COLLEGE OF ARTS AND SCIENCES
HOMER L. DODGE
DEPARTMENT OF PHYSICS AND ASTRONOMY
The UNIVERSITY of OKLAHOMA

Statistical Mechanics

CH. 10 APPROXIMATE METHODS LECTURE NOTES

STUDENT
Taylor Larrechea

PROFESSOR
Dr. Doerte Blume

4-4-22

The purpose of incorporating approximate methods is to account for interactions between particles. The Non-Relativistic Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} V_{ij}$$

$\mapsto$ Two-Body Potential

Since these are classical particles our partition function is

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

Where the above is called a Configuration Integral. The partition function becomes

$$Q_N(Z,T,V) = \sum_{N=0}^{\infty} Z^N Q_N(T,V) = \sum_{N=0}^{\infty} \left(\frac{Z}{h^3}\right)^N \frac{1}{N!} \underbrace{\int e^{-\beta \sum_{i<j} V_{ij}}\, d^{3N}\vec{q}}_{J_N(T,V)}$$

If we then start with $e^{-\beta V_{ij}} = 1 + f_{ij} \;\therefore\; f_{ij} = 1 - e^{-\beta V_{ij}}$. $J_N(T,V)$ is then

$$J_N(T,V) = \int \prod_{i<j} (1+f_{ij})\, d^3\vec{r}_1\, d^3\vec{r}_2 \ldots d^3\vec{r}_N$$

Lets say we want to write this out for a few terms

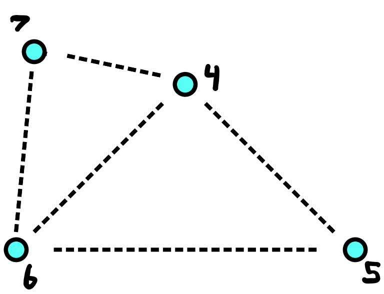
$$J_N(T,V) = \int (1 + f_{12} + f_{13} + f_{14} + \ldots + f_{23} + f_{24} + \ldots + f_{N-1,N})\, d^3\vec{r}_1\, d^3\vec{r}_2 \ldots d^3\vec{r}_N$$

This re-written will look like

$$J_N(T,V) = \left(\int 1\, d^3\vec{r}_1 \ldots d^3\vec{r}_N\right) \to V^N + \left(\int f_{12}\, d^3\vec{r}_1\, d^3\vec{r}_2 \int d^3\vec{r}_3\, d^3\vec{r}_4 \ldots d^3\vec{r}_N\right) \to V^{N-2}$$

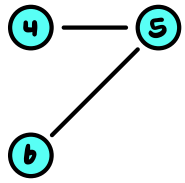
4-6-22

In systems where our particles interact, we have to make an approximation to describe our system's properties



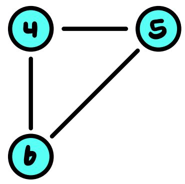
where it's clear to see that after a couple interactions these calculations become very difficult.

We can represent these interactions as



$$\Rightarrow \mathcal{I}_{45,56} = \int f_{45} f_{56} \, d^3\vec{r}_4 \, d^3\vec{r}_5 \, d^3\vec{r}_6$$

Where the above is an interaction between 4 and 5 and then 5 and 6. If all three were interacting it would look like



$$\Rightarrow \mathcal{I}_{456} = \int f_{45} f_{56} f_{64} \, d^3\vec{r}_4 \, d^3\vec{r}_5 \, d^3\vec{r}_6$$

Where we now have 3 particles interacting with one another. An equivalent way of writing the Grand Canonical Partition Function is

$$Q(z,T,V) = \exp\left(\sum_{l=1}^{\infty} b_l z^l \frac{V}{\lambda^3} \right)$$

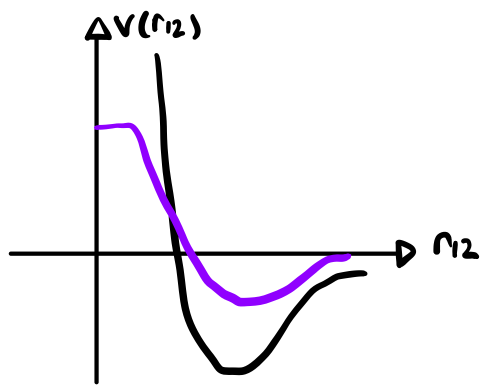
Where for example b_2 is,

$$b_2 = \frac{1}{2\lambda^3 V} \iint f_{12} \, d\vec{r}_1 \, d\vec{r}_2 = \frac{4\pi}{2\lambda^3} \int_0^\infty f_{12}(r_{12}) \, r_{12}^2 \, dr_{12} = \frac{2\pi}{\lambda^3} \int_0^\infty f_{12}(r_{12}) \, r_{12}^2 \, dr_{12}$$

Where $r_{12} = |\vec{r}_1 - \vec{r}_2|$. With $f_{12} = 1 - e^{-\beta r_{12}}$ b_2 is then

$$b_2 = \frac{2\pi}{\lambda^3} \int_0^\infty (1 - e^{-\beta r_{12}}) \, r_{12}^2 \, dr_{12}$$

If we look at how this potential of r_{12} it will look like



Where we can see that our potential goes to zero asymptotically.

4-11-22

From the previous lecture we found how to calculate the grand canonical partition function

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

We then are tasked with finding

$$\frac{P}{KT} = \frac{1}{V}\log(Q(Z,V,T)) = \frac{1}{\lambda^3}\sum_{l=1}^{\infty} b_l Z^l$$

b_l, which are referred to as the cluster coefficient / expansion. We can then re-write our ideal gas equation as

$$\frac{PV}{KT} = \sum_{l=1}^{\infty} a_l(T)\left(\frac{\lambda^3}{V}\right)^{l-1}$$

Since we are working Quantum Mechanically we must keep in mind

- We are working with operators
- We must take into account the statistics of our system

Taking the ideal gas law we then have

$$PV = KT\log(Q(Z,V,T)) = KT\log\left(\sum_{N=0}^{\infty} Z^N Q_N(T,V)\right)$$

We now approximate with a "small" x

$$PV = KT\log(1+x)$$

We now Taylor expand $\log(1+x)$
LaLane

$$\log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots\dots$$

This then means our ideal gas law becomes

$$PV = KT\left(Q_1 Z + (Q_2 - Q_1^2/2)Z^2 + (Q_3 - Q_1Q_2 + Q_1^3/3)Z^3 + (\dots\dots)Z^4 + \dots\dots\right)$$

We now have our cluster coefficients as

$$b_1 = \frac{\lambda^3}{V}Q_1 \, , \quad b_2 = -\frac{\lambda^3}{V}\left(\frac{Q_1^2}{2} - Q_2\right)$$

Lets say we are given a Hamiltonian

$$\mathcal{H}\psi_n(\vec{r}_1,\vec{r}_2) = E_n\psi_n(\vec{r}_1,\vec{r}_2)$$

This then tells us that the partition function is

$$Q_2 = \sum_{n=1} e^{-\beta E_n}$$

Where E_n are our eigenenergies from our Hamiltonian. We can then see that our Hamiltonian is

$$\tilde{\mathcal{H}} = \frac{\vec{P}_1^2}{2m} + \frac{\vec{P}_2^2}{2m} + V(|\vec{r}_1 - \vec{r}_2|)$$

If we take into account that one particle is relativistic and one classical we then have

$$\tilde{\mathcal{H}} = \frac{\vec{P}_{Rel}^2}{2m} + V(r) + \frac{\vec{P}_{cm}^2}{2m}$$

We then can say that our relativistic potential is

$$\varphi_{n\ell m}(\vec{r}_{rel}) = \frac{u_{n\ell}(|\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|} Y_m^\ell(\hat{r}_1 - \hat{r}_2)$$

<u>Homework Help</u>

In the paper we are reading

$$Z(N) \Rightarrow \text{our } Q_N$$

Where the partition function is then

$$Z(N) = \frac{1}{N} \sum_{k=1}^{N} (\pm 1)^{k+1} S(k) Z(N-k)$$