ∞ in thermodyn. limit, $g_l - g_l^{(0)}$ is finite even in the thermodyn. limit

$$b_2 - b_2^{(0)} = 2\sqrt{2}\left[\sum_\alpha e^{-\beta e_\alpha^B} + \int_0^\infty dk\, e^{-\beta\frac{\hbar^2k^2}{m}} \sum_{l=0}^{\infty}\frac{(2l+1)}{\pi}\eta_l'(k)\right]$$

$\Downarrow$

(this is not completely correct)

$$\psi_{klm}(\vec{r}) = A_{klm}\,Y_{lm}(\theta,\phi)\,\frac{u_{kl}(r)}{r}$$

$$r = |\vec{r}_1 - \vec{r}_2|$$

this is the state describing the 2 particle system - we have taken the complete set of states - we haven't ~~...~~ considered exchange symmetry

Full wave fn.

$$e^{i\vec{P}\cdot\frac{(\vec{r}_1+\vec{r}_2)}{2}}\,\psi_{klm}(\vec{r}) = \psi(\vec{r}_1, \vec{r}_2)$$

$\vec{P} \to$ label for C.M. motion

$klm \to$ for rel. motion

Bosons: $\psi_{\vec{P},klm}(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) \Rightarrow \psi_{klm}(\vec{r}) = \psi_{klm}(-\vec{r})$

$\vec{r} \to -\vec{r}$

$\xRightarrow[\text{to}]{\text{corresponds}}$ $r \to r$, $\theta \to \pi - \theta$, $\phi \to \pi + \phi$

$$Y_{lm}(\theta, \phi) = (-1)^l Y_{lm}(\pi - \theta, \pi + \phi)$$

$\Rightarrow$ Bosons $\to$ l = even

fermions $\to$ l = odd

<u>Correct formula</u> :-

$$b_2 - b_2^{(0)} = 2\sqrt{2}\Big[\underbrace{\sum_\alpha e^{-\beta e_\alpha^B}}_{l = \text{even, odd}} + \int_0^\infty dk \, e^{-\beta \hbar^2 k^2/m} \times \underbrace{\sum_{l=0}^{\infty} \frac{(2l+1)}{\pi} \eta_l'(k)}_{l = \text{even (bosons), odd (fermions)}}\Big]$$

You also don't sum over all bound states for bosons & fermions

In principle you can calculate higher virial coeff. but in practice it is diff.

$\downarrow$

e.g. for 2nd virial coeff. you have to solve a quantum 3-body problem

If pot. is ~~sufficiently short-range~~ such that for large l & k, contribution is negligible

Pot. should be short ranged

$\frac{1}{r}$ pot. won't work

In classical case also we saw pot. should at least fall of as $\frac{1}{r^3}$

If l-dependent falls off as $\frac{1}{l^\alpha}$ where $\alpha \geq 3$, then convergent