

'Dire', said Monsieun Myriel, in this fellow you see goodness, in the man before me, el see greatness. There's advantage to both of us. - Monsieun Myriel to the Emperor (Victor Hugo, The Wretched)

The Density Matrix (Return to this)

The density matrix is a quantum concept that can be applied to solve problems in statistical mechanics. Imagine we have an ensemble of systems, each with its own wavefunction  $\psi^{(k)}[\{\vec{r}_i\}, t]$ , which evolve according to  $\hat{H}\psi^{(k)}(t) = i\hbar\dot{\psi}^{(k)}(t)$ , which we recognize as the time-dependent Schrodinger equation.

Using separation of variables, we can write  $\psi^{(k)}[\{\vec{r}_i\}, t] = \sum_n a_n^{(k)}(t) \phi_n[\{\vec{r}_i\}]$ , where  $a_n^{(k)}(t) = \langle \phi_n | \psi^{(k)} \rangle$ .

$$\begin{aligned} i\hbar \dot{a}_n^{(k)}(t) &= i\hbar \langle \phi_n | \dot{\psi}^{(k)}(t) \rangle \\ &= i\hbar \langle \phi_n | \hat{H} | \psi^{(k)}(t) \rangle \\ &= \sum_m \langle \phi_n | \hat{H} | \phi_m \rangle a_m^{(k)}(t) \end{aligned}$$

The density matrix

$$\begin{aligned} \rho_{mn}(t) &= \frac{1}{N} \sum_k a_m^{(k)}(t) a_n^{(k)*}(t) \\ &= \langle \phi_m | \hat{\rho} | \phi_n \rangle \end{aligned}$$

Imagine we wish to know the average value of some quantity  $\hat{G}$ , which corresponds to a hermitian operator in QM.

$$\begin{aligned} \langle \hat{G} \rangle_k &= \langle \psi^{(k)}(t) | \hat{G} | \psi^{(k)}(t) \rangle \\ \langle \hat{G} \rangle &= \sum_{mn} \langle \phi_m | \hat{G} | \phi_n \rangle \rho_{nm}(t) \\ &= \text{Tr}(\hat{G} \hat{\rho}) \end{aligned}$$

If all the members of the ensemble are in the same quantum state,  $\rho^2 = \rho$ . This is called a pure state

\* Example: An ensemble of spin- $\frac{1}{2}$  particles are all polarized in the  $+\hat{x}$  direction

$$|\psi\rangle = \frac{1}{\sqrt{2}} [|\uparrow\rangle + |\downarrow\rangle]$$

$$\psi^{(k)} = \frac{1}{\sqrt{2}} [|\uparrow\rangle + |\downarrow\rangle] = \sum_n a_n |\phi_n\rangle = a_1 |\uparrow\rangle + a_2 |\downarrow\rangle$$

$$a_1 = a_2 = \frac{1}{\sqrt{2}}$$

$$\rho_{mn} = a_m a_n^* = \frac{1}{2} \text{ for all } m \text{ and } n$$

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$\rho^2 = \frac{1}{4} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 2 & 2 \\ 2 & 2 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = \rho$$

★ Example: In ensemble where half are  $|\uparrow\rangle$ , half are  $|\downarrow\rangle$

$$\rho_{mn} = \frac{1}{2} (a_m^\uparrow a_n^\uparrow + a_m^\downarrow a_n^\downarrow)$$

$$\text{if } m=\uparrow, a_m^\uparrow=1 \quad m=\uparrow, a_m^\downarrow=0$$

$$m=\downarrow, a_m^\uparrow=0 \quad m=\downarrow, a_m^\downarrow=1$$

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\rho^2 = \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2} \rho$$

★ Density matrix in the microcanonical ensemble

|||||  $\xrightarrow{E}$  We want to choose a narrow range of states of width  $\Delta$  around  $E$ , which will then say number  $\Gamma$ .

$$\rho_{mn} = \frac{1}{\Gamma} \delta_{mn} \text{ if } E - \Delta/2 < E_n < E + \Delta/2$$

$$= 0 \text{ else}$$

★ Density matrix in the canonical ensemble

$$\rho_{rs} = \frac{\delta_{rs} \exp(-\beta E_r)}{Z}$$

$$Z = \sum_r \exp(-\beta E_r)$$

$$\hat{\rho} = \frac{\exp(-\beta \hat{H})}{\mathcal{Z}[\exp(-\beta \hat{H})]}$$

★ Density in grand canonical ensemble

$$\hat{\rho} = \frac{\exp[-\beta(\hat{H} - \mu \hat{N})]}{\mathcal{Z}[\exp(-\beta(\hat{H} - \mu \hat{N}))]}$$

Problems.

1. Density Matrix as a Diffusion Problem

Recall our result for the density matrix of a single quantum particle in a box of volume  $V$

$$\rho(\vec{R}, \vec{R}', \beta) = \langle \vec{R} | \hat{\rho} | \vec{R}' \rangle = \frac{1}{V} \exp[-\pi |\vec{R} - \vec{R}'|^2 / \lambda^2]$$

where  $\lambda$  is the thermal wavelength. Show this result can be derived by the following.

a. Show that the unnormalized density matrix,  $Z\rho(\vec{R}, \vec{R}', \beta)$  where  $Z$  is the partition function in the canonical ensemble, obeys the diffusion equation

$$\frac{\partial}{\partial \beta} Z\rho = \frac{\hbar^2}{2m} \nabla^2 (Z\rho)$$

in which  $\beta$  plays the role of time. What is the boundary condition on  $Z\rho$  at "time"  $\beta=0$ ?

$$\rho(\vec{R}_1, \vec{R}_2) = \frac{1}{Z} \langle \vec{R}_1 | \exp(-\beta \hat{H}) | \vec{R}_2 \rangle$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

$$\frac{\partial}{\partial \beta} Z\rho = \langle \vec{R}_1 | \frac{\partial}{\partial \beta} \exp(-\beta \hat{H}) | \vec{R}_2 \rangle$$

$$= \langle \vec{R}_1 | -\hat{H} \exp(-\beta \hat{H}) | \vec{R}_2 \rangle = \langle \vec{R}_1 | \frac{\hbar^2}{2m} \nabla^2 \exp(-\beta \hat{H}) | \vec{R}_2 \rangle$$

$$= \frac{\hbar^2}{2m} \nabla^2 \langle \vec{R}_1 | \exp(-\beta \hat{H}) | \vec{R}_2 \rangle$$

$$\frac{\partial}{\partial \beta} Z\rho = \frac{\hbar^2}{2m} \nabla^2 (Z\rho)$$

$$\text{At } \beta=0, Z\rho = \langle \vec{R}_1 | \vec{R}_2 \rangle$$

$$= \delta(\vec{R}_1 - \vec{R}_2)$$

b. Solve the diffusion equation to show that one obtains the correct result for the density matrix

Use the Laplace transform

$$f(\epsilon, \vec{R}) = \int_0^\infty Z\rho(\vec{R}, \beta) \exp(-\beta \epsilon) d\beta$$

$$\int_0^\infty \frac{\partial}{\partial \beta} (Z\rho) \exp(-\beta \epsilon) d\beta = \frac{\hbar^2}{2m} \nabla^2 \int_0^\infty \exp(-\beta \epsilon) Z\rho(\vec{R}, \beta) d\beta$$

$$u = \exp(-\beta \epsilon) \quad v = Z\rho$$

$$u' = -\epsilon \exp(-\beta \epsilon) \quad v' = \frac{\partial}{\partial \beta} (Z\rho)$$

$$Z\rho \exp(-\beta \epsilon) \Big|_0^\infty - \int_0^\infty -\epsilon \exp(-\beta \epsilon) Z\rho d\beta = \frac{\hbar^2}{2m} \nabla^2 f(\epsilon, \vec{R})$$

$$\delta(\vec{R}) = \left[ \epsilon - \frac{\hbar^2}{2m} \nabla^2 \right] f(\epsilon, \vec{R})$$



$$\left(\frac{\hbar^2}{2m} k^2 + \epsilon\right) f(\epsilon, \vec{k}) = 1 \quad \text{Fourier transform}$$

$$f(\epsilon, \vec{k}) = \frac{1}{\frac{\hbar^2 k^2}{2m} + \epsilon}$$

$$f(\beta, \vec{k}) = \frac{1}{2\pi i} \int_{-\infty-i\infty}^{\infty-i\infty} \exp(z\beta) \left[ \frac{\hbar^2 k^2}{2m} + z \right] dz \quad \text{Inverse Laplace transform}$$

$$Z_\rho(\vec{R}, \beta) = \int \frac{d^3k}{(2\pi)^3} \exp(-i\vec{k} \cdot \vec{R}) \exp(-k^2 \lambda^2 / 4\pi) \quad \text{Inverse Fourier transform}$$

$$= \left(\frac{\sqrt{\pi}}{\lambda}\right)^3 \left(\frac{1}{2\pi}\right)^3 \exp\left(-\frac{\pi |\vec{R}|^2}{\lambda^2}\right)$$

$$= \left(\frac{1}{2\pi \lambda^2}\right)^{3/2} \exp\left(-\frac{\pi |\vec{R}|^2}{\lambda^2}\right)$$

$$Z = V \int \frac{d^3k}{(2\pi)^3} \exp(-\beta \hbar^2 k^2 / 2m) = V \int \frac{d^3k}{(2\pi)^3} \exp(-k^2 \lambda^2 / 4\pi) \quad \text{Normalize}$$

$$= V \left(\frac{1}{2\pi \lambda^2}\right)^{3/2}$$

$$\rho(\vec{R}, \beta) = \frac{1}{V} \exp(-\pi |\vec{R}|^2 / \lambda^2)$$

## 2. Equations of motions for spin-1/2 particle

a. Show that in general the equations of motion for the density matrix may be written in operator form as

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}]$$

where  $[\hat{A}, \hat{B}]$  denotes the commutator of the operators  $\hat{A}$  and  $\hat{B}$ .

$$\rho_{mn}(t) = \frac{1}{\eta} \sum_{k=1}^{\eta} a_m^{(k)}(t) a_n^{(k)*}(t)$$

$$i\hbar \dot{a}_n^{(k)}(t) = \sum_m \langle \phi_n | \hat{H} | \phi_m \rangle a_m^{(k)}(t)$$

$$-i\hbar \dot{a}_n^{(k)*}(t) = \sum_m \langle \phi_m | \hat{H} | \phi_n \rangle a_m^{(k)*}(t)$$

$$\langle \phi_m | \dot{\rho} | \phi_n \rangle = \frac{1}{\eta} \sum_{k=1}^{\eta} \left\{ \dot{a}_m^{(k)} a_n^{(k)*} - a_m^{(k)} \dot{a}_n^{(k)*} \right\}$$

$$= \frac{1}{i\hbar \eta} \sum_{k=1}^{\eta} \left\{ \sum_m \langle \phi_m | \hat{H} | \phi_m \rangle a_m^{(k)} a_n^{(k)*} - a_m^{(k)} \sum_m \langle \phi_m | \hat{H} | \phi_m \rangle a_m^{(k)*} \right\}$$

$$= \frac{1}{i\hbar} \left\{ \langle \phi_m | \hat{H} \left( \sum_n | \phi_n \rangle \langle \phi_n | \right) \rho | \phi_n \rangle - \langle \phi_m | \rho \left( \sum_n | \phi_n \rangle \langle \phi_n | \right) \hat{H} | \phi_n \rangle \right\}$$

$$\langle \phi_m | \dot{\rho} | \phi_n \rangle = \frac{1}{i\hbar} \langle \phi_m | [\hat{H}, \hat{\rho}] | \phi_n \rangle$$

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}]$$

b. Let the Hamiltonian for a spin be  $\hat{H} = -\frac{\hbar}{2} \vec{B} \cdot \vec{\sigma}$ , where  $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$  are the three Pauli spin matrices, and  $B$  may be interpreted as a magnetic field in units where the gyromagnetic ratio is unity. Remember the useful relations among Pauli matrices,  $\sigma_i \sigma_j = -\sigma_j \sigma_i = 2i \epsilon_{ijk} \sigma_k$ . Show that any  $2 \times 2$  density matrix may be written in the form

$$\rho = \frac{1}{2} (I + \vec{p} \cdot \vec{\sigma})$$

where  $I$  is the unit  $2 \times 2$  matrix.

$$\hat{H} = -\frac{\hbar}{2} \vec{B} \cdot \vec{\sigma}$$

$$\rho_{mn} = \frac{1}{\eta} \sum_k a_m^{(k)} a_n^{(k)*} = \rho_{mn}^*$$

$$\rho = \begin{pmatrix} a & c+id \\ c-id & b \end{pmatrix}$$

Since  $\text{Tr} \rho = 1$

$$\rho = \begin{pmatrix} \frac{1}{2} + e & c+id \\ c-id & \frac{1}{2} - e \end{pmatrix}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + e \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + c \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - d \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$= \frac{1}{2} I + e \sigma_z - d \sigma_y + c \sigma_x$$

if  $\vec{p} = 2(c, -d, e)$

$$\rho = \frac{1}{2} (I + \vec{p} \cdot \vec{\sigma})$$

c. Show that the equations of motion for the density matrix can

be written as  $\frac{d\hat{\rho}}{dt} = -\vec{B} \times \vec{p}$

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}] = -\frac{\hbar}{2} \sum_{i=x,y,z} B_i [\sigma_i, \frac{1}{2} (I + \vec{p} \cdot \vec{\sigma})]$$

$$= -\frac{\hbar}{4} \sum_{i,j,k} B_i p_j 2i \epsilon_{ijk} \sigma_k$$

$$\frac{d\vec{p}}{dt} = -\frac{1}{2} \sum_{i,j,k} B_i p_j \epsilon_{ijk} \sigma_k$$

$$= -\frac{1}{2} (\vec{B} \times \vec{p}) \cdot \vec{\sigma}$$

$$\frac{d\vec{p}}{dt} = -\vec{B} \times \vec{p}$$



### 3 Pathria 5.4

Study the density matrix and the partition function of a system of free particles, using the unsymmetrized wavefunction (5.4.3) instead of the symmetrized wavefunction (5.5.7). Show that, following this procedure, one encounters neither the Gibbs' correction factor  $(N!)$  nor a spatial correlation among the particles.

$$\psi_E(\vec{q}) = \prod_i u_{\vec{q}_i}(q_i) \quad (5.4.3)$$

$$\psi_{\vec{R}}(1, \dots, N) = (N!)^{-1/2} \sum_P \delta_P P \{u_{\vec{R}_1}(1), \dots, u_{\vec{R}_N}(N)\} \quad (5.4.7)$$

$$\psi_{\vec{R}_1, \vec{R}_2, \dots}(\vec{r}_1, \vec{r}_2, \dots) = \prod_i \phi_{\vec{R}_i}(\vec{r}_i)$$

$$\phi_{\vec{R}}(\vec{r}) = \frac{1}{\sqrt{L^3}} \exp(i\vec{k} \cdot \vec{r})$$

$$E = \epsilon_{\vec{R}_1} + \epsilon_{\vec{R}_2} + \dots, \quad \epsilon_{\vec{R}} = \frac{\hbar^2 k^2}{2m}$$

$$\begin{aligned} & \langle \vec{R}_1, \vec{R}_2, \dots | \exp(-\beta \hat{H}) | \vec{R}'_1, \dots, \vec{R}'_N \rangle \\ &= \sum_{\vec{R}_1, \dots, \vec{R}_N} \psi_{\vec{R}_1, \dots, \vec{R}_N}(\vec{R}_1, \dots, \vec{R}_N) \exp(-\beta \sum \epsilon_{\vec{R}_i}) \psi_{\vec{R}'_1, \dots, \vec{R}'_N}^*(\vec{R}'_1, \dots, \vec{R}'_N) \\ &= \prod_i \left[ \sum_{\vec{R}_i} \phi_{\vec{R}_i}(\vec{R}_i) \exp(-\beta \epsilon_{\vec{R}_i}) \phi_{\vec{R}'_i}^*(\vec{R}'_i) \right] \end{aligned}$$

In the thermodynamic limit

$$= \left[ \frac{m}{2\pi\beta\hbar^2} \right]^{N/2} \exp \left[ \frac{-m}{2\beta\hbar^2} \sum_i |\vec{R}_i - \vec{R}'_i|^2 \right]$$

$$Z_C(N) = \int d^3R_1 \dots d^3R_N \langle \vec{R}_1, \dots, \vec{R}_N | \exp(-\beta \hat{H}) | \vec{R}_1, \dots, \vec{R}_N \rangle$$

$$= [L^3]^N \left[ \frac{m}{2\pi\beta\hbar^2} \right]^{N/2} = V^N \left[ \frac{m}{2\pi\beta\hbar^2} \right]^{N/2}$$

$$= \left[ \frac{V}{\lambda^3} \right]^N$$

$$\rho_2(\vec{R}_1, \vec{R}_2) = \int d^3R_3 \dots d^3R_N \langle \vec{R}_1, \dots, \vec{R}_N | \hat{\rho} | \vec{R}_1, \dots, \vec{R}_N \rangle$$

$$= \frac{1}{V^2}$$

No spatial dependence

### Theory of Non-Interacting Gases

So far we've been dealing with ideal gases, but we know that the world is not always ideal. So how do we improve our models?

#### \* Quantum statistics

For a non-interacting particles, we can construct a quantum state by putting particles in different single-particle states. We can specify each state by how many particles are in any given particle state. For example,

$$\text{States: } \phi_0, \phi_1, \phi_2, \phi_3$$

$$\text{Occupation\#: } 2, 6, 0, 1$$

The above is an example of a boson gas since the particle number can run from 0 to  $\infty$  while for fermions, the occupation number is 0 or 1. For any given state,  $E = \sum_i n_i \epsilon_i$  and  $N = \sum_i n_i$ .

If we want to find the partition function, it's probably best to work in the Grand Canonical Ensemble.

$$Z_G = \sum_{n_0} \sum_{n_1} \sum_{n_2} \dots \exp \left\{ -\beta \left[ \sum_i n_i \epsilon_i - \mu \sum_i n_i \right] \right\}$$

$$= \sum_{n_0} \sum_{n_1} \dots \exp(-\beta(n_0 \epsilon_0 - \mu n_0)) \exp(-\beta(n_1 \epsilon_1 - \mu n_1)) \dots$$

$$= \left[ \sum_{n_0} \exp(-\beta n_0 \epsilon_0 + \beta \mu n_0) \right] \left[ \sum_{n_1} \exp(-\beta n_1 \epsilon_1 + \beta \mu n_1) \right] \dots$$

Thus, we see that we need to evaluate the individual sums, and here we get to a fork. How we end up evaluating these sums depends on if we have a fermion or a bose system.

$$\text{For fermions: } \sum_{n_i=0}^1 \exp(-\beta n_i \epsilon_i + \beta \mu n_i) = 1 + \exp(-\beta(\epsilon_i - \mu))$$

$$= 1 + z \exp(-\beta \epsilon_i)$$

$$\text{For bosons: } \sum_{n_i=0}^{\infty} \exp(-\beta(\epsilon_i - \mu)n_i) = 1 + \sum_{n_i=1}^{\infty} \exp(-\beta(\epsilon_i - \mu)n_i)$$

$$= \frac{1}{1 - \exp(-\beta(\epsilon_i - \mu))} = \frac{1}{1 - z \exp(-\beta \epsilon_i)}$$

$$Z_G = \prod_i (1 + z \exp(-\beta \epsilon_i))$$

Fermi-Dirac

$$= \prod_i (1 - z \exp(-\beta \epsilon_i))^{-1}$$

Bose-Einstein



$$\langle n_j \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_j} \ln Z_G$$

For Fermions:

$$\frac{\partial}{\partial \epsilon_j} \ln(1 + z \exp(-\beta \epsilon_j)) = \frac{z \cdot -\beta \exp(-\beta \epsilon_j)}{1 + z \exp(-\beta \epsilon_j)}$$

$$= \frac{-z \beta \exp(-\beta \epsilon_j)}{1 + z \exp(-\beta \epsilon_j)}$$

$$\langle n_j \rangle = \frac{z \exp(-\beta \epsilon_j)}{1 + z \exp(-\beta \epsilon_j)} = \frac{z}{\exp(\beta \epsilon_j) + z}$$

$$= \frac{z}{z^{-1} \exp(\beta \epsilon_j) + 1}$$

Bosons:

$$\frac{\partial}{\partial \epsilon_j} \ln \left( \frac{1}{1 - z \exp(-\beta \epsilon_j)} \right) = \frac{\partial}{\partial \epsilon_j} -\ln(1 - z \exp(-\beta \epsilon_j))$$

$$= \frac{-z \beta \exp(-\beta \epsilon_j)}{1 - z \exp(-\beta \epsilon_j)}$$

$$\langle n_j \rangle = \frac{z \exp(-\beta \epsilon_j)}{1 - z \exp(-\beta \epsilon_j)} = \frac{1}{z^{-1} \exp(\beta \epsilon_j) - 1}$$

In the classical limit, we want  $z \ll 1$ , which also means that the thermal wavelength  $\lambda \ll$  interparticle spacing. In addition, Fermi-Dirac and Bose-Einstein statistics can be treated as the same.

$$\frac{1}{z^{-1} \exp(\beta \epsilon_j) + 1} \approx \frac{1}{z^{-1} \exp(\beta \epsilon_j) - 1} \approx z \exp(-\beta \epsilon_j)$$

This is known as Maxwell-Boltzmann statistics.

Example: Determine  $\mu$  for an ideal gas as a function of  $T$  and  $\beta$  in two dimensions.

$$\rho = \frac{1}{(2\pi)^2} \int \frac{1}{\exp(\beta(\epsilon_k - \mu)) + a} d^2 k \quad a = 1 \text{ Fermi-Dirac}$$

$$= \frac{2\pi}{(2\pi)^2} \int_0^\infty k \frac{1}{z^{-1} \exp(\frac{\beta \hbar^2 k^2}{2m}) + a} dk \quad a = -1 \text{ Bose-Einstein}$$

$$= \frac{1}{2\pi} \int_0^\infty k \frac{1}{z^{-1} + a \exp(\frac{\beta \hbar^2 k^2}{2m})} dk \quad a = 0 \text{ Maxwell-Boltzmann}$$

$$= \frac{1}{2\pi} \int_0^\infty k \frac{1}{z^{-1} + a \exp(\frac{\beta \hbar^2 k^2}{2m})} dk$$

$$x = \exp(\frac{\beta \hbar^2 k^2}{2m}) \quad \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$dx = \frac{\beta \hbar^2 k}{m} \exp(\frac{\beta \hbar^2 k^2}{2m}) dk$$

$$= \frac{1}{2\pi} \int_0^\infty \frac{m}{\beta \hbar^2} \frac{1}{z^{-1} + a x} dx = \frac{m}{2\pi \beta \hbar^2} \frac{1}{a} [\ln(z^{-1} + a) - \ln z^{-1}]$$

$$\rho = \frac{m}{2\pi \beta \hbar^2 a} \ln \left( \frac{z^{-1} + a}{z^{-1}} \right) = \frac{m}{2\pi \beta \hbar^2 a} \ln(1 + az)$$

$$\mu = k_B T \ln \left( \frac{\exp(\frac{2\pi \beta \hbar^2 \rho}{m}) - 1}{a} \right)$$

$$\text{For Bosons, } \mu = k_B T \ln(1 - \exp(-\frac{2\pi \beta \hbar^2 \rho}{m}))$$

$$= k_B T \ln(1 - \exp(-\rho \lambda^2))$$

Compare this to 3D case where  $\mu \rightarrow 0$  at a finite temperature.

This implies there is no Bose-Einstein Condensate in 2D.

$$\text{For Fermions, } \mu = k_B T \ln(1 + \exp(\rho \lambda^2))$$

$$\approx k_B T \rho \lambda^2 = \frac{2\pi \hbar^2 \rho}{m}$$

No temperature dependence hints at degenerate fermi gas

Maxwell-Boltzmann

We need to take the limit as  $a \rightarrow 0$ .

$$\frac{\exp(\rho \lambda^2 a) + 1}{a} \rightarrow \frac{1 + \rho \lambda^2 a - 1}{a} = \rho \lambda^2$$

$$\mu = k_B T \ln(\rho \lambda^2)$$

If we compare this to the ideal gas, we end up with the same result.



★ Kinetics of non-interacting gases.

As gases bounce around the container, they will come into contact with the wall (but not with each other, hence, non-interacting). This results in pressure. So how do we calculate this?

$$- \Phi_G = k_B T \ln Z_G = PV$$

$$PV = k_B T a \sum_i \ln [1 + a z \exp(-\beta \epsilon_i)]$$

$$P = \frac{k_B T a}{L^3} \left( \frac{L^3}{2\pi} \right)^3 \int \ln [1 + a z \exp(-\beta \frac{\hbar^2 k^2}{2m})] d^3 k$$

$$= k_B T \left( \frac{a}{8\pi^3} \right) 4\pi \int k^2 \ln [1 + a z \exp(-\beta \frac{\hbar^2 k^2}{2m})] dk$$

Integration by parts

$$u = \ln [1 + a z \exp(-\beta \frac{\hbar^2 k^2}{2m})] \quad v = \frac{1}{3} k^3$$

$$du = \frac{a z \exp(-\beta \frac{\hbar^2 k^2}{2m}) \cdot (-\beta \hbar^2 k) / m}{1 + a z \exp(-\beta \frac{\hbar^2 k^2}{2m})} dk \quad dv = k^2 dk$$

$$= \frac{k_B T a}{2\pi^2} \cdot \frac{k^3 \ln [1 + a z \exp(-\beta \frac{\hbar^2 k^2}{2m})]}{3} \Big|_0^\infty$$

$$+ \frac{k_B T a}{2\pi^2} \int_0^\infty \frac{k^3}{3} \cdot \frac{a z \beta \frac{\hbar^2 k^2}{2m} \exp(-\beta \frac{\hbar^2 k^2}{2m})}{1 + a z \exp(-\beta \frac{\hbar^2 k^2}{2m})} dk$$

$$= \frac{1}{6\pi^2} \int_0^\infty k^2 \left( \frac{\hbar k}{m} \right) \frac{1}{z^{-1} \exp(-\beta \frac{\hbar^2 k^2}{2m}) + a} dk$$

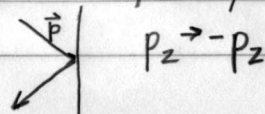
$$= \frac{1}{3} \int \frac{1}{(2\pi)^3} v(\vec{k}) p(\vec{k}) \langle n_{\vec{k}} \rangle d^3 k$$

$$= \frac{1}{3} \cdot \frac{N}{V} \langle v p \rangle = P$$

We can also get this result using Kinetic Theory. First let's define a distribution function

$f(\vec{u}) d^3 u$  = probability velocity in a cube of volume  $d^3 u$  centered at  $\vec{u}$

When a particle strikes a wall, the perpendicular component of  $\vec{p}$  changes sign



We can figure out the number of particles with velocity  $\vec{u}$  striking an area  $dA \hat{z}$  in a time  $dt$

$$\underbrace{f(\vec{u}) d^3 u}_{\text{probability of}} \cdot \underbrace{(u_z dt)}_{\text{volume}} \cdot \underbrace{dA \cdot n}_{\text{density}}$$

The change in momentum is  $2p_z$ , and the force is the change in momentum over time

$$dF_z = 2p_z f(\vec{u}) d^3 u (u_z dA) \cdot n$$

$$P = \frac{dF_z}{dA} = 2np_z f(\vec{u}) u_z d^3 u$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} 2np_z f(\vec{u}) u_z du_z du_x du_y$$

Note we only look at particles with positive z-velocities.

$$P = n \int f(\vec{u}) p_z u_z d^3 u = n \langle p_z u_z \rangle$$

$$P = n \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(u) p u \cdot \sin \theta \cos \theta d\theta d\phi du$$

$$= n \int_0^{\infty} u^2 f(u) p u \cdot \frac{4\pi}{3} du = \frac{1}{3} \cdot n \langle p u \rangle$$

In equilibrium, we expect  $u^2 f(u) \propto u^2 \exp(-\frac{m u^2}{2k_B T})$ , which has been experimentally verified. However, it was noticed that the size of the hole affected the data. This is known as molecular effusion. We find that the flux =  $\frac{1}{4} \cdot n \langle u \rangle$



### \* Internal Degrees of Freedom

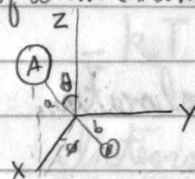
For a given state,

$$E_r = p^2/2m + \epsilon_{vib} + \epsilon_{rot} + \epsilon_{elec} + \dots$$

$$Z_c = \frac{1}{N!} \left\{ \left[ \frac{V}{h^3} \int \exp(-\beta p^2/2m) d^3x d^3p \right] \cdot \left[ \sum_{vib} \exp(-\beta \epsilon_{vib}) \right] \cdot \dots \right\}^N$$

$$= \frac{1}{N!} \left\{ \frac{V}{h^3} (2\pi m k_B T)^{3/2} j_{vib}(T) j_{rot}(T) \dots \right\}^N$$

Let's look at diatomic molecules, in which rotational degrees of freedom become important. We can either have the same type of atom (homonuclear) or different types of atoms (heteronuclear).



$$T = \frac{1}{2} M (p_x^2 + p_y^2 + p_z^2) + \frac{1}{2} (\mu r^2) (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta)$$

$$M = m_A + m_B \quad r = a + b$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$p_{\theta} = \frac{\partial T}{\partial \dot{\theta}} = I \dot{\theta} \quad p_{\phi} = \frac{\partial T}{\partial \dot{\phi}} = I \dot{\phi} \sin^2 \theta$$

$$I = \frac{1}{2} \mu r^2$$

$$j_{rot} = \frac{1}{h^2} \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \exp(-\beta p_{\theta}^2/2I - \beta p_{\phi}^2/2I \sin^2 \theta) dp_{\theta} dp_{\phi} d\theta d\phi$$

$$= \frac{2\pi}{h^2} \int_0^{\pi} \sqrt{\frac{2\pi I}{\beta}} \sqrt{\frac{2\pi I \sin^2 \theta}{\beta}} d\theta$$

$$= \frac{2\pi}{h^2} \cdot \frac{2\pi I}{\beta} \int_0^{\pi} \sin \theta d\theta = \frac{2I}{h^2 \beta}$$

$$Z_c(N) = \frac{1}{N!} \left[ \frac{V}{h^3} \right]^N \left[ \frac{2I}{h^2 \beta} \right]^N$$

$$A = -k_B T \ln Z_c(N) = -k_B T \ln \left( \frac{V}{h^3} \right)^N - k_B T \ln \left( \frac{2I}{h^2 \beta} \right)^N$$

$$= A_{trans} + A_{rot}$$

From  $U = \frac{\partial}{\partial \beta} (\beta A)$ ,  $U_{tot} = \frac{5}{2} N k_B T$  where  $U_{trans} = \frac{3}{2} N k_B T$  and

$U_{int(rot)} = N k_B T$ . We have 5 dof, so from equipartition, we expect  $U = \frac{5}{2} N k_B T$ .

If we approach from a quantum perspective,

$$H = H_{cm} + H_{rel}$$

$$H_{rel} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r)$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} \hat{L}^2$$

$$H_{rel} = \frac{1}{2\mu} \hat{L}^2 \rightarrow \frac{1}{2I} \hat{L}^2 \text{ since we drop the other (constant) term}$$

$$\epsilon_{rot} = \frac{\hbar^2 l(l+1)}{2I}$$

$$j_{rot} = \sum_{l=0}^{\infty} (2l+1) \exp(-\frac{l(l+1)\hbar^2}{2I})$$

$$\approx 1 + 3 \exp(-\frac{\hbar^2}{I})$$

$$A_{rot} = -k_B T N \ln(1 + 3 \exp(-\frac{\hbar^2}{I}))$$

$$\approx -k_B T N \cdot 3 \exp(-\frac{\hbar^2}{I})$$

$$U_{rot} = \frac{\partial}{\partial \beta} (\beta A_{rot}) = \frac{3N\hbar^2}{I} \exp(-\frac{\hbar^2}{I})$$

$$C_{v,rot} = \frac{\partial U_{rot}}{\partial T} = 3N \left( \frac{\hbar^2}{k_B T^2} \right) \exp(-\frac{\hbar^2}{I})$$

As  $\beta$  increases,  $C_{v,rot}$  goes exponentially to zero.

For homonuclear molecules, we have the same type of atom.

We can convince ourselves that if we rotate by  $\pi$ , we return the original state, thus, we must integrate from 0 to  $\pi$ .

$$j_{rot} = \frac{I}{h^2} \beta$$

since we repeat the derivation for heteronuclear but with different integration parameters.

$$A_{rot} = -k_B T \ln \left( \frac{I}{h^2} \beta \right)^N$$

$$U_{int} = N k_B T$$

### \* Vibrational States

We treat the diatomic molecule as two balls connected by a spring.

$$\epsilon_n^{vib} = \hbar \omega (n + \frac{1}{2})$$

$$j_{vib} = \sum_{n=0}^{\infty} \exp(-\beta \hbar \omega (n + \frac{1}{2}))$$

$$= \frac{\exp(-\beta \hbar \omega / 2)}{1 - \exp(-\beta \hbar \omega)}$$

$$A_{vib} = \frac{N}{2} \hbar \omega + N k_B T \ln(1 - \exp(-\beta \hbar \omega))$$

$$U = \frac{N \hbar \omega}{2} + \frac{N \hbar \omega}{\exp(\beta \hbar \omega) - 1}$$

$$C_v = N \cdot \left( \frac{\hbar \omega}{k_B T} \right)^2 \cdot \frac{\exp(\beta \hbar \omega)}{(\exp(\beta \hbar \omega) - 1)^2}$$



Problems.

1. Pathria 6.1: Show that the entropy of an ideal gas in thermal equilibrium is given by the formula

$$S = k_B \sum_{\epsilon} [ \langle n_{\epsilon} + 1 \rangle \ln \langle n_{\epsilon} + 1 \rangle - \langle n_{\epsilon} \rangle \ln \langle n_{\epsilon} \rangle ]$$

in the case of bosons and by the formula

$$S = k_B \sum_{\epsilon} [ - \langle 1 - n_{\epsilon} \rangle \ln \langle 1 - n_{\epsilon} \rangle - \langle n_{\epsilon} \rangle \ln \langle n_{\epsilon} \rangle ]$$

in the case of fermions. Verify that these results are consistent with the general formula

$$S = -k_B \sum_{\epsilon} \left\{ \sum_n p_{\epsilon}(n) \ln p_{\epsilon}(n) \right\}$$

where  $p_{\epsilon}(n)$  is the probability that there are exactly  $n$  particles in the energy state  $\epsilon$ .

$$S = -k_B \sum_r p_r \ln p_r$$

$$p_r = \frac{\exp(-\beta(E_r - \mu N_r))}{Z_r}$$

$$E_r = \sum_i n_i(r) \epsilon_i$$

$$N_r = \sum_i n_i(r)$$

$$p_r = \prod_i \left\{ \frac{\exp(-\beta(n_i(r) \epsilon_i - \mu n_i))}{Z_i} \right\}$$

$$Z_i = \sum_{n_i} \exp(-\beta(\epsilon_i - \mu)n_i)$$

$$S = -k_B \sum_{n_1} \sum_{n_2} \dots \left[ \prod_i \frac{\exp(-\beta(\epsilon_i - \mu)n_i)}{Z_i} \right] \ln \left[ \prod_i \frac{\exp(-\beta(\epsilon_i - \mu)n_i)}{Z_i} \right]$$

$$= -k_B \sum_j [ -\beta(\epsilon_j - \mu)n_j - \ln Z_j ] \cdot \frac{\exp(-\beta(\epsilon_j - \mu)n_j)}{Z_j}$$

$$= -k_B \sum_j [ -\beta(\epsilon_j - \mu) \langle n_j \rangle - \ln Z_j ]$$

For fermions,  $n_i = 0$  or  $1$

$$\langle n_j \rangle = \frac{1}{\exp(\beta(\epsilon_j - \mu)) + 1}$$

$$\exp(\beta(\epsilon_j - \mu)) = \frac{1}{\langle n_j \rangle} - 1$$

$$\beta(\epsilon_j - \mu) = \ln [ \langle n_j \rangle^{-1} - 1 ]$$

$$Z_j = 1 + \exp(-\beta(\epsilon_j - \mu)) = 1 + \frac{\langle n_j \rangle}{1 - \langle n_j \rangle}$$

$$S = -k_B \left\{ - \langle n_j \rangle \ln \left[ \frac{\langle n_j \rangle}{1 - \langle n_j \rangle} \right] + \ln (1 - \langle n_j \rangle) \right\}$$

$$= -k_B \left[ - \langle n_j \rangle \ln \left( \frac{1 - \langle n_j \rangle}{\langle n_j \rangle} \right) + \ln (1 - \langle n_j \rangle) \right]$$

$$= -k_B [ - \langle n_j \rangle \ln (1 - \langle n_j \rangle) + \langle n_j \rangle \ln \langle n_j \rangle + \ln (1 - \langle n_j \rangle) ]$$

$$= -k_B [ (1 - \langle n_j \rangle) \ln (1 - \langle n_j \rangle) + \langle n_j \rangle \ln \langle n_j \rangle ]$$

For bosons,  $n_i = 0, \dots, \infty$

$$\langle n_j \rangle = \frac{1}{\exp(\beta(\epsilon_j - \mu)) - 1}$$

$$\beta(\epsilon_j - \mu) = \ln [ \langle n_j \rangle^{-1} + 1 ]$$

$$Z_j = 1 + \exp(-\beta(\epsilon_j - \mu)) + \exp(-2\beta(\epsilon_j - \mu)) + \dots$$

$$= 1 + \exp(-\beta(\epsilon_j - \mu)) Z_j$$

$$= \frac{1}{1 - \exp(-\beta(\epsilon_j - \mu))} = \frac{1}{1 - \exp(\beta(\epsilon_j - \mu)) \langle n_j \rangle}$$

$$= \langle n_j \rangle [ \langle n_j \rangle^{-1} + 1 ] = 1 + \langle n_j \rangle$$

$$S = -k_B \sum_j [ - \langle n_j \rangle \ln [ \langle n_j \rangle^{-1} + 1 ] - \ln (1 + \langle n_j \rangle) ]$$

$$= -k_B \sum_j \left[ - \langle n_j \rangle \ln \left[ \frac{1 + \langle n_j \rangle}{\langle n_j \rangle} \right] - \ln (1 + \langle n_j \rangle) \right]$$

$$= -k_B \sum_j [ \langle n_j \rangle \ln \langle n_j \rangle - (1 + \langle n_j \rangle) \ln (1 + \langle n_j \rangle) ]$$

2. Heat Capacity of a Fermi Gas

The Sommerfeld formula allows one to approximately compute integrals involving the Fermi-Dirac distribution. It takes the form of

$$\int_0^{\infty} \frac{H(\epsilon) d\epsilon}{\exp(\beta(\epsilon - \mu)) + 1} = \int_0^{\mu} H(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + O\left(\frac{k_B T}{\mu}\right)^4$$

a. Write down an integral formula that expresses the particle number  $N$  in terms of the chemical potential and temperature. Using the density of states, express this in terms of an energy integral.



$$N = \left(\frac{L}{2\pi}\right)^3 \int \frac{1}{\exp(\beta(\epsilon - \mu)) + 1} d^3k$$

$$\epsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$g(\epsilon) = \sum_k \delta(\epsilon - \epsilon_k) = \left(\frac{L}{2\pi}\right)^3 \int \delta(\epsilon - \epsilon_k) d^3k$$

$$= \frac{L^3}{h^3} (2\pi)^2 (2m)^{3/2} \epsilon^{1/2}$$

$$N = \frac{2\pi L^3 (2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{\exp(\beta(\epsilon - \mu)) + 1}$$

b. Evaluate the integral equation at zero temperature, for which the chemical potential becomes the Fermi energy,  $E_F$ . Find an explicit expression for  $E_F$  in terms of the density,  $n = N/V$ , with  $V$  the volume.

$$\frac{1}{\exp(\beta(\epsilon - \mu)) + 1} = \frac{1}{\exp(\beta(\epsilon - E_F)) + 1}$$

$$\rightarrow \begin{cases} 1 & \text{if } \epsilon < E_F \\ 0 & \text{if } \epsilon > E_F \end{cases}$$

$$N = \frac{2\pi L^3 (2m)^{3/2}}{h^3} \int_0^{E_F} \epsilon^{1/2} d\epsilon = \frac{2\pi V (2m)^{3/2}}{h^3} \cdot \frac{2}{3} E_F^{3/2}$$

$$E_F^{3/2} = \frac{3nh^3}{4\pi(2m)^{3/2}}$$

$$E_F = \frac{h^2}{2m} \left(\frac{3n}{4\pi}\right)^{2/3}$$

c. Next, use the Sommerfeld formula to find an expression for the chemical potential at low but non-zero temperature, valid to  $O((k_B T/E_F)^2)$ . The expression may be conveniently expressed in terms of  $E_F$  and  $k_B T$ .