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Part I

Statistical Mechanics
Chapter 1

Introduction

1.1 Course Overview

We develop the ability to predict macroscopic properties of a system from an understanding of molecular properties. The ensemble average of a mechanical property is equated to the corresponding thermodynamic function. Using basic assumptions about intermolecular potential, we are able to determine transport coefficients (viscosity, mass diffusivity, and thermal conductivity).

1.2 Collisions

Imagine a flux of j particles through some k particles, get a change in flux (Fig. 1.1)

• Probability of a collision between j and k particle is:

\[ dP_{jk} = n_k Q^P_{jk} dx \]  

- \( Q^P_{jk} \) is cross sectional area of process \( P \)
- \( dx \) is distance
- \( n_k \) is density of k-particles

\[ \Gamma + d\Gamma = \Gamma - \Gamma \cdot dP = (1 - n_k Q^P_{jk} dx)\Gamma \]  

3
CHAPTER 1. INTRODUCTION

Figure 1.1: Flux of j-particles through k-particles.

\[
d\Gamma = n_k Q_{jk}^P dx \Gamma \\
\frac{d\Gamma}{dx} = n_k Q_{jk}^P \Gamma \\
\Gamma(x) = \Gamma_0 e^{-n_k Q_{jk}^P x}
\]

- If \( x \) is in units of length, \( n_k Q_{jk}^P \) is in units of \( \frac{1}{\text{length}} \) and define a decay constant:
  \[
  \lambda = \frac{1}{n_k Q_{jk}^P} \equiv \lambda_{\text{mfp}}
  \]

- \( \lambda \) is the mean free path - how long we travel before “bouncing.”

Instead of flux, say the number of j-particles lost is:

\[
dN = NdP = nN_j Q(v) dx
\]

- We see \( Q(v) \) (our cross section) needs to be defined → How to do it? See Fig. 1.2
1.2. COLLISIONS

![Image of two particles](image)

Figure 1.2: Two particles will only hit if the distance between them is less than the sum of both sphere radii.

$$Q = \pi (r_1 + r_2)^2 \quad (1.8)$$

Collision Frequency: Imagine the mean free path is equal to the distance traveled between collisions.

$$\lambda \frac{v(\Delta t)}{\nu(\Delta t)} = \frac{\text{velocity}}{\text{collision frequency}} = \frac{1}{nQ(v)} \quad (1.9)$$

$$\nu = n\nu Q(v) \quad (1.10)$$

- \(\nu\) is the frequency with which a \(j\)-particle hits a \(k\) particle.

- We can generalize our cross section as our elastic collision and all the inelastic collisions (\(KE\) not preserved).

$$Q = Q^{(e)} + \sum Q^{(ne)} \quad (1.11)$$

- \(Q^{(ne)}\) can result from electron excitation, ionization, etc.
- Good first estimate is using Bohr radius: \(Q_0 = \pi a_0^2 = 0.88 \text{ Å}^2\).
- Can usually go with \(Q \approx 10^{-20} \text{ m}^2\) as a start.

Reaction Rate: Look at our collision frequency with all the particles:

$$R^P = n_j n_k \nu Q^P_{jk}(v) \quad (1.12)$$
CHAPTER 1. INTRODUCTION

Figure 1.3: Particle with velocity $u$ in a flow of length $l$.

- $R^P$ has units of $\frac{1/m^3}{s} = \text{density time}$.  
- This is how fast we add or take away particles in the process $P$.  
- Example reaction: $A + e^- \rightarrow A^+ + 2e^-$ (ionization), where $A$ is rigid particle $k$ and $e^-$ is particle $j$. If we let $n_0$ be the density of neutrals, then:

$$R^\text{ion} = n_e n_0 v_e Q^\text{ion}(v) \quad (1.13)$$  
- We are removing field particles at a rate $\frac{dn_0}{dt} = -R^\text{ion}$. We can rewrite this to see that $\frac{dn_0}{dt}$ is in units of time. $\rightarrow$ Define as $\tau^P$ relaxation time.

  - In a flow of length $l$, $\tau_r = \frac{l}{v}$, the resonance time shown in Fig. 1.3  
  - Looking at rocket for $\tau^P$ and $\tau_r$ comparison:  
    * $\tau_r > \tau^P$ is equilibrium flow  
    * $\tau^P > \tau_r$ is frozen flow

Elastic collisions conserve energy.  
Inelastic collisions transfer energy to internal modes.

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_1 V_1^2 + \frac{1}{2} m_2 V_2^2 + U \quad (1.14)$$

- $U$ is the energy that goes to exciting particle 2  
- Momentum is also conserved ($m_1 v_1 = m_1 V_1 + m_2 V_2$)

  - For max $U$ ($\frac{dU}{dV_1} = 0$), $V_1 = \frac{m_1 v_1}{m_1 + m_2}$  
  - Max $U^* = \left(\frac{m_2}{m_1 + m_2}\right) \frac{m_1 v_1^2}{2}$, the larger $\frac{m_2}{m_1}$, the more initial KE $\rightarrow U$.  
  - If $m_1 << m_2 \rightarrow U^* = \frac{m_1 v_1^2}{2}$
1.2. COLLISIONS

Figure 1.4: Particle 1 collides with particle 2, transferring some of its kinetic energy to particle 2.

Non-adiabatic criterion for elastic collisions:

- Ionization/excitation happens when the incoming particles come in fast enough that electron fields can’t adjust.
- Consider the neutral atom as a harmonic oscillator with natural frequency $\nu_0$ (See Fig. 1.5).
- $e^-$ has a forcing function that applies to the electron field (has a frequency).
  - Define $\tau \approx \frac{a}{v}$, where $v$ is velocity and $a$ is range of interaction.
  - If $\frac{1}{\tau} \ll \nu_0$, adiabatic interaction
  - If the electron is oscillating much faster than the incoming particle is coming in, it can adjust and we have no excitations.
- So $\frac{a \nu_0}{v} \gg 1$ is the adiabatic condition
- To excite an electron, we need energy $E = h\nu \rightarrow \nu_0 \approx \frac{E}{h}$ and $E = \Delta \varepsilon_{12}$
- So for adiabatic interactions (no excitation), $\frac{a \Delta \varepsilon}{vh} \gg 1$, and for non-adiabatic collisions (excitation) $\frac{a \Delta \varepsilon}{vh} \leq 1$
- Then $\Delta \varepsilon$ at some $T$ gives how much energy we need at that temperature.
- If $\Delta \varepsilon$ is above the first excited state, then we need to worry about more than ground state in the partition function.
CHAPTER 1. INTRODUCTION

1.3 Preliminary Mathematics and Review

Statistical mechanics studies macroscopic systems from a molecular point of view.

- Looking into equilibrium (statistical thermo) we will develop a way to calculate and interpret thermodynamic quantities from a molecular point of view.
- We will do this by presenting ideas in terms of quantum mechanical properties such as energy states, wave functions, and degeneracy.

1.3.1 The Schrödinger Equation

Know that the Schrödinger equation determines the possible energy values $\varepsilon_j$ available to the system and these values may have an associated degeneracy $\Omega(\varepsilon_j)$.

We had learned $F=ma$, but can’t apply to very small particles because of the Heisenberg uncertainty principle (can’t know both position and momentum).

- We use quantum mechanics and probability distribution
- We can use the Hamiltonian to measure energy: $H\Psi = E\Psi$ (time independent), where $\Psi$ is a probability distribution.
- Then $p = \hbar k$, $\hbar = \frac{h}{2\pi}$, $k = \frac{2\pi}{\lambda}$, $p = \frac{\hbar}{\lambda}$, and $\hbar$ is in units of joule-seconds.

Figure 1.5: An electron oscillating with natural frequency $\nu_0$. 
1.3. PRELIMINARY MATHEMATICS AND REVIEW

Figure 1.6: Particle in a box: We use a wave as the most general form of where the particle could be, then the wave function \( \psi_n(x) = \sin(\frac{n\pi}{a}x) \) for \( n = 1, 2, 3, \ldots \). Note that the wave function is zero outside of the box since there is zero possibility the particle can be there. Now, the 1D Hamiltonian is \( H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \), so \( H\psi = -\frac{\hbar^2 n^2 \pi^2}{2ma^2} \sin(\frac{n\pi}{a}x) \), which means \( \varepsilon = \frac{\hbar^2 n^2}{8ma^2} \).

- Energy is momentum squared divided by mass: \( E = \frac{p^2}{2m} \)
- So with \( H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \) for the 1D Schrödinger equation, then \( p^2 = \hbar^2 \frac{\partial^2}{\partial x^2} \) and \( p = -i\hbar \frac{\partial}{\partial x} \)
- If we can write the Hamiltonian, use boundary conditions. Then we can solve for the energy of the system. See Fig. 1.6 for an example.

1.3.2 Stirling’s Approximation and Distributions

\[ \ln(N!) = \ln(N) + \ln(N-1) + \ln(N-2) + \ldots + \ln(1) = \sum_{m=1}^{N} \ln(m). \]

The graph of this looks like \( \ln(x) \), so integrate from 1 to N to solve:
\[ \int_{1}^{N} \ln(x)dx = N\ln(N) - N + 1. \]

But \( N >> 1 \), so drop 1 to get Stirling’s approximation (equation 1.15).

\[ \ln(N!) \approx N \ln(N) - N \quad (1.15) \]

Binomial Distribution

- With \( N \) particles, we have \( N! \) different arrangements of those \( N \) particles.
• We can divide these into two groups of particles, such that \( N_1 + N_2 = N \). We then have \( \frac{N!}{N_1!N_2!} \) ways to do this.

Say we have 4 coins with \( N_1 \) heads and \( N_2 \) tails. Table 1.1 shows the degenerate ways to arrange different combinations of heads and tails.

<table>
<thead>
<tr>
<th>( N_1 )</th>
<th>( N_2 )</th>
<th>( N )</th>
<th>Ways to Get</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>4</td>
<td>1 = 1</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>4</td>
<td>( \frac{4!}{3!1!} = 4 )</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4</td>
<td>( \frac{4!}{2!2!} = 6 )</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4</td>
<td>( \frac{4!}{1!3!} = 4 )</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>4</td>
<td>1 = 1</td>
</tr>
</tbody>
</table>

Table 1.1: Degeneracies of “coin-states.”

If we have a very large \( N \), then we can treat \( N_1 \) as a continuous variable. Fig. 1.7 illustrates this for a smaller number \( N \).

Does our distribution get sharper as \( N \rightarrow \infty \)? Let’s look!

• \( f(N_1) = \frac{N!}{N_1!(N-N_1)!} \) \( \text{Stirling} \rightarrow \ln(f(N_1)) = N \ln(N) - N - (N_1 \ln(N_1) - N_1) - ((N - N_1) \ln(N - N_1) - (N - N_1)) \)

• How do we measure the “width” of this function? Let’s find the max value (take \( \frac{\partial}{\partial N} \ln(f(N_1)) = 0 \)).

• \( \frac{\partial f(N_1)}{\partial N} \bigg|_{N^*} = 0 \) or \( \frac{\partial \ln(f(N_1))}{\partial N} = 0 \) \( \rightarrow \) get \( N^* = \frac{N}{2} \) as most probable state for coins.

• If \( N \) is very large, we get a delta function.

1.3.3 Lagrange Multipliers

With \( f(N_1, N_2) \), then \( \partial f = \frac{\partial f}{\partial N_1} \partial N_1 + \frac{\partial f}{\partial N_2} \partial N_2 \) (general form).
1.3. PRELIMINARY MATHEMATICS AND REVIEW

Figure 1.7: The distribution of ways to arrange $N$ for a small number $N$.

We also have $N_1 + N_2 = N$, or $\phi(N_1, N_2) =$constant.

Then $\partial \phi = \frac{\partial \phi}{\partial N_1} \partial N_1 + \frac{\partial \phi}{\partial N_2} \partial N_2 = 0$ since $\phi$ is constant.

Maximize the first equation, $\partial f = 0$, but now we are equal! So:

\[
\begin{align*}
\text{get } \alpha \left\{ \frac{\partial f}{\partial N_1} + \alpha \frac{\partial \phi}{\partial N_1} = 0, \right. \\
\left. \frac{\partial f}{\partial N_2} + \alpha \frac{\partial \phi}{\partial N_2} = 0 \right. 
\end{align*}
\]

(1.16)

Because \( \frac{\partial f}{\partial N_1} = \frac{\partial f}{\partial N_2} = -\alpha \), say it’s some \(-\alpha\) constant.

Another way:

- We want max or min of $f \rightarrow f(x_1, x_2, ..., x_n) =$max or min
- Equations 1.17 then give constraints on our function:

\[
\begin{align*}
\text{constraints on our function } \begin{cases} 
g_1(x_1, ..., x_n) = c_1 \\
\vdots \\
g_n(x_1, ..., x_n) = c_m 
\end{cases}
\end{align*}
\]

(1.17)

- Then construct $f^*$ such that $f^* = f - \alpha_1 g_1 - ... - \alpha_n g_n$
1.3.4 Degeneracy

We can have multiple microstates to make one macrostate

- Let’s say $H\Psi = E\Psi$ in 2D, then a solution can be $\Psi = \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{b} y\right)$
- We do some tedious math to get $E = \frac{\hbar^2}{8m a^2}(n_x^2 + n_y^2)$
- $n_x$ and $n_y$ can only be integers, so what states satisfy?
- Say $\sqrt{E}$ is my radius, so make it $\frac{\hbar^2}{8m a^2}(n_x^2 + n_y^2) = R^2$ as a circle (see Fig. 1.8)
- Larger circle means more possible states that can satisfy the equation/energy
Thus the degeneracy rises with increasing values of $E$: $\Omega(E)$ rises for higher $E$.

- At typical room temp, we get $\Omega(E)$ to be $\mathcal{O}(10^N) \rightarrow$ one mol has $N = 6.022 \times 10^{23}$. Think of resulting number of microstates!
Chapter 2

Ensembles

2.1 Canonical Ensemble

How do we figure the macrostate out from what we know of microstates of a system?

microstates $\rightarrow$ macrostates

We postulate the most likely state is the average $\rightarrow$ what we measure (Gibbs postulate, very important!)

A system $A$ with $N, V,$ and $\varepsilon$.

Micro Canonical Ensemble

\[
\begin{align*}
AN \text{ particles} \\
A\varepsilon &= \varepsilon_{\text{tot}} \\
AV &= V_{\text{tot}}
\end{align*}
\]  

(2.1)
CHAPTER 2. ENSEMBLES

Table 2.1: A combination of a large number of systems create an ensemble.

Switching to canonical → we will have different energy states, each with their own energy, and a certain number of systems in this state.

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>State number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>$E_2$</td>
<td>$E_3$</td>
<td>Energy number</td>
</tr>
<tr>
<td>$a_1$</td>
<td>$a_2$</td>
<td>$a_3$</td>
<td>Occupation number</td>
</tr>
</tbody>
</table>

Table 2.2: Canonical Ensemble.

- $\mathbf{a} = \{a_1, a_2, ..., a_j\}$
- Our constraints are:
  
  - $\sum_j a_j = A$
  
  - $\sum_j a_j E_j = \varepsilon_{\text{tot}}$
- Postulate: We will say each micro state is equally probable, but the macro states are not equally probable (think of the example from Table 1.1).
- We have distinguishable particles, and the number of ways $W(\mathbf{a})$ to assemble them is:

  $$W(\mathbf{a}) = \frac{A!}{a_1!a_2!...} = \frac{A!}{\prod_j a_j!} \quad (2.2)$$

- This lets us translate into probabilities $P_j$

  - $\frac{a_j}{A}$ is the fraction of systems of the ensemble in the $j^{th}$ state.
2.1. CANONICAL ENSEMBLE

Figure 2.1: Distributions of $a_j$.

- We want the probability of a system being in the $j^{th}$ state → need average $\overline{a_j}$ over all distributions with equal weight to each:

$$P_j = \frac{\overline{a_j}}{A} = \frac{1}{A} \overline{\sum_a W(a)a_j(a)} \tag{2.3}$$

- We use $a_j(a)$ because it depends on the other states also.
- We want $a^*$ which maximizes $W(a)$, as shown in Fig. 2.1.

Now we apply Lagrange multipliers with our two constraints (total number of particles is same, and total energy is the same).

$$\frac{\partial}{\partial a_j} \{ \ln[W(a)] - \alpha \sum_k a_k - \beta \sum_k a_k E_k \} = 0 \tag{2.4}$$

- $\alpha$ and $\beta$ are the unknown constants we need.
- Equation 2.4 gives $\ln(a_j^*) - \alpha - 1 - \beta E_j = 0$ or $a_j^* = e^{-\alpha'} e^{-\beta E_j}$, where $\alpha' = \alpha + 1$.
- If we sum both sides over $j$, we get $e^{\alpha'} = \frac{1}{A} \sum_j e^{-\beta E_j}$. 

• Because \( P_j = \frac{a_j^*}{A} \), we can rearrange: 
\[
\frac{1}{\lambda} = \frac{e^{\alpha'}}{\sum e^{-\beta E_j}} \quad \text{and} \quad a_j^* = e^{-\alpha'} e^{-\beta E_j},
\]
so
\[
\frac{a_j^*}{\lambda} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}.
\]

• This is our probability of being in the \( j \)th state where we maximize our ways (picked \( a^* \) that is most probable).

With our new expression, our average energy \( \bar{E} = \frac{e^{-\beta E_j}}{\sum e^{-\beta E_j}} \)

And pressure \( \varphi_j = \left( \frac{\partial E}{\partial V} \right)_N \to 2E_j = -\varphi_j dV_j \) and you can integrate.

• So average pressure \( \bar{\varphi} = \sum \varphi_j \cdot P_j \), where \( P_j = \frac{a_j^*}{\lambda} \)

• \( \bar{\varphi} = \sum \frac{-(\frac{\partial E}{\partial V})_N}{\sum e^{-\beta E_j}} e^{-\beta E_j} \)

Now we postulate that \( \bar{E} = E_{\text{thermo}} \) and \( \bar{\varphi} = \varphi_{\text{thermo}} \to \) What we measure should equal our new expression from the micro world.

Doing some math now, we can see:

\[
\text{add these together} \quad \left\{ \begin{align*}
\left( \frac{\partial E}{\partial V} \right)_{N,\beta} &= \bar{\varphi} + \beta (E \bar{\varphi}) - \beta \bar{E} \bar{\varphi} \\
\left( \frac{\partial \bar{\varphi}}{\partial \beta} \right)_{N,V} &= E \bar{\varphi} - (E \bar{\varphi})
\end{align*} \right. \tag{2.5}
\]

And find:
\[
\left( \frac{\partial E}{\partial V} \right)_{N,\beta} + \beta \left( \frac{\partial \bar{\varphi}}{\partial \beta} \right)_{N,V} = -\bar{\varphi}
\]

• We can see this is the same form as \( \left( \frac{\partial E}{\partial V} \right)_{T,N} - T \left( \frac{\partial \varphi}{\partial T} \right)_{N,T} = -\varphi \)

• If we flip so in terms of \( \frac{1}{T} \), it gives us a positive sign:
\[
\left( \frac{\partial E}{\partial V} \right)_{T,N} + \frac{1}{T} \left( \frac{\partial \varphi}{\partial T} \right)_{N,T} = -\varphi \rightarrow \beta = \frac{1}{kT} \quad \text{for some constant } k.
\]

• We find that \( k \) is constant across any system \( \rightarrow \) universal \( \rightarrow \) Boltzmann constant.
Let’s summarize what we have done with ensembles so far:

- Energy states from quantum mechanics
- Occupation states of those energy states by individual systems $a_j$ of an ensemble
- Distributions of $a_j$’s: $W(a) \rightarrow$ Maximize with $a_j^*$
- Use Lagrange multipliers $\rightarrow$ Have an $\alpha$ and $\beta \rightarrow \alpha$ cancels out, equation in terms of $\beta$
- Solve and get $\beta = \frac{1}{kT}$

We will simplify our expressions by saying:

$$Q = \sum_j e^{-\beta E_j}$$  \hspace{1cm} (2.6)

This is the canonical ensemble partition function, which bridges Q.M. energy states of a macroscopic system and the thermodynamic properties of that system. If we can get $Q$ as a function of $N, V$, and $T$, we can calculate thermo properties in terms of quantum mechanical and molecular parameters.

Helmholtz free energy: $A = -kT \ln(Q)$ is the useful work obtainable from a closed thermodynamic system (also $A = U - TS$)

### 2.2 Other Ensembles

An ensemble is a collection of a large number of systems ($A$), each with the same macroscopic properties for a particular thermodynamic system of interest.

- $\Omega(N, V, E)$: Micro canonical ensemble, an isolated system
- $Q(N, V, T)$: Canonical ensemble, a system in contact with a heat bath
- $\Xi(V, T, \mu)$: Grand canonical ensemble, a system in contact with a heat and particle bath
• $\Delta(N, T, \varphi)$: Isobaric-Isothermal ensemble, mostly used in chemistry, a system with constant $\varphi$

We can choose any type of ensemble listed above where we hold the different properties (in parenthesis) constant.

• You go through the math to get expressions for thermo equations

• We can find the values they give differ, but by such a small amount that it doesn’t matter to us

• Since it doesn’t matter, choose the ensemble that works best for us.

For $\mu$ chemical potential: $\sum_i \mu_i \partial N_i = 0$ is equilibrium.

Table 3-1 in the McQuarrie [3] summarizes each ensemble and has fundamental relation associated.
2.2. OTHER ENSEMBLES

- Thermodynamic Aside -

From thermo:

1\textsuperscript{st} Law \begin{equation}
\partial E = \partial Q - \partial W \tag{2.7}
\end{equation}

2\textsuperscript{nd} Law \begin{align*}
\partial E &= T \partial S - \partial W \\
&= T \partial S - \varphi \partial V \\
\text{and } E &= E(S,V) \\
\text{so } \partial E &= \left(\frac{\partial E}{\partial S}\right)_V \partial S + \left(\frac{\partial E}{\partial V}\right)_S \partial V \tag{2.8}
\end{align*}

From Equations 2.7 and 2.8 you can see that \( \varphi = \left(\frac{\partial E}{\partial V}\right)_S \) and \( T = \left(\frac{\partial E}{\partial S}\right)_V \).

What if we could come up with a function of temperature and volume? \( f = f(T,V) \)

- We get Helmholtz free energy: \( A(T,V) = E - TS \)
- We can similarly find \( g(T,\varphi) \implies \text{entropy } H(T,\varphi) \)

- End Thermodynamic Aside -

The partition functions from each ensemble can be linked together:

\[
\text{for example: } Q(N,V,T) = \sum_E \Omega(N,V,E) e^{-\frac{E}{kT}} \tag{2.9}
\]

These ensembles are each in their own specific equilibrium → Don’t forget that it’s a mental construct!

Note: \( S = k \ln(\Omega) \) is engraved on Boltzmann’s grave- his greatest contribution.
Chapter 3

Boltzmann, Fermi-Dirac, and Bose-Einstein Statistics

In the high temperature limit, quantum mechanics $\rightarrow$ Boltzmann statistics

3.1 Boltzmann Statistics

$H \approx H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + H_{\text{elect}}$ is a good approximation for ideal gas.

We use the canonical partition function $Q(N, V, T) = \sum_j e^{-\frac{E_j}{kT}}$,

$E_j = \varepsilon_i^a + \varepsilon_i^b + \ldots + \varepsilon_i^N$

- Break it up further: $Q = (\sum_i e^{-\frac{\varepsilon_i^a}{kT}})(\sum_j e^{-\frac{\varepsilon_j^b}{kT}})(\sum_k e^{-\frac{\varepsilon_k}{kT}})(\ldots)$
- If distinguishable, then we have Equation 3.1

$$Q(V, T) = [q(V, T)]^N$$

and $q = \sum_i e^{-\frac{\varepsilon_i}{kT}}$ (3.1)

- For indistinguishable particles, this becomes a little complicated
  - We have $N$ particles and $N!$ ways to arrange them, so we just sum all indices indiscriminately
– It is unlikely we can fill all states (many, many more states than N), so just divide by \(N!\) (All indices will be different, summing indiscriminately is ok). End up with equation 3.2 for indistinguishable particles

\[
Q = \frac{[q(V, T)]^N}{N!}
\] (3.2)

Bosons: sum of protons, electrons, and neutrons is even (integral spin). Wave function must be symmetric under the operation of the interchange of two identical particles.

Fermions: sum of protons, electrons, and neutrons is odd (half integral spin). Wave function must be antisymmetric under the operation of the interchange of two identical particles.

### 3.2 Fermi-Dirac and Bose-Einstein Statistics

Different approach to get same results as Boltzmann (above)

Starting definitions: \(E_j = \sum_k \varepsilon_k n_k\), \(N = \sum_k n_k\)

- Same partition function: \(Q(N, V, T) = \sum_j e^{-E_j kT}\), but our restriction makes us rewrite: \(\sum^* n_k e^{-\beta \sum_i \varepsilon_i n_i}\)
- Hard to evaluate, so let’s use grand canonical partition function:

\[
\Xi(V, T, \mu) = \sum_{N=0}^{\infty} \lambda^N Q(N, V, T) \text{ and } \lambda = e^{\beta \mu}
\] (3.3)

\[
\Xi = \sum_{N=0}^{\infty} \lambda^N \sum^{*} n_k e^{-\beta \sum_i \varepsilon_i n_i} = \sum_{N=0}^{\infty} \lambda^N \sum^{*} n_k e^{-\beta \sum_i \varepsilon_i n_i}
\] (3.4)

\[
\Xi = \sum_{N} \sum^{\star} n_k \prod_k (\lambda e^{-\beta \varepsilon_k})^{n_k}
\] (3.5)

Big thought step!

\[
\Xi = \prod_{k} \sum_{n_k=0}^{n_k_{\text{max}}} (\lambda e^{-\beta \varepsilon_k})^{n_k}
\] (3.6)
3.2. FERMI-DIRAC AND BOSE-EINSTEIN STATISTICS

- Each set of $n_k$ can go from 0 to some max value \( \rightarrow \) many combinations over \( N \), that lets us make this simplification and get rid of our weird set notation.

- Side Note -

Let’s see why: For example, \( S = \sum_{N=0}^{\infty} \sum_{\{n_j\}}^{\ast} x_1^{n_1} x_2^{n_2} \) and \( n_1 \) and \( n_2 = 0, 1, \) and 2.

Show its equivalence:

\[
S = (1 \cdot 1 + 1x_2 + 1x_1 x_2 + x_1 x_2^2 + x_1^2 x_2 + x_1^2 x_2^2 + x_1^2 x_2^2)
\]

\( n_1 + n_2 = N \), so all possible values of \( N \) allowed us to use different exponents up to \( N = 2 + 2 = 4 \).

Now, basic algebra gives

\[
S = (1 + x_1 + x_1^2)(1 + x_2 + x_2^2) \rightarrow S = \prod_{k=1}^{2}(1 + x_k + x_k^2)
\]

- End Side Note -

Fermi-Dirac Statistics: \( n_k = 0 \) or 1 (particles can’t be in same energy level)

Then \( n_1^{\max} = 1 \) and:

\[
\Xi_{FD} = \prod_k (1 + \lambda e^{-\beta \varepsilon_k}) \tag{3.7}
\]

Bose-Einstein Statistics: \( n_k \) has no restriction on the occupancy of each state, so \( n_k^{\max} = \infty \). Then:

\[
\Xi_{BE} = \prod_k \sum_{n_k=0}^{\infty} (\lambda e^{-\beta \varepsilon_k})^{n_k}
\]

- But any \( \sum_{j=0}^{\infty} x^j = (1 - x)^{-1} \) when \( x < 1 \), so:

\[
\Xi_{BE} = \prod_k (1 - \lambda e^{-\beta \varepsilon_k})^{-1} \tag{3.8}
\]
CHAPTER 3. BOLTZMANN, F-D, AND B-E STATISTICS

The FD and BE equations can be written together as:

\[ \Xi_{FD}^{BE} = \prod_k \left( 1 \pm \lambda e^{-\beta \varepsilon_k} \right)^{\pm 1} \]  \hspace{1cm} (3.9)

So we had:

\[ N = \sum_k \bar{n}_k = kT \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} \] (from Chap. 2, Chap. 3 in McQuarrie)

\[ = \lambda \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V,T} = \sum_k \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}. \]

• And comparing we see the average number of particles in the \( k \)th quantum state is \( \bar{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}. \)

• And we get \( \bar{E} = N \bar{\varepsilon} = \sum_k \bar{n}_k \varepsilon_k = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}} \)

• From Chap. 3 in the MacQuarrie \( \varphi V = kT \ln \Xi = \pm kT \sum_k \ln[1 \pm \lambda e^{-\beta \varepsilon_k}] \)

In Boltzmann limit, energy states \( \gg \) number of particles, so \( \bar{n}_k \to 0 \) since \( \lambda \to 0 \), so we can write \( \bar{n}_k = \lambda e^{-\beta \varepsilon_k} \) (for small \( \lambda \)) and \( \bar{E} \to \sum_j \lambda \varepsilon_j e^{-\beta \varepsilon_j} \).

• Also, \( \mp V \to \pm kT(\pm \lambda \sum_j e^{-\beta \varepsilon_j}) = kT \lambda q \)

• We can show \( \lambda q = N \), so \( \mp V = NkT \)

Thus, the quantum view agrees with Boltzmann statistics!
Chapter 4

Monatomic and Diatomic Gases

4.1 Ideal Monatomic Gas

- Single molecules, room temperature, low pressures (< 1 ATM)
- No molecules in same energy state and indistinguishable: \( Q = \frac{q^N}{N!} \) and \( q = \sum e^{\frac{-\varepsilon_j}{kT}} \)
- We will approximate \( q \) as separable: \( q = q_{\text{trans}}q_{\text{elect}}q_{\text{nucl}} \)

4.1.1 Translational Partition Function

Going back to the particle in a box: \( \varepsilon_{n_xn_yn_z} = \frac{\hbar^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \) (for energy states)

Then, \( q_{\text{trans}} = \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta\varepsilon_{n_xn_yn_z}} \)

- Writing out each piece and summing, we get:

\[
q_{\text{trans}} = \sum_{n_x=1}^{\infty} e^{-\frac{\beta \hbar^2 n_x^2}{8ma^2}} \sum_{n_y=1}^{\infty} e^{-\frac{\beta \hbar^2 n_y^2}{8ma^2}} \sum_{n_z=1}^{\infty} e^{-\frac{\beta \hbar^2 n_z^2}{8ma^2}} = \left( \sum_{n=1}^{\infty} e^{-\frac{\beta \hbar^2 n^2}{8ma^2}} \right)^3
\]

We want to replace the summation with an integral, so difference between two successive energy states must be small: \( \Delta = \frac{\beta \hbar^2 (n_x+1)^2}{8ma^2} - \frac{\beta \hbar^2 n_x^2}{8ma^2} = \frac{\hbar^2 (2n_x+1)}{kTma^2} \), which gives very small values \( \sim O(10^{-20}) \).
• Since our $\Delta$ is small, we can say it is approximately equivalent to integrate, so:

$$ q_{\text{trans}} = \left[ \int_0^\infty e^{-\frac{\beta h^2 n^2}{8ma^2}} dn \right]^3 = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} a^3 $$

(using identity $\int_0^\infty e^{-ax^2} = \frac{1}{2}\sqrt{\frac{\pi}{a}}$)

• Replace $a^3$ with volume:

$$ q_{\text{trans}} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V \quad (4.1) $$

Sum of states: Worry about the sum of different energy levels, $\varepsilon_j$, not the individual $n$’s that comprise our $\varepsilon_j$.

• Now another way to look at it is: $q_{\text{trans}} = \int_0^\infty \omega(\varepsilon)e^{-\beta \varepsilon} d\varepsilon$, where $\omega(\varepsilon)$ is the degeneracy.

• And $\omega(\varepsilon) = \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \Delta \varepsilon + O((\Delta \varepsilon)^2)$

• As $\Delta \varepsilon \to 0$, we get $q = \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} \int_0^\infty \varepsilon^{1/2} e^{-\beta \varepsilon} d\varepsilon = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V$

• $\bar{\varepsilon}_{j,\text{trans}} = \sum_j \varepsilon_j e^{-\varepsilon_j/kT} q_{\text{trans}} = kT^2 \frac{\partial \ln q_{\text{trans}}}{\partial T} = \frac{3}{2} kT$ (Yay!)

DeBroglie Wavelength:

$$ \Lambda \equiv \left( \frac{h^2}{2\pi mkT} \right)^{1/2} \quad (4.2) $$

• And $\frac{1}{2}mv^2 = \frac{p^2}{2m} = \bar{\varepsilon}_{\text{trans}}$

• So $\frac{p^2}{2m} = \frac{3}{2} kT \to p = (mkT)^{1/2}$, but look at $\Lambda$.

• $\Lambda \approx \frac{h}{p}$ (units of length, Plank is units of J-s)

• We use this to see when in the Boltzmann limit $\frac{V^3}{\Lambda^3} \ll 1$, and we see $q_{\text{trans}} = \frac{V}{\Lambda^3}$ → We can say $\Lambda \ll a$ for the Boltzmann limit.
4.1. IDEAL MONATOMIC GAS

4.1.2 Electronic Partition Function

\[ q_{\text{elect}} = \sum_i \omega(\varepsilon_i) e^{-\beta \varepsilon_i} \]

We can choose where we define the zero state → Say it is at \( \varepsilon_1 = 0 \)

\[ q_{\text{elect}} = \omega(\varepsilon_1) + \omega(\varepsilon_2)e^{-\beta \varepsilon_2} + \omega(\varepsilon_3)e^{-\beta \varepsilon_3} + \ldots \] (4.3)

- First term is important for most gases at ordinary temps.
- Second term is added in for alkali and halogens.

4.1.3 Nuclear Partition Function

Usually just ignore (set to 1)

\[ q_{\text{nucl}} = \omega_n \] (4.4)

- You need \( O(10^{10}) \) K temps to get next state, just set to 1 then.

\[ Q = \left[ q_{\text{trans}}q_{\text{elect}}q_{\text{nucl}} \right]^N / N! \]

We can use this to write some of our thermodynamic equations:

- Helmholtz Free Energy: \( A(N,V,T) = -kT \ln Q \) (useful work obtainable from a closed system at constant \( T \))

\[ A = -kT \ln \left( \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \frac{V e}{N} \right) - NkT \ln \left( \omega_{\varepsilon_1} + \omega_{\varepsilon_2} e^{-\beta \Delta \varepsilon_{12}} \right) \]

usually very small

- Pressure!: \( p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} = \frac{NkT}{V} \) Cool stuff!

Note: Stirling approximation gives us the “e” in the ln term in \( A(N,V,T) \).
CHAPTER 4. MONATOMIC AND DIATOMIC GASES

4.2 Ideal Diatomic Gas

In addition to translational and electronic (and nuclear) degrees of freedom, diatomic molecules also have rotational and vibrational degrees of freedom (5 total).

- Using Schrödinger Eq. is extremely difficult → We will use simplification to help.

4.2.1 1st Assumption: Born-Oppenheimer Approximation

\( m_{\text{atom}} \gg m_e \)

Nuclei are much more massive than electrons → move slow relative to the electrons

- Now the Schrödinger eq. approximately separates into 2 simpler equations:
  - Motion of electrons about the “fixed” nuclei → eigenvalues \( u_j(r) \)
  - Motion of the nuclei in the potential field \( u_j(r) \) that is set up by the electrons in the electronic state \( j \) (\( u_j(r) = \) ground state)

First excited state is usually several eV above ground → just consider ground state

- Approximate the potential curve as a Morse Potential → \( u_0(r) \) → \( r_e \approx 2.6 \text{ Å} \)
  \( (u_r \) is internuclear potential)

Since potential is set to \( u_0(r) \) → spherically symmetrical → split into 2 equations using a center of mass motion \( (m_1 + m_2) \) and relative motion of reduced mass \( \mu = \frac{m_1 m_2}{m_1 + m_2} \)

- Now we can wrote our Hamiltonian as \( H = H_{\text{trans}} + H_{\text{int}} \) with eigenvalues \( \varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{int}} \)
- The partition function for a diatomic molecule is then \( q = q_{\text{trans}} \cdot q_{\text{int}} \) and from earlier in the chapter (monatomic gases) and using our 2 masses:

\[
q_{\text{trans}} = \left[ \frac{2\pi (m_1 + m_2) kT}{\hbar} \right]^{3/2} V
\]
Now we have to investigate $q_{\text{int}}$ to understand diatomic molecules, and we will see it will differ for heteronuclear and homonuclear molecules.

Relative motion of the two nuclei in our potential $u(r)$ is rotary motion and vibration

- Vibration is small, call fixed internuclear distance $r_e$ (rigid dumbbell)
- Expanding $u(r)$ about $r_e$:
  
  \[
  u(r) = u(r_e) + (r - r_e) \left( \frac{\partial u}{\partial r} \right)_{r=r_e} + \frac{1}{2} (r - r_e)^2 \left( \frac{\partial^2 u}{\partial r^2} \right)_{r=r_e} + \ldots, \text{ simplifies:}
  \]
  \[
  u(r) = u(r_e) + \frac{1}{2} (r - r_e)^2 \left( \frac{\partial^2 u}{\partial r^2} \right)_{r=r_e} + \ldots,
  \]
  \[
  k = \frac{\partial^2 u}{\partial r^2} \rightarrow u(r) = u(r_e) + \frac{1}{2} k (r - r_e)^2
  \]

- First derivative at $r_e = 0$ (minimum potential $\rightarrow$ ground state) and $k$ is “force constant” (stiffness)
- This assumption gives us our second big step and is called:

4.2.2 2\textsuperscript{nd} Assumption: Rigid Rotor - Harmonic Oscillator (RRHO) Approximation

$H_{\text{rot,vib}} = H_{\text{rot}} + H_{\text{vib}}$ and $\varepsilon_{\text{rot,vib}} = \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$ and $q_{\text{rot,vib}} = q_{\text{rot}} \cdot q_{\text{vib}}$

- Chap. 1.3 gives rigid rotor:
  \[
  \varepsilon_J = \frac{\hbar^2 J(J+1)}{2I} \\
  \omega_J = 2J + 1 \\
  J = 0, 1, 2, \ldots
  \]
  \[
  I = \text{moment of inertia} = \mu r_e^2 \\
  \mu = \text{reduced mass}
  \]

- Harmonic oscillator:
  \[
  \varepsilon_{\text{vib}} = \hbar \nu (\nu + \frac{1}{2}) \\
  \omega_n = 1 \\
  n = 0, 1, 2, \ldots
  \]
  \[
  \nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \\
  k = \frac{\partial^2 u}{\partial r^2}
  \]
In rotation, transitions from one state to another happen by going from 1 state to adjacent, or $\Delta J = \pm 1$ and energy absorbed is at frequencies of $\hbar \pi I / 4 \sim$ microwave region.

In vibration, the same occurs, but only at one frequency of $\frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \sim 1000 \text{ cm}^{-1}$ (infrared).

From the spectroscopy results, we define a rotational constant $\tilde{B} = \frac{\hbar}{8\pi^2 c I}$ so energy of a rigid rotor becomes $\varepsilon_J = \tilde{B}J(J + 1)$ ($c$ is the speed of light).

Now we will further split the Hamiltonian by assuming elect and nuclear are separate: $H = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + H_{\text{elect}} + H_{\text{nuc}} \rightarrow \varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elect}} + \varepsilon_{\text{nuc}}$ and $q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elect}} \cdot q_{\text{nuc}}$.

- This is NOT exact, but stands as a useful approximation for diatomic molecules.
- Knowing $q_{\text{trans}}$ and $q_{\text{elect}}$ is similar to the beginning of the chapter and $q_{\text{nuc}} = 1$ again. We only need to solve our vibrational and rotational partition functions.

We need ground states:

- **Rotational**: Zero energy ground state occurs at $J = 0$ state
- **Vibrational**: Zero energy ground state is bottom of internuclear potential well of lowest electronic state: $\varepsilon_0 = \frac{\hbar \nu}{2} (\varepsilon_{\text{vib}} = \hbar \nu (n + \frac{1}{2}))$.
- **Electronic**: Redefine as energy of ground state as $-D_e$, and electronic partition function is now: $q_{\text{elect}} = \omega_1 e^{D_e / kT} + \omega_2 e^{-\varepsilon_2 / kT} + \ldots$

### 4.2.3 Vibrational Partition Function

Remember $\varepsilon_{\text{vib}} = \hbar \nu (n + \frac{1}{2}), \nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}$ where $k$ is force constant and $\mu$ is reduced mass.

$$q_{\text{vib}} = \sum e^{-\beta \varepsilon_n} \rightarrow q_{\text{vib}} = \frac{e^{-\beta \hbar \nu / 2}}{1 - e^{-\beta \hbar \nu}} \text{ (math is in McQuarrie).}$$
4.2. IDEAL DIATOMIC GAS

- This is because we had a geometric series and can compute sum → no approximation.

- Now, with high enough temperature, $\beta h\nu \ll 1$ and we make the prior sum an integral:

$$q_{vib} = e^{-\beta h\nu/2} \sum e^{-\beta h\nu n}$$

$$\rightarrow q_{vib}(T) = e^{-\beta h\nu/2} \int_0^\infty e^{-\beta h\nu n} dn = kT/h\nu$$

- Note since we have an exact solution, we don’t need this approximation, we can compare:

Define vibrational temperature $\Theta_{vib} = h\nu/k$ (values in table 6.1 in McQuarrie)

- Fraction of molecules in a state above ground state

$$f_{n>0} = \sum_{n=1}^\infty \frac{e^{-\beta h\nu(n+1/2)}}{q_{vib}} = 1 - f_0 = e^{-\Theta_{vib}/T}$$

- This number is very small for most diatomic molecules except Br$_2$ (table 6.2 in McQuarrie)

Now we can observe the rotational partition function, but need to look at 2 cases.

4.2.4 Rotational Partition Function: Heteronuclear

Partition function by summing our energy levels: $q_{rot} = \sum_{J=0}^\infty (2J+1)e^{-\beta B_J(J+1)}$ ($\beta = \frac{1}{kT}$)

- Denote $\frac{B}{k} = \Theta_{rot}$ (characteristic temperature of rotation). $\Theta_{rot} = h^2/8\pi^2 I k$

- We can’t do the sum like with vibration, so if we approximate that the distances between energy levels is small: $\frac{\Delta E}{kT} = \frac{2\Theta_J(J+1)}{T} \ll 1$ then we can say it is an integral

- As J increases, our distances do too, but we see the terms are so small it doesn’t matter:
\[ q_{\text{rot}}(T) = \int_0^\infty (2J + 1)e^{-\Theta_r J(J+1)/T} \, dJ \]

\[ \rightarrow q_{\text{rot}} = T/\Theta_r = \frac{8\pi^2 \hbar^2}{k^2} \text{ for } \Theta_r \ll T \]

- This improves in accuracy with increasing temperature → High Temp Limit

If we have a low temperature or a high \( \Theta_r \), then perform the sum directly:

\[ q_{\text{rot}}(T) = 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + 7e^{-12\Theta_r/T} \sim \text{ within 0.1\% for } \Theta_r > 0.7 \, T. \]

If we are in an intermediate range where we aren’t too small but smaller than 0.7 \( T \), then we can find an approximation using an Euler-MacLauren expansion:

\[ q_{\text{rot}}(T) = \frac{T}{\Theta_r} \{ 1 + \frac{1}{3} \left( \frac{\Theta_r}{T} \right) + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_r}{T} \right)^3 + \ldots \} \sim \text{ within 0.1\% for } \Theta_r < T \]

4.2.5 Rotational Partition Function: Homonuclear

With same atoms in a molecule, we get coupling due to interlocking wave functions and now we must pair our \( q_{\text{rot}} \) with \( q_{\text{nucl}} \) based on partial symmetry

Bosons: Nuclei with integral spin - Rotational levels with odd values of \( J \) get coupled with the \( I(2I + 1) \) antisymmetric nuclear spin functions and levels with even values of \( J \) must be coupled with the \( (I + 1)(2I + 1) \) symmetric nuclear spin functions:

\[ q_{\text{rot,nucl}} = (I+1)(2I+1) \sum_{J \text{ even}} (2J+1)e^{-\Theta_r J(J+1)/T} + I(2I+1) \sum_{J \text{ odd}} (2J+1)e^{-\Theta_r J(J+1)/T} \]

Fermions: Likewise, nuclei with half-integer spin have it swapped:

\[ q_{\text{rot,nucl}} = I(2I+1) \sum_{J \text{ even}} (2J+1)e^{-\Theta_r J(J+1)/T} + (I+1)(2I+1) \sum_{J \text{ odd}} (2J+1)e^{-\Theta_r J(J+1)/T} \]

- We can see that \( q_{\text{rot,nucl}} \neq q_{\text{rot}}q_{\text{nucl}} \) → Have to consider nuclear contribution!
- For most molecules at ordinary temperatures, we had \( \Theta_r \ll T \), so replace the \( \sum \) with an integral
- Then we can see both equations above (integral and half-integer spin) become:
4.2. IDEAL DIATOMIC GAS

\[ q_{\text{rot, nucl}} = \frac{(2I + 1)^2 T}{2\Theta_r} = q_{\text{rot}} q_{\text{nucl}}, \text{ where } q_{\text{rot}}(T) = \frac{T}{2\Theta_r} \text{ and } q_{\text{nucl}} = (2I + 1)^2 \]

- For this to be valid, we must have \( \Theta_r / T < 0.20 \)

Notice the similarity between the hetero- and homonuclear \( \rightarrow \) a factor of 1/2, which will only work when in the High Temp Limit of \( \Theta_r < 0.20 \ T \)

- This high temp limit allows us to call the factor of 2 as \( \sigma \), and is our symmetry number.
- Now, we can write:

\[
q_{\text{rot}}(T) \approx \frac{8\pi^2 I kT}{\sigma h^2} \approx \frac{1}{\sigma} \sum (2J + 1)e^{\Theta_r J(J+1)}/T,
\]

where \( \Theta_r \ll T, \sigma = 1 \) for heteronuclear, and \( \sigma = 2 \) for homonuclear.

Hydrogen (H\(_2\)) is a molecule where we aren’t in the high temp limit \( \rightarrow \) Can’t use our equation.

- Table 6-1 in McQuarrie shows almost all molecules are at high temp (\( \Theta_r \ll T \))
- Therefore, we can use the Euler-MacLauren expansion for most cases, and:

\[
q_{\text{rot}}(T) = \frac{T}{\sigma \Theta_r} \{ 1 + \frac{1}{3} \left( \frac{\Theta_r}{T} \right) + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_r}{T} \right)^3 + \ldots \}
\]

- Usually only the first term is necessary.

4.2.6 Putting it all Together

We have studied each partition function and can now assemble them together:

- \( q(V, T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elect}} q_{\text{nucl}}, \) giving Eq. 4.5:

\[
q(V, T) = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \cdot \frac{8\pi^2 I kT}{\sigma h^2} \cdot e^{-\frac{\beta \nu}{2}} \cdot \frac{1}{1 - e^{-\beta \nu}} \cdot \frac{\omega e_1 + \omega e_2 e^{-\frac{\Delta e_1}{kT}}}{q_{\text{elect}}} \cdot \frac{1}{q_{\text{nucl}}} \] (4.5)
• $Q(N, V, T) = \frac{2^N}{N!}$

Assumptions:

• $\Theta_r << T$ is the largest restriction and must hold
• Only the ground electronic state is important
• The zero of energy is the separated electronically unexcited atoms at rest in their ground electric states
• Rigid rotor harmonic oscillator is our weakest assumption → most error

This partition function will yield results with very small errors when compared to experimental data → sometimes < 1% error.

• Correction factors can be applied (Problems 6-23 and 6-24 in Ref. [3])

Overall, we start with the Schrödinger equation, get the $\varepsilon_j$ eigenvalues, applying it to our partition functions we derived, and assume a high temperature limit.

• This is only good up to our diatomic molecule- not even looking at systems!

Note: The Hamiltonians and Energy Equations: Table 4.1

| Translation | $H_{\text{trans}} = \frac{p_x^2}{2m} + \frac{p_y^2 + p_z^2}{2m}$ | $\varepsilon_{\text{trans}} = \frac{\hbar^2 n_x^2}{8ma^2}$, $n^2 = n_x^2 + n_y^2 + n_z^2$ |
| Rotation | $H_{\text{rot}} = \frac{1}{2I} \left[ p_\theta^2 + \frac{p_\phi^2}{\sin^2(\theta)} \right]$ | $\varepsilon_{\text{rot}} = \frac{\hbar^2}{2I} J(J + 1)$, $\omega = 2J + 1$ |
| Vibration | $H_{\text{vib}} = \frac{p_{\text{vib}}^2}{2m} + \frac{1}{2} k x^2$ | $\varepsilon_{\text{vib}} = h\nu(n + \frac{1}{2})$, $\omega = 1$ |

Table 4.1: Hamiltonians and Energy Equations.
Part II

Kinetic Theory of Gases
Chapter 5

Overview of Kinetic Theory of Gases

• Look at a classical system since we usually work in high temperature limit
• Define phase space
• Ensemble of systems → many phase points → Density in phase space ($f$ is distribution function)
• The equation of motion of phase space distribution is described by the Liouville equation
  – Shows the time evolution of the phase space distribution function $f$
  – Valid for both equilibrium and non-equilibrium systems
• Next look to reduced distribution functions (not all particles interact or are important)
• Using Liouville equation introduce reduced distribution function $f^{(1)}$ and $f^{(2)}$ and work into it
• We get the BBGKY Hierarchy → set of equations describing dynamics of a system of a large number of interacting particles → a chain of equations $f^{(s)}$ depends on $f^{(s+1)}$
• In dilute gases, most molecules don’t interact, so we only care about singlet distribution function $f^{(1)}$
Once an expression for $f^{(1)}_j(r, v, t)$ is found, you can calculate fluxes and thus transport properties

- But getting $f^{(1)}_j$ from BBGKY is very difficult because of dependency on following terms

- $f^{(1)}_j$ can be found by deriving the Boltzmann equation, fundamental equation for kinetic theory of gases

- Assume only 2 body interactions are important and see how number of $j$-molecules in $dr dv$ change
  - Account for inward and outward fluxes over $dt$ and assume molecular chaos

- Find integrodifferential equation for $f^{(1)}_j$, one for each component of the dilute gas

- Solving Boltzmann equation isn’t easy, but you can gain insight from it without solving!

- Enskog’s general equation of change for a property $\psi_j$ shows that multiplying Boltzmann equation by a collisional invariant and integrating over $dv_j$ gives transport equations
  - $\psi_j=$mass gives continuity equation, $\psi_j=$momentum gives momentum equation, $\psi_j=$kinetic energy gives energy balance equations

- Boltzmann H-theorem gives $\frac{dH}{dt} \leq 0$, Boltzmann equation has preferred direction
  - This is analogous to the 2nd law of thermodynamics → we will tend towards an equilibrium state
  - While fluctuations occur (we deal with probability), we always trend to equilibrium
  - Recurrence also questioned → shows it happens on order of $10^{10^19}$ years, so no conflict with idea of irreversibility on most physically interesting systems

- From H-theorem, we find equilibrium gives our distribution of velocity as a Maxwellian distribution

- Solving Boltzmann equation is done with Chapman-Enskog method to give successive approximations
• Each successive approximation of $f$ (singlet) is added to get more refined solution.

• Solutions of this type are in final stage of relaxation $\rightarrow$ equilibrium $\rightarrow$ hydrodynamic stage.

• We find first approximation $f^{[0]}$ gives ideal hydrodynamic equations, $p^{[0]} = \rho kT I$ and $q^{[0]} = 0$.

• Second approximation yields $f^{[0]} + f^{[1]}$ giving Navier Stokes equations $\rightarrow$ get expressions for $\lambda$, $\eta$, $D_{12}$.

• Third approximation with $f^{[2]}$ yields Burnett equations, but limited use to us.

• Note: all around equilibrium is where we are useful.

• The expressions for thermal conductivity $\lambda$, shear viscosity coefficient $\eta$, and binary diffusion coefficient $D_{12}$. All are complicated integrals that end up depending on intermolecular potential $u(r)$.

• From $u(r)$, get deflection angle $\rightarrow$ collisional cross-sectional area $\rightarrow$ collision integral $\rightarrow$ $a_{ij}$ and $b_{ij} \rightarrow \lambda$, $\eta$, $D_{12}$.

• Often referenced from hard sphere model, but Leonard-Jones potential is pretty good.
  
  – Coeff. usually found from “one term” expansion, two is more accurate, three almost dead on.
CHAPTER 5. OVERVIEW OF KINETIC THEORY OF GASES
Chapter 6

Classical Statistical Mechanics

So far, we derived partition functions for linear molecules \( \rightarrow \) using Schrödinger equation and molecular properties up to a dilute diatomic gas at high temperature.

- Remember for HTL: number of available molecular quantum states \( \gg \) number of particles so states occupied likely contain only one molecule.
- In HTL, we replaced sums with integrals \( \rightarrow \) gave numerically satisfactory answers (except vibration).

At higher temperature, average energy per molecule increases, so quantum numbers describing motion also increase (think radius).

- \( (n_x \text{ for translation, } J \text{ for rotation}) \) Molecules are in high quantum number limit, \( \approx \mathcal{O}(10^4) \) at room temperature.
- Classical behavior is obtained in limit of large quantum numbers, so can we stay in context of classical mechanics? Do like Gibbs did before quantum mechanics fully came about.

6.1 Classical Partition Function

We’ve used the molecular partition function \( q = \sum e^{-\beta\epsilon_j} \) which is a sum over all possible quantum energy states \( \rightarrow \) Let’s postulate that classical partition function
CHAPTER 6. CLASSICAL STATISTICAL MECHANICS

will also be over classical energy states.

- Energy in a classical sense is a continuous function of momentum and position \((p_j \text{ and } q_j)\).

- Then sum is an integral, and classical energy is Hamiltonian function: 
  \[ q_{\text{classical}} \approx \int \ldots \int e^{-\beta H(p,q)} dp dq \text{ (conjecture)} \]

The Hamiltonian depends on \(p_1, p_2, \ldots, p_s\) and \(q_1, q_2, \ldots, q_s\), and \(s\) is the number of coordinates needed to completely specify the motion or position \(\rightarrow s\) represents the degrees of freedom of molecule.

\{q_j\} are generalized coordinates, \{p_j\} are conjugate momentum, choose \(q\) that is convenient.

We had for monatomic ideal gas: 
\[ q_{\text{trans}} = \left[ \frac{2\pi mkT}{\hbar^2} \right]^{3/2} V \] (quantum partition function)

Hamiltonian (classical) of one atom of monatomic ideal gas: Simply the KE!
\[ H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \]

- Plugging in \(H\) to our \(q_{\text{class}}\) yields a sixfold integral (3 coordinates, 3 momentum). Integrating gives:
  \[ q_{\text{class}} \approx V \left[ \int_{-\infty}^{\infty} e^{\beta p^2/2m} dp \right]^3 = (2\pi mkT)^{3/2}V \]

- This is the same as our quantum partition function without the Plank’s constant factor.

- We can’t expect to derive a classical expression and get Plank’s constant- on the right path

Let’s compare with rigid rotor as well to see: 
\[ q_{\text{rot}} = \frac{8\pi^2 kT}{\hbar^2} \] (for quantum level)

- With rigid rotor Hamiltonian: 
  \[ H = \frac{1}{2I}(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta}) \rightarrow q_{\text{class}} = 8\pi^2 I kT \]

Harmonic oscillator: 
\[ q_{\text{vib}} = \frac{kT}{\hbar \omega} \] (in quantum level)
6.1. CLASSICAL PARTITION FUNCTION

- Hamiltonian: \( H = \frac{p^2}{2\mu} + \frac{k}{2}x^2 \rightarrow q_{\text{class}} = \frac{kT}{\nu} \)

We see that we are off by \( h^3 \), \( h^2 \), and \( h \) for 3, 2, and 1 degree of freedom in each \( q_{\text{class}} \).

- Also, \( q \) is dimensionless, so the factor of \( h \) will correct the units.

- Therefore, we will assume that for classical mechanics we can write:

\[
q = \sum_j e^{-\beta e_j} \rightarrow \frac{1}{h^s} \int \cdots \int e^{-\beta H} \prod_{j=1}^s dp_j dq_j \quad (6.1)
\]

This applies to a single molecule, so expanding to a system of \( N \) independent indistinguishable particles:

\[
Q = \frac{2^N}{N!}, \quad \text{so} \quad Q_{\text{class}} = \frac{1}{N!} \prod_{j=1}^N \left[ \frac{1}{h^s} \int \cdots \int e^{-\beta H} \prod_{i=1}^{sN} dp_i dq_i \right] \quad (\text{rewriting an exponent})
\]

- \( H_j \) is Hamiltonian of the \( j \)-th molecule, function of \( p_{j1}, \ldots, p_{js} \) and \( q_{j1}, \ldots, q_{js} \).

- Rewriting and relabeling indices allows us to write, with a Hamiltonian \( H \) of the \( N \)-body system:

\[
Q = \frac{1}{N!h^{sN}} \int \cdots \int e^{-\beta H} \prod_{i=1}^{sN} dp_i dq_i \quad (6.2)
\]

We conjecture this partition function is the classical partition function, and \( H(pq, ) \) is the classical \( N \)-body Hamiltonian for interacting particles \([p, q] \) represents set of \( p_j, q_j \) for entire system]

- To show what is happening with particle interactions, let us expand our Hamiltonian.

- For a monatomic gas,

\[
H(p, q) = \frac{1}{2m} \sum_{j=1}^N (P_{xj} + P_{yj} + P_{zj}) + U(x_1, y_1, z_1, \ldots, x_N, y_N, z_N)
\]

(translation)
• Our Hamiltonian now contains an internal energy that is dependent on particles’ position in $N$-body system

• This potential energy describes the particle interactions

This partition function is actually the correct classical limit of $Q \to$ Proven in 1934 with rigorous method.

Plugging in our new $H(p,q)$ into the expression for $Q$ will give the partition function for classical monatomic gas with particle interactions (translation):

$$Q_{\text{class}} = \frac{1}{N!} \left( \frac{2\pi m k T}{\hbar^2} \right)^{3N/2} Z_N$$

where $Z_N = \int_{V} e^{-U(x_1, \ldots, x_N)/kT} dx_1 \ldots dx_N$ (6.3)

• $Z_N$ is the classical configuration integral (focus of current research) - describes intermolecular forces.

• Without intermolecular forces, or a dilute gas, we have $U \to 0$, $Z_N \to V^N$ (Previous $Q$ Eq.)

It often happens that not all degrees of freedom can be treated classically (like vibration).

• We then treat the degrees we can (translation, rotation, etc.) classically and ones we can’t (vibration) quantumly $\to$ then we can say

$$H = H_{\text{class}} + H_{\text{quantum}} \to q = q_{\text{class}} q_{\text{quantum}},$$

$$q_{\text{class}} = \frac{1}{\hbar^s} \int e^{-H_{\text{class}}(p,q)/kT} dp_1 dq_1 \ldots dp_s dq_s$$

• Therefore, assuming a separable Hamiltonian, the entire system can be written as:

$$Q = Q_{\text{class}}Q_{\text{quantum}} = \frac{Q_{\text{quantum}}}{N! \hbar^s N} \int e^{-H_{\text{class}}/kT} dp_{\text{class}} dq_{\text{class}}$$

(6.4)

6.2 Phase Space and Liouville Equation

Historically, statistical mechanics was formulated by Boltzmann, Maxwell, and Gibbs before quantum mechanics.
6.2. PHASE SPACE AND LIOUVILLE EQUATION

- It was based in classical mechanics, which is still a most useful limit → used for many systems today

Consider: System with $N$ interacting particles, each with $s$ degrees of freedom to completely describe its position.

- To describe all molecules, need $l = sN$ coordinates: $q_1, q_2, \ldots, q_l$ give spatial orientation of $N$-body system.
- Also have conjugate momentum $p_j$, with $l = sN$ momenta, for $2l$ total coordinates of system.
- The $2l$ coordinates, along with the equations of motion, completely describe the system and determine the future and past course of the system.

Let’s construct a conceptual Euclidean space of $2l = 2sN$ dimensions, one axis for each $p$ and $q$.

- This phase space describes the state of an $N$-body system under classical consideration.
- A single phase point at time $t$ completely specifies the state, and as the system evolves through time, the dynamics of the system is described by the motion of the phase point through phase space.

The trajectory of the phase point is given by Hamilton’s equations of motion:

$$\dot{q}_j = \frac{\partial H}{\partial p_j}, \quad \dot{p}_j = -\frac{\partial H}{\partial q_j} \quad \text{and} \quad j = 1, 2, \ldots, l = sN \quad (6.5)$$

Now consider an ensemble of systems in phase space, for simplicity say a microcanonical ensemble.

- Each ensemble has the same fixed $N, V, E$, but their own $p, q$.
- We will have a large number $A$ of these isolated systems with fixed macroscopic properties.
Each system in the ensemble has its own phase point in the same phase space to describe it.

- The entire ensemble appears as a “cloud” of phase points, and as time evolves, each point will trace its own independent trajectory (since they are all isolated).

Postulate of equal a priori probabilities state that for a microcanonical ensemble, the density is uniform over the “surface” of constant energy in phase space (value of energy of isolated system).

- Therefore, as long as \((p, q)\) for each system satisfies \(N, V, E\), then that state is equally probable as others \(\rightarrow\) every classical state is equally probable (like quantum states).

Define a number density for “cloud” as \(f(p, q, t)\) (distribution function) so \# of systems in ensemble have phase points in \(dpdq\) about the point \(p, q\) at time \(t\) is \(f(p, q, t)dpdq \rightarrow \int \ldots \int f(p, q)dpdq = A\).

- Then ensemble average of any function \(\phi(p, q)\) is
  \[
  \hat{\phi} = \frac{1}{A} \int \ldots \int \phi(p, q)f(p, q)dpdq
  \]

- **Gibbs Postulate** equates this ensemble average to the corresponding thermodynamic function.

The equations of motion determine each phase point trajectory, so they also determine density \(f(p, q, t)\).

- If initial condition is known, then we have \(f(p, q, t) \rightarrow\) controlled by laws of mechanics, not arbitrary!
- The time dependence of \(f\) is given by the Liouville Eq., now we derive (like fluids).

Considering a small volume element \((\delta p_1 \ldots \delta p_l \delta q_1 \ldots \delta q_l)\) about the point \((p_1, \ldots, p_l, q_1, \ldots, q_l)\) and the number of phase points within the volume \(\delta N = f(p_1, \ldots, p_l, q_1, \ldots, q_l, t)\delta p_1 \ldots \delta p_l \delta q_1 \ldots \delta q_l\) (see Fig. 6.1).
6.2. PHASE SPACE AND LIOUVILLE EQUATION

This number will change as points move → consider points through faces perpendicular to \( q_1 \)-axis.

Using linear expansions of \( f \) and \( \dot{q}_1 \) to linear terms in \( \delta q_1 \), we can get a net flow of phase points in the \( q_1 \) direction:

\[
\text{Net Flow} = - \left( \frac{\partial f}{\partial q_1} \delta \dot{q}_1 + f \frac{\partial f}{\partial q_1} \right) \delta p_1 \ldots \delta p_l \delta q_1 \ldots \delta q_l
\]

This can be found in all \( p \) and \( q \) directions (equal status to all coordinates in phase space) and we will get the change through all faces, which must equal the change of \( \delta N \) with time:

\[
\frac{d(\delta N)}{dt} = - \sum_{j=1}^{l} \left[ f \left( \frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right) + \left( \frac{\partial f}{\partial q_j} \dot{q}_j + \frac{\partial f}{\partial p_j} \dot{p}_j \right) \right] \delta p_1 \ldots \delta p_l \delta q_1 \ldots \delta q_l
\]

We can simplify using our Hamiltonian Eq. of motion and dividing by the “volume element” to get the rate of change of density itself around the point \( p_1, \ldots, p_l, q_1, \ldots, q_l \) (\( \frac{\partial f}{\partial t} \)). This describes the evolution of phase point density:

\[
\frac{\partial f}{\partial t} = - \sum_{j=1}^{l} \left( \frac{\partial f}{\partial q_j} \dot{q}_j + \frac{\partial f}{\partial p_j} \dot{p}_j \right)
\] (6.6)

We have \( \frac{\partial f}{\partial t} \) to indicate we fixed attention on a given stationary point in phase space.

This can also be written in a more conventional form using Eqs. for \( \dot{q}_j \) and \( \dot{p}_j \):

\[
\frac{\partial f}{\partial t} = - \sum_{j=1}^{l} \left( \frac{\partial H}{\partial p_j} \frac{\partial f}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial f}{\partial p_j} \right)
\] (6.7)
or in cartesian coordinates:

\[
\frac{\partial f}{\partial t} + \sum_{j=1}^{N} \frac{p_j}{m_j} \cdot \nabla r_j f + \sum_{j=1}^{N} F_j \cdot \nabla p_j f = 0 \quad (6.8)
\]

This is our **Liouville Eq.**, the most fundamental equation of classical statistical mechanics.

- In cartesians, \( \nabla r_j \) is gradient with respect to spatial variables in \( f \), \( \nabla p_j \) is gradient with respect to momentum variables in \( f \), and \( F_j \) is the total force on the \( j \)th particle.

Since \( f \) depends on \( p, q \), and \( t \), our Liouville Eq. looks like a total derivative, and rearranging gives \( \frac{df}{dt} = 0 \), so density in the neighborhood of any moving phase point is constant along its trajectory.

- Like density of incompressible gas: and given an initial condition:
  \[ f(p, q, t) = f(p_0, q_0, t_0) \]

- As time progresses, an elemental volume will distort, but the phase points will stay within, no change in density.

- Gibbs called this the “conservation of extension in phase space”:
  \[ \delta p \delta q = \delta p_0 \delta q_0 \text{ at all } t. \]

A corollary to this says two different phase space coordinates describing the same system have, for \( q_1, \ldots, q_{3n}, p_1, \ldots, p_{3n} \) and \( Q_1, \ldots, Q_{3n}, P_1, \ldots, P_{3n} \):

\[
dq_1 \ldots dq_{3n} dp_1 \ldots dp_{3n} = dQ_1 \ldots dQ_{3n} dP_1 \ldots dP_{3n}.
\]

- For example, a single particle in 3 dimensions can be equally described by \((x, y, z)\) or \((r, \theta, \phi)\):

\[
dp_x dp_y dp_z dx dy dz = dp_r dp_\theta dp_\phi dr d\theta d\phi
\]

- This only holds true because we use conjugate momenta \( \rightarrow \) velocities wouldn’t allow this.
6.3 Equipartition of Energy

In classical statistical mechanics \( \rightarrow \) high temp limit: \( \sum \rightarrow \int \) and only need Hamiltonian, not eigenvalues of quantum problem

- Consider average energy of a molecule in a system of independent molecules:
  \[ \bar{\varepsilon} = \frac{\int H e^{-\beta H} dp_1...dq_s}{\int e^{-\beta H} dp_1...dq_s} . \]

- Multiplying by \( N \) gives total energy of system, differentiating by \( T \) gives constant volume heat capacity: \( C_V = \frac{d\bar{\varepsilon}}{dT} \).

- If Hamiltonian is of the form \( H(p_1,\ldots,q_s) = \sum_{j=1}^m a_jp_j^2 + \sum_{j=1}^n b_jq_j^2 + H(p_{m+1},\ldots,p_s,q_{n+1},\ldots,q_s) \) and \( a_j, b_j \) are constants, then each quadratic term contributes \( kT/2 \) to energy and \( k/2 \) to \( C_V \).

- This equipartition of energy is a consequence of quadratic terms, not due to classical statistical mechanics.

Monatomic ideal gas: \( H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \rightarrow \) each atom gives \( 3kT/2 \) to energy and \( 3k/2 \) to \( C_V \) (like Chap. 4).

Rigid rotor: \( H = \frac{1}{2I}(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta}) \rightarrow \) still gives \( kT \) to energy because \( \theta \) not \( \phi \) in “constant” terms on \( p_\phi^2 \).

Note: only holds in classical limit: \( \frac{\Delta \varepsilon}{kT} \ll 1 \rightarrow \) Not true for vibrational degree of freedom.

- Chap. 4 had \( C_V = \frac{5}{2}Nk + \frac{Nk(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \) for RRHO approximation. \( \frac{5}{2}Nk \) from translation and rotation.

- From harmonic oscillator Hamiltonian, expect to give \( Nk \) to \( C_V \), but it wasn’t true \( \rightarrow \) deviations!

- Then the high \( \Theta_v \) in some gases causes a deviation from \( C_V = \frac{7}{2}Nk \) total.

The Liouville Eq. serves as a great starting point for most approaches.
Chapter 7

Kinetic Theory of Gases

We just went over phase space and distribution functions in phase space.

- Also derived Liouville Eq. (Eq. of motion that phase space distribution function must satisfy).
- We didn’t look at it too much because we were looking only at equilibrium statistical mechanics

We will review these concepts again and introduce reduced distribution functions and derive BBGKY Hierarchy.

- Then we get to derive physical, yet approximate, equations for the distribution function of gases.
- This will be the Boltzmann Eq. - the central Eq. for the rigorous kinetic theory of gases.

7.1 Phase Space and Liouville Eq. (Take 2)

Consider a system of $N$ point particles - classical dynamical state of $3N$ momentum and $3N$ position ($p$ and $q$).
We construct a 6\(N\)-dimensional space with coordinates \(q_1, q_2, \ldots, p_1, \ldots, p_{3N}\) → one point completely specifies the microscopic dynamical state of our \(N\)-particle system (one point consists of all particles and their \(p\)'s and \(q\)'s).

Through time, the phase point moves through phase space in a manner dictated by Eq. of motion for the system.

In reality, we don’t know (or care) about the 6\(N\) coordinates of a macroscopic system - we just know a few macroscopic mechanical properties of the system, such as energy, volume, velocity, etc.

- There are a great number of points in phase space compatible with the few variables we know about the system → the set of all those phase points constitutes an ensemble of systems.
- Number of systems in ensemble → \(\infty\), so is very dense: Define density of phase points (distribution function) as the fraction of phase points contained in the volume \(dq_1dq_2\ldots dp_{3N}\) as \(f_N(dq_1dq_2\ldots dp_{3N}, t)\).
- Simplify with \(f_N(p, q, t)\) and volume element \((dp, dq)\) to write with ease

The density (distribution function) \(f_N(p, q, t)\) is normalized such that \(\int f_N(p, q, t) dp dq = 1\).

Each phase point moves in time according to Eqs. of motion of the system → \(f_N\) obeys same Eqs. of motion.

Number of phase points within some arbitrary volume \(V\) is
\[n = N \int_V f_N(p, q, t) dp dq\]
where \(N\) is number of phase points in phase space.

- Rate of change of phase points in \(V\) is: \(\frac{\partial n}{\partial t} = N \int_V \frac{\partial f_N(p, q, t)}{\partial t} dp dq\), and since phase points aren’t created or destroyed, the rate of change of \(n\) must be the rate of phase points flowing through surface of \(V\).

- Rate of flow of phase points: \(N f_Nu\), where \(u = (\dot{q}_1, \ldots, \dot{p}_1, \ldots, \dot{p}_{3N})\) - “velocity” through phase space.

- Integrate flow over surface: \(\frac{\partial n}{\partial t} = -N \int_S f_nu \cdot dS\) (negative for outward flow).
7.2. REDUCED DISTRIBUTION FUNCTIONS

- Use Gauss theorem, equate our two \( \frac{\partial n}{\partial t} \) Eqs., then conservation of phase points:

\[
\frac{\partial f_N}{\partial t} + \nabla \cdot (f_N \mathbf{u}) = 0 \tag{7.1}
\]

\[
\nabla \cdot (f_N \mathbf{u}) = \sum_{j=1}^{3N} \frac{\partial (f_N \dot{q}_j)}{\partial q_j} + \sum_{j=1}^{3N} \frac{\partial (f_N \dot{p}_j)}{\partial p_j} = \sum_{j=1}^{3N} \left[ \frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right] f_n
\]

- Plugging in Hamilton’s Eqs. of motion (\( \dot{\mathbf{p}}_j = -\frac{\partial H}{\partial \mathbf{q}_j} \) and \( \dot{\mathbf{q}}_j = \frac{\partial H}{\partial \mathbf{p}_j} \)) gives second summation = 0 and we have:

\[
\frac{\partial f_N}{\partial t} + \sum_{j=1}^{3N} \left( \frac{\partial H}{\partial \mathbf{p}_j} \frac{\partial f_N}{\partial \mathbf{q}_j} - \frac{\partial H}{\partial \mathbf{q}_j} \frac{\partial f_N}{\partial \mathbf{p}_j} \right) = 0 \tag{7.2}
\]

which can be written using a Poisson bracket:

\[
\frac{\partial f_N}{\partial t} + \{H, f_N\} = 0 \tag{7.3}
\]

This is our **Liouville Eq.**, the most fundamental Eq. in statistical mechanics.

In cartesian coordinates: \( \frac{\partial f_N}{\partial t} + \sum_{j=1}^{N} \frac{\mathbf{p}_j}{m_j} \cdot \nabla \mathbf{r}_j f_N + \sum_{j=1}^{N} \mathbf{F}_j \cdot \nabla \mathbf{p}_j f_N = 0 \) (\( \mathbf{F}_j \) is total force on \( j \)th particle, gradient with respect to spatial or momentum variables).

- Often write Liouville Eq. as \( i \frac{\partial f_N}{\partial t} = L f_N \) with Liouville operator

\[
L = -i \left( \sum_{j=1}^{N} \frac{\mathbf{p}_j}{m_j} \cdot \nabla \mathbf{r}_j + \sum_{j=1}^{N} \mathbf{F}_j \cdot \nabla \mathbf{p}_j \right).
\]

- The Liouville operator is defined in such a way to allow us to bring Liouville Eq. into form of Schrödinger Eq.

### 7.2 Reduced Distribution Functions

Once we have a distribution function \( f_N(p, q, t) \), we can compute the ensemble average of any dynamical variable \( A(p, q, t) \).
Our equation for ensemble average is $\langle A(t) \rangle = \int A(p, q, t) f_N(p, q, t) dp dq$.

It turns out that dynamical variables of interest are functions of either the $p$'s and $q$'s of just a few particles or they can be written as a sum over such functions - overkill here! We just need a few terms.

An example is intermolecular potential, depending on only pair-wise potentials and can be summed:

$$\langle U \rangle = \sum_{i,j} \int \int \int u(r_i, r_j) f_N(r_1, \ldots, p_N, t) dr_1 \ldots p_N$$

for paired coordinates $r_i$ and $r_j$.

Let's define reduced distribution function $f^{(n)}_N(r_1, \ldots, r_n, p_1, p_n, t)$ as:

$$f^{(n)}_N(r_1, \ldots, r_n, p_1, p_n, t) = \frac{N!}{(N-n)!} \int \int \int f^{(n)}_N(r_1, \ldots, p_N, t) dr_{n+1} \ldots dr_N dp_{n+1} dp_N$$

In this, we've reduced the number of variables needed! Also, drop subscript and write as $f^{(n)}(r^n, p^n, t)$.

We usually only need $f^{(1)}$ and $f^{(2)}$, so let's derive an equation for both.

Writing the force in the Liouville Eq. $F_j$ as the sum of forces due to other molecules in the system $\sum_i F_{ij}$ and an external force $X_j$, then applying some math and integration, we get:

$$\frac{\partial f^{(n)}}{\partial t} + \sum_{j=1}^{n} \frac{p_j}{m_j} \cdot \nabla_{r_j} f^{(n)} + \sum_{j=1}^{n} X_j \cdot \nabla_{p_j} f^{(n)} + \sum_{i,j=1}^{n} F_{i,j} \cdot \nabla_{p_j} f^{(n)}$$

$$+ \sum_{j=1}^{n} \int \int \int F_{j,n+1} \cdot \nabla_{p_j} f^{(n+1)} dr_{n+1} dp_{n+1} = 0 \quad (7.4)$$

This is the Bogoliubov, Born, Green, Kirkwood, Yvon or BBGKY Hierarchy.

This hasn’t been truncated by superposition yet, but we can derive approximate Eqs.

We’ve done all this independent of density → now let’s specialize to dilute gases.
7.3 Fluxes in Dilute Gases

In dilute gases, most molecules aren’t interacting with any others, just traveling between collisions.

- This means macroscopic properties of the gas depend upon only the singlet distribution function $f_j^{(1)}(r, p, t)$.
- This is for species $j$ with position $r$ and momentum $p \rightarrow$ only looking at dilute gases, so let’s drop superscript.
- Also write our Eqs. with velocity in space rather than momentum $f_j^{(1)} \rightarrow f_j(r, v_j, t)$.
- We shall normalize $f_j$ such that the integral of this distribution function over all velocities is the number density of $j$ particles at position $r$ at time $t$: $\rho_j(r, t) = \int f_j(r, v_j, t) dv_j$.
- Furthermore, if $N$ is the total number of $j$ molecules in the system, then $N_j = \iint f_j(r, v_j, t) dr dv_j$ (integral of $\rho_j$ over $dr$ position).

Now we go on to define a number of important average velocities.

The **linear velocity** $v_j$ is the velocity of a molecule of species $j$ with respect to fixed coordinate system.

- **Average velocity** is then given by: $\overline{v}_j(r, t) = \frac{1}{\rho_j} \int v_j f_j(r, v_j, t) dv_j$.
- This represents the macroscopic flow of species $j$.

The **mass average velocity** is defined by: $v_0(r, t) = \frac{\sum_j m_j \rho_j \overline{v}_j}{\sum_j m_j \rho_j}$.

- Note that the denominator is the mass density $\rho_m(r, t) = \sum_j m_j \rho_j$.
- This velocity $v_0(r, t)$ is often called the **flow velocity** or stream velocity.

The **peculiar velocity** $V_j$ is the velocity of a molecule relative to the flow velocity.
Figure 7.1: Cylinder containing all molecules of species $j$ with velocity $\mathbf{V}_j$, which cross the surface $dS$ during the time interval $dt$.

- This is defined as $\mathbf{V}_j = \mathbf{v}_j - \mathbf{v}_0$.

The average of the peculiar velocity is the **diffusion velocity**:

$$\overline{\mathbf{V}}_j = \frac{1}{\rho_j} \int (\mathbf{v}_j - \mathbf{v}_0) f_j(r, \mathbf{v}_j, t) d\mathbf{v}_j$$

- It is easy to show that $\sum_j \rho_j m_j \overline{\mathbf{V}}_j = 0$ (all diffusion sums to zero → different from the average).

Our ultimate goal is to get transport coefficients of a fluid.

- Let’s designate the molecular properties of mass, momentum, and kinetic energy as a collective $\psi_j$.
- Now, we will derive fluxes of these properties for the species $j$: imagine the surface $dS$ shown in Fig. 7.1.

The surface $dS$ moves with velocity $\mathbf{v}_0$, unit normal $\mathbf{n}$.

- All the molecules that have velocity $\mathbf{V}_j = \mathbf{v}_j - \mathbf{v}_0$ and that cross $dS$ in time interval $(t, t + dt)$ must have been in a cylinder of length $|\mathbf{V}_j| dt$ and base $dS$.
- The volume of this cylinder will then be $(\mathbf{n} \cdot \mathbf{V}_j) dS dt$. 
The number of molecules per unit volume is $f_j d_v$, so the number that cross $dS$ in $dt$ with relative velocity $V_j$ is $(f_j d_v) (n \cdot V_j) dS dt$.

We then have a flux of $f_j (n \cdot V_j) d_v$, and if each molecule carries property $\psi_j$ then we can say the flux of the property is $\psi_j f_j (n \cdot V_j) d_v$, and the total flux across the surface is:

$$\text{total flux} = \int \psi_j f_j (n \cdot V_j) d_v = n \cdot \int \psi_j f_j V_j d_v = n \cdot \psi_j.$$

The vector $\psi_j = \int \psi_j f_j V_j d_v$ is the flux vector associated with property $\psi_j$, and the component of this vector in any direction is the transport of the property $\psi_j$ in that direction.

### 7.3.1 Transport of Mass

$\psi_j = m_j \rightarrow \psi_j = m_j \int f_j V_j d_v = \rho_j m_j V_j \equiv j$

### 7.3.2 Transport of Momentum

$\psi_j = m_j V_{jx} \rightarrow \psi_j = m_j \int V_{jx} f_j V_j d_v = \rho_j m_j \nabla V_j$

- This is the flux of the $x$-component of momentum relative to $v_0$: a pressure!

Example pressure components

\[
\begin{aligned}
(p_j)_{xx} &= \rho_j m_j V_{jx} V_{jx} \\
(p_j)_{xy} &= \rho_j m_j V_{jx} V_{jy}
\end{aligned}
\] (7.5)

More general partial pressure tensor of $j$th species

\[
\begin{aligned}
p_j &= \rho_j m_j \nabla V_j
\end{aligned}
\] (7.6)

### 7.3.3 Transport of Kinetic Energy

$\psi_j = \frac{1}{2} m_j V_j^2 \rightarrow \psi_j = \frac{m_j}{2} \int v_j^2 V_j f_j d_v = \frac{1}{2} \rho_j m_j V_j^2 V_j = q_j$

- $q_j$ is the heat flux vector of the $j$th species.
We now see that once we have an expression for \( f_j(r, v, t) \), we can calculate all the fluxes and hence get all the transport properties of a dilute gas.

- We now need \( f_j \) or at least an equation to give us \( f_j \) as its solution.
- All we have for now is the BBGKY hierarchy with \( f^{(1)} \), but it also contains \( f^{(2)} \), and as mentioned no one has found a way to uncouple the equation.
- We next derive an equation for \( f_j \), the Boltzmann Eq.: The fundamental Eq. of the rigorous kinetic theory of gases.

### 7.4 The Boltzmann Equation

Using a simple physical argument, we will derive the Boltzmann Eq. for \( f_j \) (first order \( f^{(1)} \), drop superscript).

- Imagine a volume \( \text{d}r \text{d}v_j \) at point \((r, v)\) in phase space for a dilute gas (only 2-body interactions are important).
- The number of \( j \) molecules in the element \( \text{d}r \text{d}v_j \) is given by \( f_j \text{d}r \text{d}v_j \).
- If we had no collisions, all particles at the starting CV will move with the equations of motion to a second point at \( t + \text{d}t \), this second point being \( (r + v_j \text{d}t, v_j + \frac{1}{m_j}X_j \text{d}t) \).
- Since all points in \( \text{d}r \text{d}v_j \) stay within over \( t + \text{d}t \), we have \( f(r, v_j, t) = f(r + v_j \text{d}t, v_j + \frac{1}{m_j}X_j \text{d}t, t + \text{d}t) \).

That assumed no collisions, but that isn’t true! Some molecules leave or enter the stream due to collisions throughout the movement.

- Denote \( j \) molecules lost from the position range \( (r, r + v_j \text{d}t) \) and velocity range \( (v_j, v_j + \text{d}v_j) \) because of collisions with \( i \) molecules over time interval \( (t, T + \text{d}t) \) as \( \Gamma_{ji}^{(-)} \text{d}r \text{d}v_j \text{d}t \).
- We similarly denote \( j \) molecules joining the stream from collisions with \( i \) molecules as \( \Gamma_{ji}^{(+)} \text{d}r \text{d}v_j \text{d}t \).
7.4. THE BOLTZMANN EQUATION

Figure 7.2: Collisions of molecules of type $i$ with one molecule of type $j$. The distance $A$ is essentially the intermolecular distance at which the potential begins to “take hold.”

- Putting the collision terms into our “flow equation” of particles over $dt$ gives us:

$$f_j(r + v_j dt, v_j + \frac{1}{m_j} X_j dt, t + dt) dr dv_j =$$

$$f_j(r, v_j, t) d r v_j + \sum_i (\Gamma^{(+)}_{ji} - \Gamma^{(-)}_{ji}) dr dv_j dt$$

Expanding the left side gives:

$$\frac{\partial f_j}{\partial t} + v_j \cdot \nabla_r f_j + \frac{X_j}{m_j} \cdot \nabla v_j f_j = \sum_i (\Gamma^{(+)}_{ji} - \Gamma^{(-)}_{ji})$$

- LHS is change in $f_j$ due to collisionless motion, RHS is change in $f_j$ due to collisions.

- Notice this is very similar to the Liouville Eq. for $f_j^{(1)}$.

We now must find explicit expressions for the collision terms.

- Consider a fixed $j$ particle with incoming $i$ particle with relative velocity $g_{ij}$ with impact parameter in range of $db$ around $b$. 


CHAPTER 7. KINETIC THEORY OF GASES

- $A$ is the range of intermolecular potential $\rightarrow$ when collisions would start to happen.

- Then any $i$ molecule in the cylinder will collide with the fixed $j$ molecule during the time $dt$.

The probable number of $i$ molecules in the cylindrical shell is $2\pi f_i(r, v_i, t)g_{ij}bdbdt$ with $g_{ij} = |g_{ij}|$.

- The total collisions that would occur with the fixed $j$ molecule is then $2\pi dt \iint f_i(r, v_i, t)g_{ij}bdbdv_i$.

- But since $j$ isn’t fixed, we have a probability of them being at the $r$ point with $v_i \rightarrow f_j(r, v_j, t)$.

- We can put terms together to write $\Gamma^{(-)}_{ji} = 2\pi \iint f_j f_i g_{ij} bdbdv_i$.

Note that we assured that the mean number of $i$ molecules about the fixed $j$ is given by $f_j f_i$.

- We are assuming they are uncorrelated $\rightarrow$ known as molecular chaos assumption (not strictly true).

- This is the “weakest” point in derivation, but very important to our work.

We can do the same process for the reversed case $\rightarrow$ particles introduced to stream from collisions.

- Rewriting the equation by utilizing primes for quantities before collisions which go into $b, v_i, v_j$ after collision (eg. $b', v_j'$, etc.) and invoking Liouville theorem ($dpdq - dp'dq'$), we get:

$$\Gamma^{(+)}_{ji} = 2\pi \iint f_i' f_j' g_{ij} bdbdv_i'$$ ($f'$ means its velocity is primed).

We can now plug $\Gamma^{(+)}$ and $\Gamma^{(-)}$ back into our earlier equation to get the Boltzmann Eq.:
7.5. **CONSEQUENCES OF THE BOLTZMANN EQUATION**

\[
\frac{\partial f_j}{\partial t} + v_j \cdot \nabla_r f_j + \frac{1}{m_j} X_j \cdot \nabla_{v_j} f_j = 2\pi \sum_i \int \left\{ f'_i f'_j - f_i f_j \right\} g_{ij} b \, db \, dv_i
\]  

(7.7)

This is an integrodifferential Eq. for \( f_j^{(1)} \), and have one for each component \( j \) of the gas.

- Eqs. of motion (thus intermolecular potential) enter the equation through \( f'_i \) and \( f'_j \) because the postcollisional velocities (\( v'_i \) and \( v'_j \)) depend on precollisional velocities (\( v_i \) and \( v_j \)) through the Eqs. of motion governing the collision.

- Also, RHS after integration yields variables of \( r \), \( v_j \), and \( t \), which is what is on LHS → good!

This was the simple physical derivation → standard way of going about it.

- We find though that it is very difficult to solve, which we will do later, but we can still find important information from this equation as is!

### 7.5 Consequences of the Boltzmann Equation

We will find three primary consequences from the Boltzmann Eq. without solving it.

#### 7.5.1 1. Equations of Change

First, we will look at the relation to the equations of change (continuum mechanics Eqs.).

Multiplying the Boltzmann Eq. by \( \psi_i \) and integrating over \( dv_i \) for \( f_i \) will yield an equation where we split the LHS → looks like 3 different averaging terms for \( \psi_i \).

- By doing the math to average, we can plug the 3 relations back into our new
Eq. to get:
\[
\frac{\partial(\rho_i \psi_i)}{\partial t} + \nabla_r \cdot \rho_i \psi_i \mathbf{v}_i - \rho_i \left\{ \frac{\partial \psi_i}{\partial t} + \mathbf{v}_i \cdot \nabla_r \psi_i + \frac{X_i}{m_i} \cdot \nabla_{\mathbf{v}_i} \psi_i \right\} = 2\pi \sum_j \int \int \int \psi_i (f'_i f'_j - f_i f_j) g_{ij} b db d\mathbf{v}_i d\mathbf{v}_j
\] (7.8)

- This is Enskog's general Eq. of change for the property \( \psi_i \).

We find that for \( \psi_i = \) mass, momentum, or energy (collisional invariants) then RHS = 0.

- What we can then do is plug in \( \psi_i = m_i \) (or \( m_i \mathbf{v}_i \) or \( \frac{1}{2} m_i \mathbf{v}_i^2 \)) and sum over \( i \)’s to get:
  - \( \psi_i = m_i \rightarrow \frac{\partial \rho_i}{\partial t} + \nabla_r \cdot (\rho_i \mathbf{v}_i) = 0 \rightarrow \frac{\partial \rho}{\partial t} + \nabla_r \cdot (\rho \mathbf{v}_0) = 0 \), Continuity Eq. for the entire system!
  - \( \psi_i = m_i \mathbf{v}_i \rightarrow \text{sum over } i \rightarrow \rho_m \frac{D \mathbf{v}_0}{D t} = \sum_j \rho_j \mathbf{X}_j - \nabla \mathbf{p} \)
  - \( \psi_i = \frac{1}{2} m_i \mathbf{v}_i^2 \rightarrow \text{sum over } i \rightarrow \rho_m \frac{D \mathbf{E}}{D t} = -
  \mathbf{p} : \nabla \mathbf{u} - \nabla \cdot \mathbf{q} \), where : denotes the standard tensorial manipulation \( \mathbf{A} : \mathbf{B} = \sum_{i} \sum_{j} A_{ij} B_{ji} \)

7.5.2 2. Boltzmann H-Theorem

Next, we will discuss the Boltzmann H-Theorem by considering a single component system.

- The Boltzmann H-function is defined as \( H(t) = \int \int f(\mathbf{r}, \mathbf{v}, t) \ln[f(\mathbf{r}, \mathbf{v}, t)] d\mathbf{r} d\mathbf{v} \).
- Taking derivatives, equating to Boltzmann Eq. and other math will give us:
  \[ \frac{dH}{dt} = \frac{2\pi}{4} \int \int \ln \left( \frac{f}{f'} \right) \{ f' f'_1 - f f_1 \} g_b db d\mathbf{r} d\mathbf{v}_1 \]
- Integrand is of the form of \( -(x - y) \ln \left( \frac{x}{y} \right) \), which for all \( x \) and \( y \) is either zero or negative.
- Therefore, we get the result that \( \frac{dH}{dt} \leq 0 \)
7.5. **CONSEQUENCES OF THE BOLTZMANN EQUATION**

\( H \) is bounded, so it must approach a limit as \( t \to \infty \), which we find gives us \( \frac{dH}{dt} = 0 \), so we have equilibrium or steady state with \( f'f'_1 = ff_1 \) or \( \ln f' + \ln f'_1 = \ln f + \ln f_1 \).

- This tells us that \( f \) is a summational invariant, but the only summational invariants of bimolecular collisions of spherically symmetric molecules are mass, momentum, and kinetic energy.
- Therefore, \( \ln f \) must be a linear combination of these three quantities: \( m, \frac{1}{2}mv^2 \)

### 7.5.3 3. Equilibrium Solution

By performing some math it is possible to solve for the 3 unknown parameters of our quantities of mass, momentum, and K.E. and we find:

\[
f_{\text{equilib}} = f_{\text{Maxwell}}(r, v) = \rho \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}}
\]  

(7.9)

- The equilibrium solution to the Boltzmann Eq. is the classical expression for the Maxwellian distribution of velocities!

In classical mechanics, the equations don’t have a preferred direction in time, but the \( H \)-theorem has shown that the Boltzmann Eq. does have a preferred direction \( \frac{\partial H}{\partial t} \leq 0 \).

- Recall fluxes \( \Gamma^{-} \) and \( \Gamma^{+} \to \) they are probabilities of a collision, so we must say \( \frac{\partial H}{\partial t} \leq 0 \) on average.
- Possible for it to increase, but very small on average, so while \( \frac{\partial H}{\partial t} > 0 \) at some point, it gets lost in data.

Recurrence (reversibility) is also an issue, saying a closed mechanical system will return to original state (closely to)

- Boltzmann calculated that this recurrence time can be on the order of \( 10^{10} \) years! \( \to \frac{\partial H}{\partial t} \leq 0 \) is ok
In dilute gases, Boltzmann Eq. reigns supreme, but we must have chaos (no multi-body dependence) for it to hold true.
Chapter 8

Transport Processes in Dilute Gases

We derived the Boltzmann Eq. and found some consequences of it without solving for $f$.

- We will now solve for it using the Chapman-Enskog method (long and complex, we will summarize).

8.1 Outline of Chapman-Enskog Method

The types of solutions obtained by this method are called normal solutions, in which the spacial and time dependence of $f^{(1)}(r, v, t)$ appear implicitly through local density, flow velocity, and temperature.

- These solutions describe the final state of relaxation of a dilute gas in its equilibrium state.
- This final stage is called the hydrodynamic stage.

Chapman-Enskog expands $f^{(1)}$ in a series of the form (and dropping the superscript) (single particle): $f = \frac{1}{\xi} f^{[0]} + f^{[1]} + \xi f^{[2]} + \ldots$
• \( \xi \) is an ordering parameter that is set to unity later on, \([0], [1], \ldots \) are math orders, not number of particles.

• We can plug this into the Boltzmann Eq. to get a set of equations for all the \( f^{[j]} \).

• We solve each one successively and uniquely \( \rightarrow f^{[0]} \) is easy to solve and gives us:

\[
 f^{[0]} = f_{\text{Maxwell}} = \rho(r, t) \left( \frac{m}{2\pi kT(r, t)} \right)^{3/2} e^{-\frac{m(v-v_0(r,t))^2}{2kT(r,t)}} \quad (8.1)
\]

The \( f^{[j]} \) are constructed in such a way that the Eqs. of change from the Boltzmann Eq. (continuum mechanics Eqs.) keep the same form for increasing mathematical orders of \( f (f^{[0]}, f^{[1]}, \ldots) \).

• However, the values of the parameters that appear in them, namely heat flux vector \( q \) and pressure tensor \( p \) do vary (depends on order of \( f \)).

• Using our expressions for \( p = m \int V V f \, dv \) and \( q = \frac{m}{2} \int V^2 V f \, dv \) and plugging in \( f^{[0]} \), we find that \( p^{[0]} = \rho kT I \) and \( q^{[0]} = 0 \) \( \rightarrow \) Plugging these into the equations of change, we find that we get the ideal hydrodynamic Eqs.

• These equations specify \( \rho, v_0, \) and \( T \), therefore also specify \( f^{[0]} \) through the above Eq. (Maxwellian distribution).

To solve for \( f^{[1]} \), which is much more complicated, let \( f^{[1]} = \phi f^{[0]} \) for some function \( \phi \).

• We then have to solve for \( \phi \) by plugging \( \phi f^{[0]} \) into the Boltzmann Eq. \( \rightarrow \) get an Eq.:

\[
 2\pi \int \int f^{[0]} f^{[0]} \phi' + \phi' - \phi - \phi_1 gb \, db \, dv = -\rho^2 I(\phi) \equiv \frac{\partial f^{[0]}}{\partial t} + \nabla f^{[0]} + \frac{1}{m} \mathbf{X} \cdot \nabla f^{[0]}
\]

• \( I(\phi) \) represents some linear integral operator on \( \phi \), and we find the existance condition for \( \phi \) is just the ideal hydrodynamic equations.

We can further rewrite \( \frac{\partial f^{[0]}}{\partial t} \) since it depends on \( \rho, v_0, \) and \( T \):
8.1. OUTLINE OF CHAPMAN-ENSKOG METHOD

\[ \frac{\partial f^{[0]}}{\partial t} = \frac{\partial f^{[0]}}{\partial \rho} \frac{\partial \rho}{\partial t} + \nabla v_0 f^{[0]} \cdot \frac{\partial v_0}{\partial t} + \frac{\partial f^{[0]}}{\partial T} \frac{\partial T}{\partial t} \]

- We find the time derivatives of \( \rho, v_0, \) and \( T \) through the equations of change, thus getting:

\[ \rho^2 I(\phi) = -f^{[0]}[(W^2 - \frac{5}{2}) \mathbf{V} \cdot \nabla \ln T + b : \nabla v_0] \]

- Where \( W \) is reduced velocity, \( W = (\frac{m}{2kT})^{1/2} \mathbf{V} \) and \( b = 2(WW - \frac{1}{3}W^2I) \)

- This \( \rho^2 I(\phi) \) equation suggests we look for a solution \( \phi \) of the form:

\[ \phi = -\frac{1}{\rho} \left( \frac{2kT}{m} \right)^{1/2} A(W) \mathbf{W} \cdot \nabla \ln T - \frac{1}{\rho} B(W) (WW - \frac{1}{3}W^2I) : \nabla v_0 \]

In this equation of \( \phi, A(W) \) and \( B(W) \) are unknown scalar functions of \( W \), and since \( I(\phi) \) is a linear integral operator, we get two separate integral equations: one for \( A(W) \) and one for \( B(W) \).

- Furthermore, \( \phi \) can be used to calculate the next approximation of \( p \) and \( q \) by using their Eqs.:

\[ q[1] = -\frac{2}{3} \frac{k^2T}{m \rho} \nabla T \int (\text{Exp. of } A(W) \text{ and } f^{[0]}) d\mathbf{v} \quad \text{and} \quad p[1] = -\frac{2kT}{5\rho} (\text{Exp. of } B(W) \text{ and } f^{[0]}) d\mathbf{v} \]

- Thus we can solve for \( q^{[1]} \) and \( p^{[1]} \) if we have solved the integral equations for \( A(W) \) and \( B(W) \).

- Remember, since we build \( f = \frac{1}{\xi} f^{[0]} + f^{[1]} + \xi f^{[2]} + \ldots \), then we build

\[ p = p^{[0]} + p^{[1]} + \ldots \quad \text{and} \quad q = q^{[0]} + q^{[1]} + \ldots \]

- Comparing \( q^{[0]} + q^{[1]} \) to \( q \) with Fourier’s heat transfer law \((q = -\lambda \nabla T)\), we find:

\[ \text{Thermal conductivity: } \lambda = \frac{2}{3} \frac{k^2T}{m \rho} \int A(W)W^2(W^2 - \frac{5}{2})f^{[0]} d\mathbf{v} \]

- And similarly with \( p^{[0]} + p^{[1]} \) to the Newtonian pressure tensor

\((p = \{p + (\frac{2}{3} \eta - \kappa)I - 2\eta \text{sym}(\nabla \mathbf{u}))\):

Shear viscosity coefficient:

\[ \eta = \frac{kT}{5\rho} \int f^{[0]} B(W)(WW - \frac{1}{3}W^2I) : (WW - \frac{1}{3}W^2I) d\mathbf{v} \]
We found that $f^{[0]}$ gives us the ideal hydrodynamic equations, but now $f^{[0]} + f^{[1]}$ gives the Navier-Stokes equations! ($f^{[0]} + f^{[1]} + f^{[2]}$ yields Burnett Eqs., but it is tedious to calculate, and its applications haven’t been too successful yet) → Need to stay near equilibrium with our equations.

- We’ve seen that our two expansion to $f^{(1)} \sim f^{[0]} + f^{[1]}$ yields good results near equilibrium.

Now, we must solve for $A(W)$ and $B(W)$ to get our transport coefficients $\lambda$ and $\eta$.

- This is a very complex process that has been worked out by expanding the expressions using Sonine polynomials (doing 2 terms):

\[
\begin{align*}
\lambda &= \frac{75k^2T}{8m} \left( \frac{1}{a_{11}} + \frac{a_{12}^2 a_{11}}{a_{11} a_{22} - a_{12}^2} + \ldots \right) \\
\eta &= \frac{5kT}{2} \left( \frac{1}{b_{11}} + \frac{b_{12}^2 b_{11}}{b_{11} b_{22} - b_{12}^2} + \ldots \right)
\end{align*}
\]

- The $a_{ij}$ and $b_{ij}$ appearing here are complicated integrals over the dynamics of bimolecular collisions and hence contain the information about the intermolecular potential, $u_{ij}(r)$.

- These can be reduced to linear combinations of a set of collision integrals $\Omega_{ij}^{(l,s)}$ for two components $i,j$.

<table>
<thead>
<tr>
<th>$a_{11} = 4\Omega^{(2,2)}$</th>
<th>$b_{11} = 4\Omega^{(2,2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{12} = 7\Omega^{(2,2)} - 2\Omega^{(2,3)}$</td>
<td>$b_{12} = 7\Omega^{(2,2)} - 2\Omega^{(2,3)}$</td>
</tr>
<tr>
<td>$a_{22} = \frac{77}{17} \Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}$</td>
<td>$b_{22} = \frac{301}{17} \Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}$</td>
</tr>
</tbody>
</table>

The $a_{ij}$ and $b_{ij}$ appearing here are complicated integrals over the dynamics of bimolecular collisions and hence contain the information about the intermolecular potential, $u_{ij}(r)$.

- These can be reduced to linear combinations of a set of collision integrals $\Omega_{ij}^{(l,s)}$ for two components $i,j$.

- And we define the collisions between molecules of type $i$ and type $j$ as the integral:

\[
\Omega_{ij}^{(l,s)} = \left( \frac{2\pi kT}{\mu_{ij}} \right)^{1/2} \int_0^\infty \int_0^\infty e^{-\gamma_{ij}^2} \gamma_{ij}^{2s+3} (1 - \cos \chi) b \, db \, d\gamma_{ij}
\]

- $\mu_{ij}$ is reduced mass for components $i, j$, $\chi = \chi(b, g_{ij})$ is the deflection angle, $g_{ij}$ is the relative velocity, $\gamma_{ij} = \left( \frac{\mu_{ij}}{2kT} \right)^{1/2} g_{ij}$ is a reduced relative velocity.
8.1. OUTLINE OF CHAPMAN-ENSKOG METHOD

These integrals for $\Omega^{(l,s)}$ must be evaluated numerically.

These last 4 sets of equations then give $\lambda$ and $\eta$ in terms of the intermolecular potential.

- We see the intermolecular potential by rewriting the collision integral $\Omega^{(l,s)}_{ij}$ as:

$$
\Omega^{(l,s)}_{ij} = \left(\frac{kT}{2\pi\mu_{ij}}\right)^{1/2} \int_0^\infty e^{-\gamma_{ij}^2} \gamma_{ij}^{2s+3} Q^{(l)}(\gamma_{ij}) d\gamma_{ij}
$$

with cross sectional area: $Q^{(l)}(\gamma_{ij}) = 2\pi \int_0^\infty (1 - \cos^l \chi) b db$

and deflection angle: $
\chi(b, \gamma_{ij}) = \pi - 2b \int_{r_m}^\infty \left[ 1 - \frac{k^2}{r^2} - \frac{u_{ij}(r)}{kT\gamma_{ij}^2} \right]^{1/2} dr$.

- $\gamma_{ij}^2 = \frac{\mu g^2}{2kT}$, $\mu$ is reduced mass, $r_m$ is distance of closest approach of colliding molecules.

-Big Picture-

If we know the intermolecular potential $u_{ij}(r)$, then we can calculate the deflection angle $\chi$, then cross section $Q$, the collisional integral $\Omega$, and use that for the $a_{ij}$ and $b_{ij}$ terms to finally solve for our transport coefficients $\lambda$ and $\eta$, which we found the form of from the Chapman-Enskog expansion of the Boltzmann Eq. (around equilibrium).

- End Big Picture -

As we found $\lambda$ and $\eta$, we can also find diffusion $D_{12}$ and thermal diffusion $D_T^{(1)}$ (much more complex though).

$$
D_{12} = \frac{3}{16\rho\mu_{12}} \frac{kT}{\Omega^{(1,1)}_{12}}
$$

- Note, all these equations and results have been for the first two terms $f^{[0]} + f^{[1]} \rightarrow$ usually good enough.
8.2 Summary of Formulas

To take a simple first look, we can calculate values using a rigid sphere of diameter $\sigma$.

- This is the most simplistic model for the intermolecular potential $u_{ij}(r)$ (nothing, then instant collision).
- We then solve through for $Q$ and $\Omega$ with our rigid sphere model to get hard/rigid sphere reference values for transport coefficients of thermal conductivity, shear viscosity, and binary diffusion:

\[
\lambda = \frac{75k^2T}{8m_\sigma} = \frac{25C_v}{32N} \left( \frac{\pi k T}{m} \right)^{1/2} \frac{1}{\pi \sigma^2} \\
\eta = \frac{5kT}{2\sigma} = \frac{5}{16} \frac{(\pi mkT)^{1/2}}{\pi \sigma^2} \\
D = \frac{3}{8\mu kT} \frac{kT}{\Omega(l,1)} = \frac{3}{8} \left( \frac{\pi k T}{m} \right)^{1/2} \frac{1}{\pi \sigma^2 \rho} 
\]

For most intermolecular potentials, we can write the collision integrals above in a reduced form.

- We use the rigid sphere model as a reference, and write collision integrals in a normalized form by utilizing reduced parameters.
- If the intermolecular potential can be written in the form of $u(r) = \varepsilon f \left( \frac{r}{\sigma} \right)$, where $\varepsilon$ is a characteristic temperature (energy), and $\sigma$ is a characteristic distance (hard sphere diameter), then:

\[
r^* = \frac{r}{\sigma}, \quad b^* = \frac{b}{\sigma}, \quad u^* = \frac{u}{\varepsilon}, \quad T^* = \frac{k T}{\varepsilon}, \quad g^{*2} = \frac{1}{2} \frac{\mu \varphi^2}{\varepsilon}
\]

These reduced quantities represent (physically) the deviation of any particular molecular model from the hard sphere model.

Therefore, using our reduced cross sectional area $\rightarrow$ reduced collision integral, we find generalizations of the previous 3 expressions, and when $\Omega^{l,s(2)} = 1$ they reduce to the rigid sphere results:

\[
\lambda = \frac{25 C_v}{32N} \left( \frac{\pi k T}{m} \right)^{1/2} \frac{1}{\pi \sigma^2 \Omega^{(2,2)}}
\]
8.2. SUMMARY OF FORMULAS

\[ \eta = \frac{5}{16} \frac{(\pi mkT)^{1/2}}{\pi \sigma^2 \Omega^{(2,2)}} \]

\[ D = \frac{3}{8} \left( \frac{\pi kT}{m} \right)^{1/2} \frac{1}{\rho \pi \sigma^2 \Omega^{(1,1)}} \]

These results utilized the single-term expansion of \( A(W) \) and \( B(W) \) rather than two terms since one term expansions turn out to be satisfactory for most transport coefficients.

- The thermal diffusion ratio is an exception, which requires us to carry out more terms of the expansion.
- This means thermal diffusion is more sensitive to the form of the intermolecular potential.
- Using experimental data, it is possible to use the thermal diffusion ratio to determine the best fit \( u_{ij}(r) \).

Many different models for intermolecular potential have been proposed, but we still find deviations as no single one has provided a best fit.

- Some examples: square well, Lennard-Jones, rigid spheres, Kihara potential.
- All of these are obtained from experimental data.
Figure 8.1: The first order approximations provide a good agreement with experimental results.
Part III

Atomic Spectra and Structure
Chapter 9

Historical Overview

9.1 Balmer

Balmer found the wavelengths of visible light emitted by hydrogen (in $E(n)$ to $E(2)$ transitions) follow the following pattern:

$$\lambda = \frac{n_1^2}{n_1^2 - 4} G,$$

where $n_1 = 3, 4, 5$ and $G$ is a constant.

It is also written in terms of the wave number $\tilde{\nu}$ (spatial frequency=$\frac{1}{\lambda} = \frac{k}{2\pi}$):

$$\tilde{\nu} = R \left( \frac{1}{2^2} - \frac{1}{n_1^2} \right),$$

where $R$ is the Rydberg number.

When $n_2 = 2$ is replaced with 1, 3, 4, or 5, you get the Lyman, Paschen, Bracket, and Pfund series respectively, where the Lyman series is in the far UV and the rest are infrared.

9.2 Bohr

Bohr said electrons orbit the nucleus at quantized angular momenta:

$$mvr = nh$$
Figure 9.1: H-atom spectrum.
Then, he solved for the Rydberg number classically using a force balance between the centripetal acceleration and the electric force for the quantized radii resulting from the quantized angular momenta. His result matched the experimental Rydberg number.

### 9.3 Sommerfeld’s ellipses

There was no reason to assume electrons orbited in circles, rather than the more generalized ellipses, so Sommerfeld used action integrals ($\int pdq$) and found the principal quantum number $n$ corresponded to the major axis of the ellipse (from $\int p r \, dr$) and a new quantum number $k$ corresponding to the minor axis (from $\int p \phi \, d\phi$). $k$ was poorly indexed, starting at 1, so now we use $l = k - 1$. $l$ is the azimuthal quantum number and accounted for small variations in $\lambda$ for transitions of equivalent $n$ values.

### 9.4 De Broglie’s waves

De Broglie hypothesized that the kinetic energy of the electrons was equivalent to the energy of a wave:

$$E = h\nu$$

The quantized orbits were a result of all waves destroying each other except for standing waves. The orbits must then exist where a quantized number of wavelengths are equal to the circumference:

$$2\pi r = n\lambda \rightarrow mv = \frac{h}{\lambda}$$
Chapter 10

Atoms at Present

10.1 Schrödinger Eq.

Electrons don’t actually orbit the nucleus, there is a “probability cloud” of where an electron might be. For example, the probability of finding an electron at a given radius is calculated from $\int r^2 \psi \psi^* \, dr$ using $\psi$ from the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi$$

For a single, non-relativistic particle:  

$$i\hbar \frac{\partial}{\partial t} \psi = \left[ \frac{-\hbar^2}{2\mu} \nabla^2 + V(r, t) \right] \psi(r, t)$$

Time independent:  

$$(E - V) \psi(r) = -\frac{\hbar^2}{2\mu} \nabla^2 \psi(r)$$

Using the Schrödinger equation, we determine new definitions for the quantum numbers (see Table 10.1).

A nodal surface is a surface at which there is 0 probability of finding an electron. These are at fixed radii from the nucleus unless they go through the midpoint; then they are conic sections or planes. The values of $n$ and $l$ can be better understood by seeing how the value of $\int r^2 \psi \psi^* \, dr$ varies as a function of $r$ (Figs. 10.1 and 10.2). Understand why the most probable value and the average value are not the same.
<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Name</th>
<th>Interpretation</th>
<th>Selection Rules</th>
<th>Possible Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>principal</td>
<td>number of nodal surfaces +1</td>
<td>$\Delta n = \text{any}$</td>
<td>$\geq 0$</td>
</tr>
<tr>
<td>$l$</td>
<td>azimuthal</td>
<td>number of nodal surfaces through midpoint</td>
<td>$\Delta l = \pm 1$ unless there is an E-field (then 0 possible)</td>
<td>$0, \ldots, n - 1$</td>
</tr>
<tr>
<td>$m$</td>
<td>magnetic</td>
<td>component of $l$ along quantization axis</td>
<td>$\Delta m = \pm 1$ if $\Delta J = 0$, $\Delta m = 0, \pm 1$ if $\Delta J = \pm 1$</td>
<td>$-l, \ldots, l$</td>
</tr>
<tr>
<td>$s$</td>
<td>electron spin</td>
<td>up or down spin</td>
<td>$\Delta s = 0$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td>$L$</td>
<td></td>
<td>$\sum l$</td>
<td>$\Delta L = \pm 1$</td>
<td>integer</td>
</tr>
<tr>
<td>$S$</td>
<td></td>
<td>$\sum s$</td>
<td>$\Delta S = 0$</td>
<td>half integer or integer</td>
</tr>
<tr>
<td>$J$</td>
<td></td>
<td>$L + S$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\geq 0$</td>
</tr>
</tbody>
</table>

Table 10.1: Quantum numbers and interpretation.

Figure 10.1: There are $n - 1$ surfaces with no probability of containing an electron. There are $l$ of these surfaces going through the midpoint (not fixed radius).
10.2 Selection Rules

Selection rules are outlined in Table 10.1. They are illustrated by Grotrian diagrams, examples of which are in Figs. 10.3 and 10.4. The frequency of a photon is correlated to the change in energy when an electron moves from one state to another ($\Delta E = h\nu$). The energy of each level is along the left side, as the the value of $n$. The columns correspond to $l = 0, 1, 2, \ldots$

Important: Note that for hydrogen the different $l$ states have nearly identical energy for an equivalent $n$ value. In general, the larger the atomic number, the greater the variation in energy for a given $n$ value (compare with helium for instance). This concept can be used to show that $n = 2$ for the outermost lithium electron. The entire second row of the period table can be compared side by side in Grotrian diagrams normalized by dividing all energies by $(Z - p)^2$, where $Z$ is the atomic number and $p$ is the effective charge that the outermost electron sees.

When you do this, the outermost electron of lithium is sitting at about $n = 1.5$, so it could belong to $n = 1$ or $n = 2$. By comparing with subsequent elements, it is clear that it is an $n = 2$ state.

Back to the Grotrian diagrams. There are letters corresponding to the $l$ values. These are $S$ for sharp ($l = 0$), $P$ for principal ($l = 1$), $D$ for diffuse ($l = 2$), and $F$
Figure 10.3: Grotrian diagram of hydrogen.
Figure 10.4: Grotrian diagram of helium.
for fundamental \((l = 3)\). There is also \(G\) for “comes after \(F\) in the alphabet.” To the top left of these letters in Fig. 10.4 is the tuplet value, which is to say how many values of \(J\) or possible, but this is a lie. Look at the \(S\) column of orthohelium. There is only one way to add the vector 1 to 0. There are, however, 3 different ways of adding \(S\) to \(L\) that satisfy the requirements of \(J\) for all subsequent \(l\) states (see next paragraph). They have slightly different energy levels and result in three slightly different wavelengths in the transition from \(P\) to \(S\). Note that for other transitions, such as \(F\) to \(D\), as many as 6 bands are possible for triplets. The number to the lower right hand corner of the \(l\) letter is the magnitude of \(J\):

\[
\text{tuplet}_{l_J}
\]

The above paragraph takes some time to understand. First, understand what values you can get for \(J\). \(L\) is fixed, and \(J\) must be an integral addition to \(S\).

Example: \(L = 2\) and \(S = \frac{5}{2}\). So \(J\) must have half integer values. The biggest it can be is \(\frac{9}{2}\), then \(\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}\). Again, this is technically a sextuplet, but we only have 5 terms. This is because \(2 - \frac{5}{2}\) is the smallest \(J\) can be, but since \(J\) cannot be negative, we omit that last value.

What’s with the dotted line in Fig. 10.4? In Grotrian diagrams, we are only looking at the outer electron. All other electrons are assumed to be in ground state, which is generally true until the outer electron is ionized. The dotted line denotes the difference between the two electrons of helium having the same or opposite spin (for ortho and parahelium respectively). This is why there is no \(n = 1\) state for the outer electron in orthohelium. That would put two electrons in the exact same state, violating the Pauli exclusion principle.

Metastability: This is where an electron is NOT in the ground state, but cannot move to the ground state without first receiving energy. You can see that when \(n = 2\) and \(l = 0\), there is either no ground state (ortho), or an electron would have to get energy before it can emit (para).

Know at least the following ionization potentials:

\[
\text{H: } 13.6 \text{ eV, He: } 24.5 \text{ eV, Li (first): } 5.4 \text{ eV, Li (second): } 76 \text{ eV}
\]

Also understand that selection rules are frequently broken, especially for heavier elements. The rules simply describe the most probable transitions predicted by the Schrödinger equation.
10.3 Zeeman Effect

In the presence of a magnetic field, spectral lines split into several bands, and their separation from their 0-field value is proportionate to the strength of the magnetic field. This effect is useful for measuring the intensity of magnetic fields in sun spots and elsewhere. The magnetic field exerts a torque on the magnetic dipole resulting from the electron’s “orbit.”

The perturbation in energy for a given electron in the direction of the quantization axis is:

\[ H_1 = -(\mu_l + \mu_s) \cdot B_{\text{ext}}, \]

where \( \mu_s = -\frac{e}{m} S \) and \( \mu_l = -\frac{e}{2m} L \).

\( \mu \) is on the order of \( 10^{-23} \), so \( \frac{H_1}{H} \) is usually small for a reasonable \( B \).
Part IV

Appendices
Chapter 11

Appendix A: Chinese Napkin Formulas

\[ \nu = nQ(v) \nu \] (11.1)

\[ \lambda = \frac{1}{nQ(v)} \] (11.2)

radius of H = 0.529 Å (11.3)

\[ \lambda_{\text{room}} = 10^{-6} \text{ m} \] (11.4)

\[ P_{\text{STP}} = 10^5 \text{ Pa} \] (11.5)

1 eV = 11,600° K (11.6)

\[ R = 1.1 \times 10^7 \text{ m}^{-1} \] (11.7)
\[ \dot{c} = \sqrt{\frac{8kT}{\pi m}} \quad (11.8) \]

\[ P_j = \frac{\sigma_j}{A} = \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} \quad (11.9) \]

\[ k = 1.3806 \times 10^{-23} \text{ J/K} \quad (11.10) \]

\[ \Xi_{FD} = \prod_k (1 \pm \lambda e^{-\beta \varepsilon_k})^{\pm 1} \quad (11.11) \]

\[ Q(N, V, T) = \frac{q^N}{N!} \quad (11.12) \]

\[ N_{\text{palm}} = 10^{21} \text{ atoms of air} \quad (11.13) \]

\[ q = \sum_j e^{-\beta \varepsilon_j} = q_{\text{trans}} q_{\text{int}} \quad (11.14) \]

\[ q_{\text{trans}} = \left[ \frac{2\pi mkT}{\hbar^2} \right]^{3/2} V \quad (11.15) \]

\[ q_{\text{vib}} = \frac{kT}{\hbar \nu} = \frac{T}{\Theta_{\text{vib}}} \quad (11.16) \]

\[ q_{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}}, \sigma = 2 \text{ when homonuclear} \quad (11.17) \]

\[ \frac{\partial f_j}{\partial t} + v_j \cdot \nabla f_j + \frac{X_j}{m_j} \cdot \nabla f_j = \text{change in } f_j \text{ due to collisions} \quad (11.18) \]
Chapter 12

Appendix B: Principle Topics in Plain English

Have a spiel put together for each of the following:

**BBGKY**  BBGKY offers a complete solution to the Liouville Eq. in terms of reduced distribution functions.

**Boltzmann Equation**  The Boltzmann Eq. is the most fundamental Eq. of the rigorous kinetic theory of gases. It describes the statistical behavior of a thermodynamic system not at thermodynamic equilibrium. It can be written in the form of \( \frac{\partial f}{\partial t} = \frac{\partial f}{\partial t_{\text{external force}}} + \frac{\partial f}{\partial t_{\text{diffusion}}} + \frac{\partial f}{\partial t_{\text{collisions}}} \). For the collision term, Boltzmann applied the molecular chaos assumption, which assumes 2-body only collisions between particles that are uncorrelated prior to collision. This assumption is valid since we are only dealing with dilute gases (singlet distribution function). The solution to the Boltzmann Eq. is found via the Chapman-Enskog method.

**Chapman-Enskog Method**  This method of solving the Boltzmann Eq. expands \( f^{(1)} \) such that \( f = \frac{1}{\xi} f^{[0]} + f^{[1]} + \xi f^{[2]} + \ldots \), where the first term describes a Maxwellian distribution, the combined first two terms describe the Navier Stokes Eqs., and all three terms form the Burnett Eqs.
• Assume a solution of the form \( f^{[1]} = \phi f^{[0]} \).

• Use Eqs. of change to solve for \( \phi \) in terms of \( A(W) \) and \( B(W) \) (functions of reduced velocity).

• Use Fourier’s Law to get \( \lambda(A(W)) \) (thermal conductivity).

• Use Newtonian Pressure tensor to get \( \eta(B(W)) \) (coefficient of shear viscosity).

• Expand \( \int A(W) \) and \( \int B(W) \) using Sonine polynomials in terms of \( a_{ij} \) and \( b_{ij} \).

• End up needing just intermolecular potential for \( \chi \) (deflection angle) for \( Q \) (collisional cross section area) for \( \Omega \) (collision integral) to get \( \lambda, \eta, \) and \( D \) (diffusion coefficient). So you get gas properties from first principles!

**Ensemble**  A collection of a large number of systems \( A \), each with the same macroscopic properties for a particular thermodynamic system of interest.

• \( \Omega(N, V, E) \) - microcanonical ensemble, isolated system

• \( Q(N, V, T) \) - canonical ensemble, system in contact with heat bath

• \( \Xi(V, T, \mu) \) - grand canonical ensemble, system in contact with heat and particle bath

• \( \Delta(N, T, \varphi) \) - isobaric-isothermal ensemble, used in chemistry (constant \( \varphi \))

**Liouville Equation**  The Liouville Eq. is the most fundamental Eq. of statistical mechanics. It is completely equivalent to the \( 6N \) Hamilton Eqs. of motion of the \( N \)-body system. The equation says that the density in the neighborhood of any selected moving phase point is a constant along the trajectory of that phase point, and the cloud of phase points behaves as an incompressible fluid \( (\frac{df}{dt} = 0) \). This is proven by the fact that the evolution of \( f \) obeys the \( N \)-dimensional continuity Eq..

**Partition Function**  Describes the statistical properties of a system at equilibrium. It serves as a bridge between the quantum mechanical energy states of a macroscopic system and the thermodynamic properties of that system.
Phase Space  If you take an $N$-particle system, you can define the generalized coordinates and conjugate momenta of every particle as a single point in phase space. Further, you can use an ensemble of such points representing the same macroscopic mechanical properties, and the density of these phase points (assuming you take the limit of them) is a distribution function $f$. Since $f$ represents all phase points with the same macroscopic mechanical property, the distribution of phase points will be invariant with respect to time. So $\frac{df}{dt} = 0$ and we can solve for $\frac{df}{dt}$ with respect to $\dot{p}$ and $\dot{q}$ to find the Liouville Eq.
Bibliography

