A DISCUSSION OF FRIEMAN'S
METHOD IN THE THEORY OF IRREVERSIBLE PROCESSES

by

YUN-KWONG SEBASTIAN TAM

B. Sc., University of Hong Kong, 1961
B. Sc. (Special Honours), University of Hong Kong, 1962

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS OF THE DEGREE OF
M. Sc.

in the Department
of
PHYSICS

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
April, 1965
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Physics

The University of British Columbia, Vancouver 8, Canada

Date 21st April, 1965.
ABSTRACT

We investigate a new perturbation technique introduced by E. Frieman to derive a kinetic equation from the equations of the BBGKY hierarchy. The orders of magnitude of the terms in the latter equations are calculated and Frieman's estimate is found incorrect. His derivation of the Landau's equation for a weakly coupled gas actually depends on the existence of the relaxation time rather than the much shorter mean free time as he expected. A physical interpretation of the Grad's theorem and Grad's original proof is given to justify the choice of the molecular chaos conditions at the initial time. Two examples are given to clarify the applicability of the perturbation method.
ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. L. De Sobrino for suggesting this problem and for his invaluable help in the course of this work.

I am also grateful to the National Research Council for financial assistance in the form of an N. R. C. Award.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>i</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td></td>
<td>iii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER I</td>
<td>THE EQUATIONS OF THE HIERARCHY</td>
<td>4</td>
</tr>
<tr>
<td>CHAPTER II</td>
<td>THE WEAK-COUPLING CASE</td>
<td>10</td>
</tr>
<tr>
<td>CHAPTER III</td>
<td>THE PERTURBATION METHOD</td>
<td>19</td>
</tr>
<tr>
<td>CHAPTER IV</td>
<td>CONCLUSION</td>
<td>31</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>ORDERS OF MAGNITUDE OF THE DISTRIBUTION FUNCTIONS</td>
<td>33</td>
</tr>
<tr>
<td>APPENDIX F</td>
<td>ORDERS OF MAGNITUDE OF THE CORRELATION FUNCTIONS</td>
<td>41</td>
</tr>
<tr>
<td>APPENDIX C</td>
<td>GRAD'S THEOREM</td>
<td>47</td>
</tr>
<tr>
<td>APPENDIX D</td>
<td>FURTHER DISCUSSION ON THE PERTURBATION METHOD</td>
<td>68</td>
</tr>
</tbody>
</table>
INTRODUCTION

In this thesis we investigate a new perturbation technique introduced by E. Frieman (1963) and G. Sandri (1963) to study the approach to equilibrium of a weakly coupled, moderately dense gas. In the process of this investigation, it is found that, contrary to Frieman's argument, the time between successive collisions in his model of gas is not much longer than the duration of a single collision. Since his calculation relied on these times being very different, it was not clear how he could arrive at a result which was seemingly correct. We now find that his calculation actually depends on the existence of another characteristic time which is a measure of the time for the gas to approach thermal equilibrium. Such a characteristic time is, of course, much longer than the duration of a single collision. It is therefore not surprising that his result was correct.

In chapter I of this thesis, we briefly derive, from the Liouville's equation, a system of equations (the BBGKY hierarchy, see Montgomery and Tidman, 1964) relating the distribution functions for a few particles. Assuming that the gas is originally not too far from equilibrium, we estimate the magnitudes of the various terms in the equations.
In chapter II, we consider a weakly coupled gas. We introduce a small dimensionless parameter $\epsilon$ as a measure of the strength of the interaction. We assume the gas to be nearly homogeneous. Three characteristic times of different orders of magnitude in $\epsilon$ are found. The evolution of the $s$-particle distribution is then studied qualitatively.

Chapter III introduces the perturbation technique and the calculation due to Frieman. Assuming that the initial values of all correlations are zero, we arrive at Landau's equation for the one-particle distribution function. The result is identical to that obtained by Balescu using his diagram technique.

In deriving Landau's equation, Frieman's perturbation method requires a correct estimate of the orders of magnitude of the various terms in the equations of the hierarchy. He has made such an estimate for the first two equations. To do so, it is necessary to introduce some assumptions about the distribution functions. However, many of these assumptions do not appear clearly in Frieman's paper, nor in Sandrie's. Besides, Frieman's estimate for the second equation of the hierarchy is incorrect (see appendices A and B). In this thesis, we make a detailed study in this respect and obtain conditions under which the perturbation method leads to Landau's equation. The assump-
tion of zero initial correlations is justified by Grad's theorem. Following Grad's paper (1960), we prove the theorem and give the physical conditions under which it can be applied. Finally we give two examples to clarify the applicability of the perturbation method.
CHAPTER I

THE EQUATIONS OF THE HIERARCHY

We consider a classical system of \( N \) identical, non-relativistic particles of mass \( m \) in a volume \( \Omega \) interacting with a two-body central potential \( \Phi \). The \( N \)-particle distribution function \( f_N(x_1, x_N, v_1, v_N; t) \) is defined in such a way that the probability of finding the representative point of the system at time \( t \) in a volume \( \sum_{i=1}^{N} dx_1 dv_1 \) of \( \Gamma \)-space around the point \( (x_1, x_N, v_1, v_N) \) is \( f_N(x_1, x_N, v_1, v_N; t) \sum_{i=1}^{N} dx_1 dv_1 \). Since the particles are identical, the distribution function \( f_N \) is symmetric under an interchange of the coordinates and velocities of any two particles. The time evolution of \( f_N \) is governed by Liouville's equation

\[
\frac{\partial f_N}{\partial t} + \sum_{j=1}^{N} \left( \frac{\partial f_N}{\partial x_j} \frac{\partial H}{\partial p_j} - \frac{\partial f_N}{\partial p_j} \frac{\partial H}{\partial x_j} \right) = 0
\]

where \( p_j = mv_j \) and \( H \) is the Hamiltonian of the system given by

\[
H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{n=1}^{N} \sum_{j<n} \Phi(|x_j - x_n|).
\]
From (I.2), we immediately obtain

\[(I.3) \quad \frac{\partial H}{\partial p_j} = \frac{p_j}{m} = \nu_j, \quad \frac{\partial H}{\partial q_j} = \sum_{n \neq j} \frac{\partial \Phi (q_j - q_n)}{\partial q_j} \frac{\partial f}{\partial q_j} \]

Substituting (I.3) into (I.1), we find

\[(I.4) \quad \left[ \frac{\partial}{\partial t} + \sum_{j=1}^{N} \nu_j \frac{\partial}{\partial q_j} - \frac{1}{m} \sum_{n=1}^{N} \frac{\partial \Phi (q_j - q_n)}{\partial q_j} \frac{\partial f}{\partial q_j} \right] f_N = 0 \]

We now define the reduced distribution functions

\[(I.5) \quad f_s (x_1, \ldots, x_s, \nu_1, \ldots, \nu_s; t) = \mathcal{S}_N \int \cdots \int d\nu_1 \cdots d\nu_N f_N, \quad s = 1, 2, \ldots, N-1\]

The equations for \(f_s\) are obtained from (I.4). Integrating (I.4) over the variables \(x_{s+1}, \ldots, x_N, \nu_{s+1}, \ldots, \nu_N\) and multiplying by \(\mathcal{S}_s\), we obtain the BBGKY hierarchy of equations

\[(I.6) \quad \left[ \frac{\partial}{\partial t} + \sum_{j=1}^{s} \nu_j \frac{\partial}{\partial q_j} - \frac{1}{m} \sum_{n=1}^{s} \sum_{j \neq n} \frac{\partial \Phi (q_j - q_n)}{\partial q_j} \frac{\partial f}{\partial q_j} \right] f_s \]

\[= \frac{N-S}{m \mathcal{S}_s} \int d\nu_{s+1} \cdots d\nu_N \sum_{j=1}^{s} \frac{\partial \Phi (q_j - q_{s+1})}{\partial q_j} \frac{\partial s_{s+1}}{\partial q_j}, \]
Using the centre of mass coordinate $X$ of the $s$-particle cluster and their relative coordinates $x_{ij}$ given by

$$ X = s^{-1} \sum_{i=1}^{s} x_i, $$

(I.7)

$$ x_{ij} = x_i - x_j, \quad i, j = 1, 2, \ldots, s, $$
equation (I.6) yields the equations of the hierarchy

(I.8) \[ \left[ \frac{\partial}{\partial \xi} + V \cdot \frac{\partial}{\partial X} + \sum_{j=2}^{s} (v_i - v_j) \cdot \frac{\partial}{\partial x_j} - \frac{1}{m} \sum_{j=1}^{s} \sum_{m} \frac{\partial \Phi(x_{mn})}{\partial x_{mn}} \cdot \frac{\partial}{\partial y_j} \right] f_s \]

\[ = \frac{N-s}{m \Omega} \int dx_i dy_i \sum_{j=1}^{s} \frac{\partial \Phi(x_{mn})}{\partial x_{mn}} \cdot \frac{\partial f_{s+1}}{\partial y_j}, \quad s = 1, 2, \ldots, N-1, \]

where $V = s^{-1} \sum_{i=1}^{s} v_i$, the velocity of the centre of mass of the cluster. For $s = 1, 2$, we have

(I.9) \[ \frac{\partial f}{\partial \xi} + v_i \cdot \frac{\partial f}{\partial x_i} = \frac{N-1}{m \Omega} \int dx_j dy_j \frac{\partial \Phi(x_{j2})}{\partial x_{j2}} \cdot \frac{\partial f_2}{\partial y_j}, \]

and

(I.10) \[ \left[ \frac{\partial}{\partial \xi} + \frac{1}{2} (v_i + v_j) \cdot \frac{\partial}{\partial X} + (v_i - v_j) \cdot \frac{\partial}{\partial X} - \frac{1}{m} \frac{\partial \Phi}{\partial X} \cdot \partial_{ij} \right] f_2 \]

\[ = \frac{N-2}{m \Omega} \int dx_3 dy_3 \frac{\partial \Phi}{\partial x_3} \cdot \partial_{ij} f_3, \]
where we have put

$$\chi = \chi_{12},$$

(I.11)

$$\frac{\partial f}{\partial \chi} = \frac{\partial}{\partial \chi_{1}} - \frac{\partial}{\partial \chi_{2}}.$$

It is obvious from (I.8) that the reduced distribution function $f_s$ cannot be obtained without the knowledge of $f_{s+1}$. We therefore require a justifiable procedure to decouple the system of equations in (I.8).

We now estimate the relative orders of magnitude of the various terms in the equations of the hierarchy since our method will rely entirely on them. To so so, we define the following quantities:

- $r_o$: the range of the potential,
- $\langle \Phi \rangle$: the strength of the potential,
- $\langle v \rangle$: the average speed of the particles,
- $L$: the characteristic scale length for the macroscopic spatial gradient, that is the spatial distance over which the distribution functions change appreciably,
- $\tau$: a time interval.

In what follows we assume that $N \rightarrow \infty$ and $\Omega \rightarrow \infty$ in such a way that $N/\Omega = n$ remains finite. Next we consider a moderately dense gas in which $nr_0^3 = o(1)$. 

Thus we have $r^3_o/\Omega = 0(1/N) \ll 1$ and the interaction of the system with the boundaries is expected to be negligible. Assuming that the gas is not too far from equilibrium, the ratios of the terms in (1.9) and (1.10) are given respectively by (see appendix A)

\[(1.12) \quad 1 : \frac{<v^2 \tau_1 >}{L} : \frac{< \mathbf{\Phi} >}{m \langle v^2 \rangle} : \frac{<v^2 \tau_2 >}{\tau_0},\]

and

\[(1.13) \quad 1 : \frac{<v^2 \tau_1 >}{L} : \frac{< \mathbf{\Phi} >}{m \langle v^2 \rangle} : \frac{<v^2 \tau_2 >}{\tau_0} : \frac{< \mathbf{\Phi} >}{m \langle v^2 \rangle} : \frac{<v^2 \tau_2 >}{\tau_0} : \frac{< \mathbf{\Phi} >}{m \langle v^2 \rangle} : \frac{<v^2 \tau_2 >}{\tau_0}.\]

It is convenient to write the distribution functions in the following way

\[(1.14) \quad f_2(u,2) = f_i(u) f_i'(2) + g(u,2),\]

\[(1.15) \quad f_3(u,2,3) = f_i(u) f_i'(2) f_i'(3) + f_i(u) g(2,3) + f_i(2) g(3,1) + f_i'(2) g(1,2)
+ h(u,2,3), \quad \text{etc.}\]

Substituting these into (1.9) and (1.10) and neglecting terms of order $1/N$, we obtain

\[(1.16) \quad \frac{\partial f_i}{\partial t} + u_j \frac{\partial f_i}{\partial x_j} = \frac{n}{m} \int dx_2 dy \frac{\partial \mathbf{\Phi}}{\partial x_j} \left[ \frac{\partial f_i(u)}{\partial x_j} f_i'(2) + \frac{\partial g(u,2)}{\partial y_j} \right],\]
and

\begin{align*}
(I.17) \left[ \frac{\partial}{\partial t} + \frac{1}{2} \left( v_1^2 + v_2^2 \right) \frac{\partial}{\partial x} + (v_1 - v_2) \frac{\partial}{\partial x} - \frac{1}{m} \frac{\partial^2 \Phi}{\partial x^2} \partial_{12} \right] g_{(1,2)} \\
= \frac{1}{m} \frac{\partial \Phi}{\partial x} \cdot \partial_{12} f_1^{(1)} f_2^{(2)} + \frac{n}{m} \int dz_1 dz_2 \frac{\partial \Phi}{\partial x} \frac{\partial}{\partial x} \left[ f_1^{(1)} g_{(2,3)} + g_{(1,2)} f_1^{(3)} + h_{(1,2,3)} \right] \\
- \frac{\partial \Phi}{\partial x} \frac{2}{\partial x} \left[ f_1^{(2)} g_{(3,1)} + g_{(1,2)} f_1^{(3)} + h_{(1,2,3)} \right] .
\end{align*}

These equations will constitute the basis for the development to follow.
CHAPTER II

THE WEAK-COUPLING CASE

As mentioned before, the equations of the hierarchy (I.8) do not form a closed system and have to be decoupled. This can be done with the help of a perturbation expansion. We examine a weakly coupled gas since it is analytically simple and yet the essential points of the method can be demonstrated.

It is convenient to write

\[(II.1)\quad \mathcal{F}(\lvert \mathbf{x}_1 - \mathbf{x}_2 \rvert) = \epsilon \mathcal{V}(\lvert \mathbf{x}_1 - \mathbf{x}_2 \rvert)\]

where \(\mathcal{V}(\lvert \mathbf{x}_1 - \mathbf{x}_2 \rvert) \sim m \langle v \rangle^2\), \(\epsilon \ll 1\) is a dimensionless parameter, and the symbol \(\sim\) means "of the order of". To study the evolution of the distribution functions, we determine the various characteristic times of the gas.

We define \(\tau_c = r_0 / \langle v \rangle\) as the collision time. This is the time which a particle moving with the average speed spends in the sphere of influence of another particle. The average time \(\tau_1\) between successive collisions is given by \(\tau_1 = (n \pi r_0^2 \langle v \rangle)^{-1}\)

\(= \tau_c / (n r_0^3 \langle v \rangle)\). Since \(n r_0^3 \sim 1\), the "mean free time" \(\tau_1\) is of the same order in \(\epsilon\) as the collision time \(\tau_c\). This result therefore shows an error in Frieman's
calculation in which he found $\tau_1 \sim \tau_c / \epsilon^2$. The relaxation time $\tau_r$ for the system to approach equilibrium may now be estimated and taken as the average time required for a particle to exchange with other particles an energy $m \langle v \rangle^2$. Thus to determine $\tau_r$, we first calculate the change in energy $\Delta E$ of a particle due to $k$ collisions in a time $\Delta t$.

In a time $\Delta t$, the momentum of the particle $A$ is changed by an amount

$$\Delta \mathbf{p} = \sum_{i=1}^{k} \delta \mathbf{p}_i$$

where $\delta \mathbf{p}_i$ is the change in momentum of $A$ in its $i$th collision and $\sum_{i=1}^{k}$ is the summation over all the $k$ successive collisions. The change in energy $\Delta E$ in a time $\Delta t$ is then given by

$$(\text{II.3}) \quad 2m \Delta E = (\mathbf{p}_1 + \sum_i \delta \mathbf{p}_i)^2 - \mathbf{p}_1^2$$

$$= \sum_i \mathbf{p}_1 \cdot \delta \mathbf{p}_i + \sum_{i,j} \delta \mathbf{p}_i \cdot \delta \mathbf{p}_j.$$ 

Here $\mathbf{p}_1$ is the original momentum of $A$ immediately before the first collision. The expectation value $\langle \Delta E \rangle$ is now given by
In the case where \( n r_0^2 \approx 1 \), the \( k \) different collisions may be considered as independent. The expectation value \( \langle \Delta E \rangle \) may therefore be obtained by

\[
\langle \Delta E \rangle = \frac{1}{2m} \left\{ \left< \sum_{i=1}^{k} p_i \cdot \delta_{ki} \right> + \left< \sum_{i,j} \delta_{ki} \cdot \delta_{kj} \right> \right\}
\]

Since the gas is not too far from equilibrium, the velocity distribution is approximately isotropic and we have

\[
\int \int dx_2^i dy_2^i \cdot f_2(x_2^i, y_2^i, v_2^i, t) \approx 0.
\]

This gives

\[
\langle k_1 \cdot \delta_{ki} \rangle = \int \int \int dx_1^j dx_2^i dy_1^j dy_2^i f_2(x_1^j, x_2^i, y_1^j, y_2^i, t) \delta_{ki} \cdot \left( \frac{1}{m^2} \right)^k
\]

\[
= \int \int dx_2^i dy_2^i \cdot f_2(x_2^i, y_2^i, v_2^i, t) \left( \frac{1}{m^2} \right)^k
\]

\[
= 0
\]

and also

\[
\langle \delta_{ki} \cdot \delta_{kj} \rangle = \begin{cases} 0, & \text{for } i \neq j, \\ \langle (\delta_{kj})^2 \rangle, & \text{for } i = j. \end{cases}
\]
Substituting (II.7) and (II.8) into (II.4), we find

\[(\text{II.9}) \quad \langle \Delta E \rangle = \frac{1}{2m} \sum_{i=1}^{k} \langle (\delta p_i)^2 \rangle.\]

Up to the present, we have assumed that the distribution function \(f_2\) is unchanged during a collision. However, due to interactions, \(f_2\) does change with time. To take into account of this, we approximate \(\langle (\delta p_i)^2 \rangle\) by

\[(\text{II.10}) \quad \langle (\delta p_i)^2 \rangle = \frac{1}{\bar{f}_2^2} \int \int dx'_1 dx'_2 \int \int dx'_3 dx'_4 \bar{f}_2 (\delta p_i)^2\]

where \(\bar{f}_2\) is the average of \(f_2\) over the collision time \(\tau_c\), or to be more specific,

\[(\text{II.11}) \quad \bar{f}_2 = \frac{1}{\tau_c} \int_{t}^{t+\tau_c} dt' f_2 (1, 2, t').\]

Expanding \(f_2(1, 2, t')\) about \(t\), we obtain

\[(\text{II.12}) \quad \bar{f}_2 = \frac{1}{\tau_c} \int_{t}^{t+\tau_c} dt' f_2 (1, 2, t) \left\{ 1 + \left( \frac{\partial f_2}{\partial t} \right) \frac{(t'-t)}{\bar{f}_2} + \ldots \right\}

= f_2 (1, 2, t) + \frac{1}{\tau_c} \left\{ \int_{t}^{t+\tau_c} dt' \frac{\partial f_2}{\partial t} \frac{(t'-t)}{f_2} + \ldots \right\}\]

From (I.8), (I.9) and (I.10), it is obvious that

\(\frac{\partial f}{\partial t}, \frac{\partial^2 f}{\partial t^2}, \frac{\partial^3 f}{\partial t^3}\), etc., are functions of \(f_3, f_4,\) etc.
The integral in (II.12) therefore includes the effect of many-body interactions. Using (I.13), we find

\[ \frac{\partial f_2}{\partial t} \frac{(t'_r - t)}{f_2} \sim \frac{<\Phi>}{m_v^2} \frac{<\nu> c}{\tau_v} \sim \varepsilon, \]

(II.13)

\[ \frac{\partial^2 f_2}{\partial t^2} \frac{(t'_r - t)^2}{f_2} \sim \varepsilon, \]

etc.

(II.12) and (II.13) therefore give

\[ \bar{f}_2 = f_2 (t, z, t) \{ 1 + O(\varepsilon) \}. \]

(II.14)

This shows that the effect of many-body interactions is of the first order in \( \varepsilon \) as compared with that of the two-body interaction. Substituting (II.14) into (II.10) and using (II.9), we find

\[ <\Delta E> = \frac{1}{2m} \sum_{i=1}^{k} \frac{<\delta p_i^2>}{<\Phi>^2} \]

(II.15)

\[ = \frac{1}{2m} \sum_{i=1}^{k} <\delta p_i^2> \left[ 1 + O(\varepsilon) \right]. \]

The magnitude of \( \delta p_i \) is approximately given by

\[ \delta p_i \sim \left( \frac{<\Phi>}{\tau_v} \right) \tau_c \sim \frac{<\Phi>}{<\nu>}, \]

(II.16)

since the force acting on the particle during a
collision is of the order of $<\hat{\theta}>/r_o$. In a time $\tau_r$, the average number of collisions experienced by $A$ is $\tau_r/\tau_1$ and the average energy change in $A$ is $m\langle v\rangle^2$, by definition of $\tau_r$. Thus we have

$$\langle \Delta E \rangle \sim \frac{1}{2m} \left( \frac{\tau_r}{\tau_1} \right) \left( \frac{<\hat{\theta}>}{<v>} \right)^2 \sim m\langle v\rangle^2$$

or

$$(II.17) \quad \tau_r \sim \tau_c \left\{ \frac{m\langle v\rangle^2}{<\hat{\theta}>} \right\}^2 \sim \frac{\tau_c}{\epsilon^2}$$

since $m\langle v\rangle^2/<\hat{\theta}> \sim 1/\epsilon$ and $\tau_1 \sim \tau_c$.

There is still one more characteristic time which we need to consider. This is the time required by an average particle to travel through a characteristic macroscopic inhomogeneity and is given by $\tau_h = L/<v>$. Thus for a weakly coupled gas in which $nr_o^3 = O(1)$ and $<\hat{\theta}>/(m\langle v\rangle^2) = O(\epsilon)$, there are three characteristic times:

(i) $\tau_c = r_o/<v>$, the collision time,
(ii) $\tau_r \sim \tau_c/\epsilon^2$, the relaxation time,
(iii) $\tau_h = L/<v>$, the hydrodynamic time.

We may now proceed to study the distribution of the gas at various time scales. For simplicity of calculation, we assume $r_o/L \sim \epsilon^4$ to avoid considering terms of the order $r_o/L$. Thus for $s/N \ll \epsilon$, we find that the various terms in (I.8) bear the ratios (see
appendix A)

\[ 1 : 0(\epsilon^4) : 0(\epsilon) : 0(\epsilon) : 0(\epsilon), \quad \text{for } t \sim \tau_c, \]

\[ (II.18) \quad 1 : 0(\epsilon^3) : 0(1) : 0(1) : 0(1), \quad \text{for } t \sim \tau_c / \epsilon, \]

\[ 1 : 0(\epsilon^2) : 0(1/\epsilon) : 0(1/\epsilon) : 0(1/\epsilon), \quad \text{for } t \sim \tau_c / \epsilon^2. \]

Thus we expect to find

\[ f_s(t) \sim f_s(t=0) \left[ 1 + O(\epsilon) \right], \quad \text{for } t \sim \tau_c, \]

\[ (II.19) \quad f_s(t) \sim f_s(t=0) \left[ 1 + O(1) \right], \quad \text{for } t \sim \tau_c / \epsilon, \]

\[ f_s(t) \sim f_s(t=0) \left[ 1 + O(1/\epsilon) \right], \quad \text{for } t \sim \tau_c / \epsilon^2. \]

The significance of (II.19) can be understood if we study the trajectory of an average particle subject to the influence of its surrounding particles.

In short times \( t \sim \tau_c \), an average particle is only slightly deflected from its original path due to its interactions with other particles. During this time, the distribution functions can be expanded as a power series in \( \epsilon \),

\[ (II.20) \quad \chi(t) = \sum_{i} \epsilon^i \psi^{(i)}(t), \]

since the coefficients \( \psi^{(1)}(t) \) will not change in order of magnitude in \( \epsilon \). Expansions of this form for the distribution and correlation functions may be used to solve the equations of the hierarchy.
This procedure is no longer applicable if we consider times $t \sim \tau_c \sim \tau_\epsilon / \epsilon^2$, because, then, the cumulative effect of the weak interaction may modify considerably the original path of each particle. The distribution and correlation functions may change considerably, and the first few terms of the expansion (II.20) will no longer constitute a good approximation. Thus a series expansion like (II.20) offers no help to our calculation unless we can suppress the growth of the expansion coefficients. This is done in the next chapter.
Frieman's perturbation technique is a generalization of the well-known method in nonlinear mechanics developed by van der Pol (1926, 1927), and Bogoliubov and Krylov (1937). In most perturbation methods, we expand the perturbation functions in powers of a small parameter $\epsilon$, say. Such expansions can be useful if the coefficients of the different powers of $\epsilon$, which are functions of time, are of the same order in $\epsilon$ and remain of that order in the time scale we are considering. This is often the case when we consider short time processes, the expansions can, then, be truncated. However, for long times, it is more likely that some of the coefficients grow beyond bound and the perturbation method breaks down. To overcome such a difficulty, new parameters are introduced to allow for a more general time variation. Since the distribution functions have a larger domain of definition, new conditions are necessary to determine their functional dependence on such parameters. Frieman introduced such conditions by requiring that the expansion coefficients remain of the same order in $\epsilon$ in the time scale being considered. It turns out that such conditions lead directly to the kinetic equations.
required. The applicability of the perturbation method requires further study. We have given some simple examples in appendix D.

The method we use here is essentially a method of variations of parameters. We introduce the parameters $\Theta_r$, $r = 0, 1, 2, \ldots$, which are related to the variable $t$ by the following differential equations,

$$(III.1) \quad \frac{d\Theta_r}{dt} = \epsilon \tau, \quad \tau = 0, 1, 2, \ldots.$$ 

These give

$$(III.2) \quad \Theta_r(t) = \epsilon^r t + \Theta_r(t=0), \quad \tau = 0, 1, 2, \ldots.$$ 

The freedom in choosing the initial values $\Theta_r(0)$ allows us to treat the parameters $\Theta_r$ as independent variables. We try solutions of the form

$$(III.3) \quad f_i(t) = \sum_{i=0}^{\infty} \epsilon^i f_i^{(i)}(\Theta_0, \Theta_1, \Theta_2, \ldots) = \sum_{i=0}^{\infty} \epsilon^i f_i^{(i)}(\{\Theta_r\})$$

where the coefficients $f_i^{(i)}(\{\Theta_r\})$ have the properties that all $f_i^{(i)}(\{\Theta_r\})$, $i = 0, 1, 2, \ldots$, are of the same order in $\epsilon$, and their first derivatives $\frac{\partial f_i^{(i)}}{\partial \Theta_r}$, $i, r = 0, 1, 2, \ldots$, are also of the same order of magnitude in $\epsilon$.

The time derivative of $f_i(t)$ can now be written
Thus for time $t < T/\epsilon^m$, where $T$ is some finite time, we have

\begin{equation}
(\text{III.5}) \quad \frac{\partial f(\theta)}{\partial t} = \sum_{n=0}^{m} \epsilon^n \sum_{s=0}^{n} \frac{\partial f_1^{(n-s)}}{\partial \theta_s} \left\{ 1 + O(\epsilon) \right\}
\end{equation}

and

\begin{equation}
(\text{III.6}) \quad f_1(t) = \sum_{n=0}^{m} \epsilon^n f_1^{(a)}(\{\theta_i\}) \left\{ 1 + O(\epsilon) \right\}.
\end{equation}

Similar expressions can be obtained for $g, h, \text{etc.}$ Since the correlation functions $g, h, \text{etc.}$ are of the first order in $\epsilon$ as compared with the corresponding reduced distribution function (see appendix B), we write for $t < T/\epsilon^m$

\begin{equation}
(\text{III.7}) \quad f_1(t) = \sum_{i=0}^{m} \epsilon^i f_1^{(i)}(\{\theta_i\}),
\end{equation}

\begin{equation}
(\text{III.7}) \quad g = \sum_{i=1}^{m} \epsilon^i g^{(i)}(\{\theta_i\}),
\end{equation}

\begin{equation}
(\text{III.7}) \quad h = \sum_{i=1}^{n} \epsilon^i h^{(i)}(\{\theta_i\}), \quad \text{etc.}
\end{equation}
and
\[ \frac{\partial f^{(0)}}{\partial t} = \sum_{n=0}^{m} \epsilon^n \sum_{s=0}^{n} \frac{\partial f^{(n-s)}}{\partial \theta_s}, \]

(III.8)
\[ \frac{\partial g}{\partial t} = \sum_{n=1}^{m} \epsilon^n \sum_{s=0}^{n} \frac{\partial g^{(n-s)}}{\partial \theta_s}, \]
\[ \frac{\partial h}{\partial t} = \sum_{n=1}^{m} \epsilon^n \sum_{s=0}^{n} \frac{\partial h^{(n-s)}}{\partial \theta_s}, \]

etc.

We now proceed to solve the equations of the hierarchy for \( f_1(t) \). Since we have assumed that \( r_0/L \sim \epsilon^4 \), the spatial inhomogeneity of the gas is appreciable only in the fourth order in \( \epsilon \). Substituting the expansions (III.7) and (III.8) into (I.16) and (I.17), we obtain different sets of equations for different orders of approximation.

To study the approach to equilibrium of the gas, we must perform the calculation in such a way that the result is valid for times longer than the relaxation time \( \tau_r \) (\( \tau_r \sim \tau_c / \epsilon^2 \)).

Zeroth Order Approximation

To the lowest order in \( \epsilon \), equation (I.16) gives
\[(III.9) \quad \frac{\partial f^{(0)}}{\partial t} = \frac{\partial f^{(0)}}{\partial \theta_i} = 0.\]

In conformity with (II.19) this shows that any variation of \( f_1^{(0)} \) with time can be noticed in at most the
first order in $\epsilon$. Of course, to zeroth order in $\epsilon$, the correlation functions $g$, $h$, etc. can be neglected.

First Order Approximation

To the first order in $\epsilon$, equations (I.16) and (III.9) give

\[(\text{III.10}) \quad \frac{\partial \overline{f}_i^{(i)}}{\partial \theta} + \frac{\partial \overline{f}_i^{(o)}}{\partial \theta} = \frac{n}{m} \int d\xi d\xi' \frac{\partial V}{\partial x_j} \frac{\partial}{\partial x_j} \left[ f_i^{(i)}(\xi) f_i^{(o)}(\xi') \right] \]

\[= \frac{n}{m} \int d\xi' \frac{\partial}{\partial x_j} f_i^{(i)}(\xi) f_i^{(o)}(\xi') \int d\xi \left[ \frac{\partial V(x_1-x_2)}{\partial x_j} \right] \]

\[= \frac{n}{m} \int d\xi \frac{\partial}{\partial x_j} f_i^{(i)}(\xi) f_i^{(o)}(\xi) \int d\xi \left[ -\frac{\partial V(x)}{\partial x} \right] \]

\[= 0 \]

since $\int d\xi \frac{\partial V(x)}{\partial x} = 0$. Direct integration of (III.10) over $\theta$ gives

\[(\text{III.11}) \quad f_i^{(i)}(\theta) = f_i^{(i)}(\theta = 0) - \epsilon \frac{\partial f_i^{(o)}}{\partial \theta} \]

where we have used the fact that $f_i^{(o)}$ is independent of $\theta$. In order that $f_i^{(1)}(\theta)$ does not grow with $\theta$, we fix the functional dependence of $f_i^{(o)}$ on $\theta$ by
putting

\[(\text{III.12}) \quad \frac{\partial f^{(0)}}{\partial \theta_1} = 0.\]

This and (III.10) give

\[(\text{III.13}) \quad \frac{\partial f^{(1)}}{\partial \theta_0} = 0.\]

Hence, for \(t < \tau_c/\epsilon\), we obtain

\[(\text{III.13'}) \quad \frac{df}{dt} = \frac{\partial f^{(0)}}{\partial \theta_1} + \epsilon \left[ \frac{\partial f^{(0)}}{\partial \theta_1} + \frac{\partial f^{(0)}}{\partial \theta_0} \right] = 0.\]

To the same order in \(\epsilon\), equation (I.17) gives

\[(\text{III.14}) \quad \frac{\partial q^{(0)}}{\partial \theta_0} + (y - y_2) \frac{\partial q^{(0)}}{\partial x} = \frac{1}{m} \frac{\partial V}{\partial x} \partial_{ij} \left[ f^{(0)} f^{(0)} \right].\]

Equation (III.14) can be solved easily with the help of Fourier and Laplace transforms. We define the Fourier transform of a square integrable function \(F(x)\) as

\[(\text{III.15}) \quad \widetilde{F}(k) = \int dx \ F(x) e^{-ikx}.\]

The Laplace transforms of a function \(F(\theta_0)\) is defined
as

\[ F(z) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zt} \, dt. \]

where \( F(\theta) \) has been assumed to satisfy all the necessary properties of a Laplace transformable function and \( \text{Im}(z) > 0 \).

The transformed equation of (III.14) is given by

\[ (III.17) \quad -i z \tilde{f}^{(0)}(k z) - \tilde{g}^{(0)}(k \theta = 0) + ik \cdot (y_j - y_2) \tilde{f}^{(0)}(k z) \]

\[ = \frac{1}{m} \left( \frac{1}{iz} \right) \overline{V(k)} \cdot k \cdot \partial_{\theta} \left[ f_1^{(0)} f_1^{(0)} \right]. \]

Guided by Grad's theorem (see appendix C), we assume that the initial values of the correlations vanish. Hence \( \tilde{g}(t=0) \) and

\[ (III.18) \quad \tilde{g}(k \theta = 0) = 0, \]

and (III.17) gives:

\[ (III.19) \quad \tilde{f}^{(0)}(k z) = -\frac{1}{m} \frac{\overline{V(k)} \cdot k \cdot \partial_{\theta} \left[ f_1^{(0)} f_1^{(0)} \right]}{z \cdot [z - k \cdot (y_j - y_2)]}. \]

This gives

\[ (III.20) \quad \tilde{f}^{(0)}(k \theta) = \frac{1}{m} \overline{V(k)} k \cdot \partial_{\theta} \left[ f_1^{(0)} f_1^{(0)} \right] \cdot \frac{1 - e^{ik \cdot (y_j - y_2) \Theta}}{k \cdot (y_j - y_2)}. \]
Second Order Approximation

Equations (III.9), (III.12), (III.13) and (I.16) give

\[
\frac{\partial f^{(2)}}{\partial \theta_0} + \frac{\partial f^{(1)}}{\partial \theta_1} + \frac{\partial f^{(0)}}{\partial \theta_2} = \frac{n}{m} \int dx_2 dy_2 \frac{\partial V}{\partial x_1} \frac{\partial}{\partial y_1} \left[ f^{(2)}_1 f^{(0)}_1 f^{(1)}_1 + f^{(1)}_1 f^{(1)}_1 + g^{(0)} y_1 y_2 \right].
\]

Using the same argument as in the simplification of (III.10), this gives:

\[
\frac{\partial f^{(2)}}{\partial \theta_0} + \frac{\partial f^{(1)}}{\partial \theta_1} + \frac{\partial f^{(0)}}{\partial \theta_2} = \frac{n}{m} \int dx_2 dy_2 \frac{\partial V}{\partial x_1} \frac{\partial}{\partial y_1} g^{(0)} y_1 y_2.
\]

The Laplace transform of this gives

\[
-iz \tilde{f}_1^{(1)}(z) - f_1^{(2)}(z = 0) + \frac{i}{(iz)^2} \left[ \frac{\partial f^{(0)}_1}{\partial \theta_0} + \frac{\partial f^{(0)}_1}{\partial \theta_2} \right] = (2\pi)^3 \frac{n}{m} \int dk \ \tilde{V}(k) i^k \frac{2}{\partial x_1} \int dy_2 \ \tilde{g}^{(0)} y_1 y_2.
\]

It is obvious that on inverting \( f_1^{(2)}(z) \), the double pole at \( z = 0 \) will give a term proportional to \( \theta_0 \).

In order to remove such secular behaviour, we use the undetermined functional dependence of \( f_1^{(1)} \) and \( f_1^{(0)} \) on \( \theta_1 \) and \( \theta_2 \) respectively to eliminate the secular terms. We take the theorem...
(III.24) \[ \lim_{z \to 0} (-i z) \tilde{f}(z) = \lim_{\xi \to \infty} f(\xi) \]
as a guide for such a procedure.

Using (III.24), equation (III.23) gives

(III.25) \[ \lim_{\xi \to \infty} f^{(2)}(\xi) = f^{(2)}(\xi=0) + \lim_{z \to 0} \frac{1}{iz} \left\{ \left[ \frac{2f^{(0)}}{\partial \xi} + \frac{3f^{(0)}}{\partial \xi^2} \right] + (2\pi \frac{m}{m}) \int dk \overline{V}(k) \frac{2}{\partial \xi} \int d\epsilon_k (\xi) \tilde{f}(\xi, \epsilon_k, \epsilon_k, z) \right\} \]

Thus \[ f^{(2)}_1(\xi, \epsilon_k, \epsilon_k, \epsilon_k, z) = f^{(2)}_1(\xi=0) \] as \( \xi \to \infty \) if we put

(III.26) \[ \frac{2f^{(0)}}{\partial \xi} + \frac{3f^{(0)}}{\partial \xi^2} = (2\pi \frac{m}{m}) \int dk \overline{V}(k) \frac{2}{\partial \xi} \int d\epsilon_k \lim_{z \to 0} [iz \tilde{f}(\xi, \epsilon_k, \epsilon_k, z)] \]

We now use the Dirac relation

(III.27) \[ \lim_{\epsilon \to 0} \frac{1}{x \pm i \epsilon} = \frac{P}{x} + i \pi \delta(x) \]

This and (III.19) give

(III.28) \[ \lim_{z \to 0} (-i z) \tilde{f}^{(0)}(\xi, \epsilon_k, \epsilon_k, z) = \frac{1}{m} \lim_{z \to 0} \overline{V}(k) \left\{ \epsilon_k \frac{3}{2} \int f^{(0)}_1 f^{(0)}_2 \right\} \]
or

(III.28') \[ \lim_{z \to 0} (-i z) \tilde{f}^{(0)}(\xi, \epsilon_k, \epsilon_k, z) = \frac{1}{m} \overline{V}(k) \left\{ \frac{3}{2} \int f^{(0)}_1 f^{(0)}_2 \right\} \]

\[ \times \left\{ \frac{P}{k(\xi-\epsilon_k)} + i \pi \delta(k(\xi-\epsilon_k, ) \right\} \]
Substituting (III.28) into (III.26), we find that the integration over \( k \) of the first term on the right hand side of (III.28) vanishes since the integrand is an odd function of \( k \). Hence we have from (III.26)

\[
\text{(III.29)} \quad \frac{\partial f^{(0)}_1}{\partial \theta} + \frac{\partial f^{(0)}_2}{\partial \theta_2} = C \left[ f^{(0)}_1 f^{(0)}_2 \right]
\]

where

\[
\text{(III.30)} \quad C \left[ f^{(0)}_1 f^{(0)}_2 \right] = \left(2\pi\right)^{\frac{3}{2}} \frac{m}{\hbar^2} \int dk \left| \vec{N}(k) \right|^2 \frac{1}{2} \int d^2 x \frac{\partial}{\partial x_2} \left[ f^{(0)}_1 f^{(0)}_2 \right] \delta(\theta_1, \theta_2, \theta_3)
\]

Since \( f^{(0)}_1 \) is independent of \( \theta_2 \), we use the same argument as that following (III.11) and put

\[
\text{(III.31)} \quad \frac{\partial f^{(0)}_1}{\partial \theta_2} = C \left[ f^{(0)}_1 f^{(0)}_2 \right].
\]

This and (III.29) give

\[
\text{(III.32)} \quad \frac{\partial f^{(0)}_1}{\partial \theta} = 0.
\]

Substituting (III.26) into (III.22), we obtain

\[
\text{(III.33)} \quad \frac{\partial f^{(0)}_1}{\partial \theta} = \left(2\pi\right)^{\frac{3}{2}} \frac{m}{\hbar^2} \int dk (i \hbar \vec{N}(k)) \frac{1}{2} \int d^2 x \left\{ \tilde{f}^{(0)}(\theta_1, \theta_2, \theta_3) - \lim_{\theta \to 0} \left[ i \hbar \int \tilde{f}^{(0)}(\theta_1, \theta_2, \theta_3) \right] \right\}.
\]
where $\Gamma^{(0)}(-k, x_1, x_2, 0)$ and $\lim_{z \to 0} -iz \Gamma^{(0)}(-k, x_1, x_2, z)$ are given by (III.20) and (III.28). Using (III.24), (III.33) shows that

\[(\text{III.34}) \quad \lim_{\theta \to \infty} \frac{\partial f^{(2)}}{\partial \theta} = 0.\]

We now write down the equation for $f_1(t)$ for time $t < \tau_c/\varepsilon^2$. From (III.5), (III.13)', and (III.22), we obtain

\[(\text{III.35}) \quad \frac{\partial f_1}{\partial t} = \frac{\partial f^{(0)}}{\partial \theta} + \varepsilon \left( \frac{\partial f^{(0)}}{\partial \theta} + \frac{\partial f^{(0)}}{\partial \phi_2} \right) + \varepsilon^2 \left( \frac{\partial f^{(0)}}{\partial \theta} + \frac{\partial f^{(0)}}{\partial \phi_2} + \frac{\partial f^{(0)}}{\partial \phi_3} \right) \]

\[= \varepsilon^2 (2\pi)^2 \int \frac{dk}{k} \nabla (k) \cdot \frac{\partial}{\partial x_3} \int \frac{dx_2}{x_2} \Gamma^{(0)}(k, x_1, x_2, x_3) \]

which for $t \sim \tau_c/\varepsilon^2$ gives

\[(\text{III.36}) \quad \frac{\partial f_1}{\partial t} = \varepsilon^2 C \left[ f^{(0)}(1), f^{(0)}(2) \right].\]

Neglecting $O(\varepsilon^3)$, this gives

\[(\text{III.37}) \quad \frac{\partial f_1}{\partial t} = \varepsilon^2 C \left[ f^{(1)}(1), f^{(1)}(2) \right].\]

We have thus obtained for $f_1(t)$ an equation which is valid for times $t \sim \tau_r \sim \tau_c/\varepsilon^2$ since we have only performed the calculation up to the second order in $\varepsilon$. 
However, it is easily seen that for longer times $t > \tau$, equation (III.37) will only be modified by an amount of the order $\epsilon^3$. In fact, by removing the secular behaviour of the functions $f_i^{(1)}(\{\Theta_r\})$, we can fix the functional dependence of $f_i^{(1)}$ on $\Theta_r$ in such a way that all the derivatives $\frac{\partial f_i^{(1)}}{\partial \Theta_r}$ are of the same order in $\epsilon$. Thus adding higher order terms introduces correction terms at least $1/\epsilon$ times smaller.

It is interesting to see that equation (III.37) consists only of a binary collision term $\epsilon^2 C \left[ f_1^{(1)}, f_1^{(2)} \right]$ even though we have a moderately dense gas in which $nr_o^3 \sim 1$. This is in fact a consequence of the weak interaction between the particles.

Equation (III.37) is the Landau's equation (see Sandri 1963 and Balescu 1963) which has been studied in great detail by Balescu. It possesses the property of irreversibility as described by Boltzmann's H-theorem.
CHAPTER IV

CONCLUSION

We have followed Frieman's calculation and obtained an irreversible equation which describes the approach to thermal equilibrium of the gas by means of the nonlinear perturbation technique just described. In addition, we have estimated the relative orders of magnitude of the terms in the equations of the hierarchy and obtained conditions under which Landau's equation can be derived. Following Grad's approach, we have proved Grad's theorem (see appendix C) and added the physical conditions which allow the use of the theorem. Two examples have been given (see appendix D) to clarify the applicability of the perturbation technique.


van der Pol, Phil. Mag. 2, 978-992 (1926)

van der Pol, Phil. Mag. 2, 65-80 (1927)


Since our method relies on the knowledge of the relative orders of magnitude of the terms in the equations of the hierarchy, it is important to obtain a correct estimate of the former. Frieman has made such an estimate for the first two equations of the hierarchy. To do so, it is necessary to introduce some assumptions about the distribution functions. However, many of these assumptions do not appear clearly in Frieman's paper nor in Sandri's. We therefore find it necessary to re-examine the various terms in the equations and determine the necessary assumptions.

We assume that the gas is not too far from equilibrium. The s-particle distribution function may therefore be written as

\[ f_s(t, \ldots, s) = f_s^0(t, \ldots, s) \left[ 1 + g_s(t, \ldots, s) \right] \]  

where \( f_s^0(1, 2, \ldots, s) \) denotes the s-particle distribution at equilibrium, \( g_s(1, 2, \ldots, s) \) is a small quantity, and the derivatives \( \frac{\partial g_s}{\partial t}, \frac{\partial g_s}{\partial t}, \frac{\partial g_s}{\partial x}, \frac{\partial g_s}{\partial x}, \frac{\partial g_s}{\partial y}, \frac{\partial g_s}{\partial y} \) are assumed small compared with \( \frac{\partial f_s^0}{\partial t} \) and \( \frac{\partial f_s^0}{\partial x} \) respectively. To obtain an
explicit form of \( f^0_s(1, 2, \ldots, s) \), we first calculate the N-particle distribution function \( f^0_N(1, 2, \ldots, N) \) at equilibrium. The Hamiltonian for N-particles is given by

\[
H(\mathbf{z}, \mathbf{\nu}) = \sum_{i=0}^{N} \left\{ \frac{1}{2} m \nu_i^2 + \sum_{j > i}^{N} \bar{F}(z_i - z_j) \right\}
\]

Using a canonical ensemble, we find

\[
f^0_N(\mathbf{i}, \mathbf{\nu}) = \frac{1}{Z} e^{-\frac{H(\mathbf{z}, \mathbf{\nu})}{kT}}
\]

where \( k \) is the Boltzmann constant, \( T \) the temperature and \( Z \) the partition function given by

\[
Z = \int \int d\mathbf{z} \int d\mathbf{\nu} e^{-\frac{H(\mathbf{z}, \mathbf{\nu})}{kT}}
\]

The s-particle reduced distribution function \( f^0_s(1, 2, \ldots, s) \) is given by

\[
f^0_s(\mathbf{i}, \mathbf{\nu}) = S_s \int \int \int f^0_N(\mathbf{i}, \mathbf{\nu}) d\mathbf{z}_{\mathcal{S} \setminus \mathcal{I}} d\mathbf{\nu}_{\mathcal{S} \setminus \mathcal{I}} d\mathbf{\nu}_\mathcal{I}
\]

\[
= \frac{1}{Z} S_s \int \int \frac{1}{\prod_{i \in \mathcal{S} \setminus \mathcal{I}} d\mathbf{z}_i} d\mathbf{\nu}_\mathcal{I} e^{-\frac{H(\mathbf{z}, \mathbf{\nu})}{kT}}
\]

We now write
Equation (A.6) gives

\[
K = s^{-1} \sum_{i=1}^{s} z_i,
\]

\[
z_{ij} = z_i - z_j, \quad i, j = 1, 2, \ldots, s.
\]

Equation (A.2) gives

\[
\frac{\partial H}{\partial x_{i\alpha}} = \left( \frac{\partial}{\partial x_i} - \frac{\partial}{\partial x_{i\alpha}} \right) H
\]

\[
= \sum_{j \neq i}^{N} \frac{\partial \Phi(z_j)}{\partial x_{ij}} - \sum_{j \neq i}^{N} \frac{\partial \Phi(z_j)}{\partial x_{i\alpha}}
\]

and

\[
\frac{\partial H}{\partial y_{\alpha \alpha}} = m y_{\alpha \alpha}.
\]

Hence from (A.5), (A.7) and (A.8), we obtain

\[
\frac{\partial f_{s}}{\partial y_{\alpha \alpha}} = - \frac{S e^{S}}{kT} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\partial H}{\partial y_{\alpha \alpha}} f_{s} \prod_{i=s+1}^{N} d\xi_{i} d\eta_{i}
\]

\[
= - \frac{S m y_{\alpha \alpha}}{kT} f_{s}
\]

\[
\sim \langle v \rangle^{-1} f_{s},
\]

\[\alpha = 1, 2, \ldots, s,
\]

and

\[
\frac{\partial f_{s}}{\partial x_{i\alpha}} = S \int \int \frac{1}{kT} \frac{\partial H}{\partial x_{i\alpha}} f_{s} \prod_{i=s+1}^{N} d\xi_{i} d\eta_{i}
\]

\[
= S \sum_{j \neq i}^{N} \frac{1}{kT} \int \int \frac{\partial \Phi(z_{ij})}{\partial x_{ij}} f_{s} \prod_{i=s+1}^{N} d\xi_{i} d\eta_{i}.
\]
For \( \beta, j = 1, 2, \ldots, s \), we have

\[
(A.11) \quad \Omega^s \int \int \frac{\partial \Phi(x)}{\partial x_j} f_N^0 \, dx_1 \cdots dx_{s+1} \cdots dx_N \, dx = \frac{\partial \Phi(x)}{\partial x_j} f_\beta^0.
\]

We now assume that, because of the weakness of the interaction, the correlations are so small that the change in \( f_N \) with \( x_j \) within the range of the potential may be neglected. Thus we have for \( \beta = 1, 2, \ldots, s \) and \( j = s+1, \ldots, N \),

\[
(A.12) \quad \Omega^s \int \int \frac{\partial \Phi(x)}{\partial x_j} f_N^0 \, dx_1 \cdots dx_{s+1} \cdots dx_N \sim \frac{\langle \phi \rangle}{\rho_0} \left( \frac{e^3}{\Omega} \right) f_s^0.
\]

Using \( (A.11) \) and \( (A.12) \), \( (A.110) \) gives

\[
(A.13) \quad \frac{\partial f_s^0}{\partial x_\alpha} \sim \left[ S \frac{1}{k_\beta} \frac{\langle \phi \rangle}{\rho_0} + (N-s) \frac{\langle \phi \rangle}{\rho_0 k_\beta} \left( \frac{e^3}{\Omega} \right) \right] f_s^0
\]

\[
\sim \left[ S + (N-1) \left( \frac{e^3}{\Omega} \right) \right] \frac{\langle \phi \rangle}{\rho_0} \frac{1}{k_\beta} f_s^0, \quad \alpha = 1, \ldots, S.
\]

To estimate the magnitude of \( \frac{\partial f_s^0}{\partial x} \), we first consider \( f_N^0 \). From \( (A.2) \) and \( (A.3) \) we obtain the homogeneous property for \( f_N^0 \),

\[
(A.\#) \quad f_N^0(x_1, x_2, \ldots, x_N) = f_N^0(x_1, x_2, \ldots, x_N)
\]

where \( a \) is an arbitrary vector. Hence \( (A.5) \) and
(A.14) give

\[ f_s^o (x_1^s, x_2^s, \ldots, x_{s_i}^s, x_{s_j}^s) = \Omega^s \int d\xi_{s_i} d\nu_{s_j} d\nu_{s_k} \cdots d\nu_{s_p} f_N^o (x_{s_i}^s, x_{s_j}^s, x_{s_k}^s, \ldots, x_{s_p}^s) \]

\[ = \tilde{f}^s \int d\xi_{s_i} d\nu_{s_j} d\nu_{s_k} \cdots d\nu_{s_p} f_N^o (x_{s_i}^s, x_{s_j}^s, x_{s_k}^s, \ldots, x_{s_p}^s) \]

\[ = f_s^o (x_{s_i}, x_{s_j}, x_{s_k}, \ldots, x_{s_p}). \]

After changing variables according to (A.6), equation (A.15) gives

\[ f_s^o (X_{s_j}, y_{s_k}, \ldots, x_{s_p}) = f_s^o (X, y_{s_k}, \ldots, x_{s_p}) \]

where we have used the same symbol \( f_s^o \) to denote both the original and the transformed functions. Thus we have:

(A.17) \[ \frac{\partial f_s^o}{\partial X} = 0. \]

(A.18) \[ \left| \frac{\partial f_s}{\partial y_{s_k}} \right| \sim \left\langle \nu \right\rangle f_s, \quad \alpha = 1, \ldots, S, \]

(A.19) \[ \left| \frac{\partial f_s}{\partial y_{s_k}} \right| \sim \left[ s + (N-s) \left( \frac{r_0^2}{\Omega^2} \right) \right] \frac{\left\langle \nu \right\rangle}{m \nu^2} \frac{1}{r_0} f_s, \quad \alpha = 1, \ldots, S. \]

If we assume that \[ \left| \frac{\partial f_s}{\partial X} \right| \sim L^{-1}, \] we obtain from (A.1) and (A.17)
This, in fact, amounts to the definition of $L$. Using the results just obtained, we now estimate the relative orders of magnitude of the various terms in the equation

\[(A.21) \left[ \frac{\partial}{\partial t} + \sum_{j=1}^{S} \frac{y_j}{x_j} \frac{\partial}{\partial x_j} - \frac{1}{m} \sum_{j=1}^{S} \sum_{n \neq j}^{S} \frac{\partial \Phi (y_j - x_n)}{\partial x_j} \cdot \frac{\partial}{\partial x_j} \right] f_s \]

\[= \frac{N-s}{m \Omega} \int d \mathbf{x}_{\text{si}} d \mathbf{x}_{\text{si}} \sum_{j=1}^{S} \frac{\partial \Phi (y_j - x_n)}{\partial x_j} \cdot \frac{\partial f_{\text{si}}}{\partial x_j} . \]

In terms of the coordinates $X, x_{ij}, i,j = 1,2,\ldots$, as given in (A.6), equation (A.21) gives

\[(A.22) \left[ \frac{\partial}{\partial t} + \frac{V}{\partial X} + \sum_{j=2}^{S} \frac{(y_j - y)}{x_j} \frac{\partial}{\partial x_j} - \frac{1}{m} \sum_{j=1}^{S} \sum_{n \neq j}^{S} \frac{\partial \Phi (x_n)}{\partial x_j} \cdot \frac{\partial}{\partial x_j} \right] f_s \]

\[= \frac{N-s}{m \Omega} \int d \mathbf{x}_{\text{si}} d \mathbf{x}_{\text{si}} \sum_{j=1}^{S} \frac{\partial \Phi (y_j - x_n)}{\partial x_j} \cdot \frac{\partial f_{\text{si}}}{\partial x_j} , \]

where $V = s^{-1} \sum_{i=1}^{S} v_i$. From (A.17), (A.18) and (A.19), we have

\[(A.23) \frac{\partial f_s}{\partial t} \sim \frac{f_s}{\tau} , \]

\[(A.24) \frac{V}{\partial X} f_s \sim \frac{\langle v \rangle}{L} f_s . \]
Here we have used the fact that

\[
\int d\mathbf{x}_{\text{st}1} d\mathbf{y}_{\text{st}1} f_{s+1} \sim \int d\mathbf{x}_{\text{st}1} d\mathbf{y}_{\text{st}1} f_s^o
\]

\[
\left|\mathbf{x}_{\text{st}1} - \mathbf{y}_{\text{st}1}\right| < r_0
\]

\[
\sim \frac{r_0^3}{s_2} \int d\mathbf{x}_{\text{st}1} d\mathbf{y}_{\text{st}1} f_s^o
\]

\[
= \frac{r_0^3 f_s}{s_2}
\]

\[
\sim \frac{r_0^3 f_s}{s_2}
\]
The relative orders of magnitude of the various terms in (A.21) are

(A.28) \[ \frac{v_T}{L} : \frac{s + (n-s) \left( \frac{\beta_0^2}{2} \right)}{m v_T^2} : \frac{v_T}{\gamma_0} \]

In particular, in the limit \( N \to \infty, V \to \infty \), the equations for \( s = 1,2 \) give

(A.29) \[ \frac{v_T}{L} : \frac{\left( \frac{\beta_0}{m v_T} \right)}{\gamma_0} \]

(A.30) \[ \frac{v_T}{L} : \frac{\left( \frac{\beta_0}{m v_T} \right)}{\gamma_0} \]

(A.28) will be used as a guide in the discussion in chapter II.

It is important to see that (A.30) differs from Frieman's estimate,

(A.31) \[ \frac{v_T}{L} : \frac{v_T}{\gamma_0} : \frac{\beta_0}{m v_T^2} \]

In the third term which is supposed to give the order of magnitude of \( (v_1 - v_2) \). Since the gradient of \( f_2 \) with respect to the relative coordinate \( \bar{x} = x_1 - x_2 \) should depend on the magnitude of the interacting potential \( \Phi \), Frieman's result is incorrect.
APPENDIX B

ORDERS OF MAGNITUDE OF THE CORRELATION FUNCTIONS

We now estimate the orders of magnitude of the correlation functions assuming that $\frac{<\theta>}{m_n} \sim \frac{<\theta>}{kT} \sim \epsilon$ and that $N \gg s = O(1)$. The s-particle distribution function $f_s^0(1,2,\ldots,s)$ is given by

(B.1) $f_s^0(1,2,\ldots,s) = \frac{Z}{s!} \int d\vec{x}_{s+1} \ldots d\vec{x}_N f_0(d\vec{x}_1) d\vec{x}_N \ldots d\vec{x}_N e^{-\frac{1}{kT} \sum_{i=1}^{N} \left\{ \frac{1}{2} m v_i^2 + \sum_{j>i}^{N} E(\vec{x}_i, \vec{x}_j) \right\} - \frac{m}{2kT} \sum_{i=1}^{N} v_i^2 - \frac{1}{kT} \sum_{i=1}^{N-1} \sum_{j=1}^{i} E(\vec{x}_i, \vec{x}_j)}$

for $s = 1$, we have

(B.2) $f_1^0(1) = \left( \frac{m}{2\pi kT} \right)^\frac{3}{2} e^{-\frac{m v_1^2}{2kT}}$

Hence from (B.1) and (B.2), we obtain
The exponent of the integrand can be written in the following way

\begin{align*}
(B.4) \quad \frac{1}{kT} \left\{ \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \frac{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1} \sum_{i=1}^{N-1} \sum_{j=s+i}^{N} \sum_{n=1}^{N} \sum_{j=n+i+1}^{N} \sum_{i=1}^{S_{-1\}}

The integral in (B.3) then becomes
From (B.1), (B.3) and (B.5), we obtain

\begin{align*}
\text{(B.6)} & \quad \frac{\partial}{\partial s} \left( \sum_{i=1}^{N} \Phi(x_{i}) \right) - \sum_{i=1}^{N} \Phi(x_{i}) \left[ \sum_{i=1}^{N} \Phi(x_{i}) \right] = \left[ e^{-\frac{1}{kT} \sum_{i=1}^{N} \Phi(x_{i})} - 1 \right] \left[ \sum_{i=1}^{N} \Phi(x_{i}) \right] \left[ 1 + O(\epsilon) \right] \\
& = -\sum_{i=1}^{N} \Phi(x_{i}) \left[ \sum_{i=1}^{N} \Phi(x_{i}) \right] \left[ 1 + O(\epsilon) \right] \\
& = \sum_{i=1}^{N} \Phi(x_{i}) \left[ 1 + O(\epsilon) \right] \\
& = \frac{\partial}{\partial s} \left( \sum_{i=1}^{N} \Phi(x_{i}) \right) \left[ 1 + O(\epsilon) \right].
\end{align*}

Differentiating (B.6) with respect to \( x_{\alpha} \), we obtain

\begin{align*}
\text{(B.7)} & \quad \frac{\partial}{\partial x_{\alpha}} \left[ f_{s}^{o}(\cdot, s) - \frac{\partial}{\partial s} f_{s}^{o}(\cdot, s) \right] = \left\{ \begin{array}{ll}
\frac{f_{s}^{o}(\cdot, s)}{s} O(\epsilon^{2}) & \alpha \neq 1, \ldots, s-1 \\
\frac{f_{s}^{o}(\cdot, s)}{s} O(\epsilon) & \alpha = s.
\end{array} \right.
\end{align*}

We therefore obtain for \( g, h, \) etc. that
(B.8) \[ g(1,2) = f_1(u_2) O(\epsilon) = f_1(1) f_1(2) O(\epsilon), \]

(B.9) \[ h(1,2,3) = f_2(u_3,3) O(\epsilon) = f_1(1) f_1(2) f_1(3) O(\epsilon), \]

and

(B.10) \[ \frac{\partial g(1,2)}{\partial x_{12}} = \frac{1}{r_0} f_1(1) f_1(2) = g(1,2) \frac{1}{r_0} O(1), \]

(B.11) \[ \left| \frac{\partial h(1,2,3)}{\partial x_{12}} \right| = \frac{\partial h(1,2,3)}{\partial x_{12}} = \frac{h(1,2,3)}{r_0} O(1), \]

Differentiating (B.6) with respect to \( \nu \), we obtain

(B.12) \[ \frac{\partial}{\partial \nu} \left[ f_1^*(u_{1-2}) - f_2^*(u_{1-2}) f_2^*(v) \right] = -\frac{\Xi(x_{1-2})}{kT} \frac{\partial f_1^*(u_{1-2})}{\partial x_{1-2}} \]

\[ = \frac{f_1^*}{\langle v \rangle} O(\epsilon), \quad \nu = 1, \ldots, s. \]

Thus we have

(B.13) \[ \left| \frac{\partial g(1,2)}{\partial x_1} \right| \sim \left| \frac{\partial g(1,2)}{\partial x_2} \right| \sim \frac{g(1,2)}{\langle v \rangle}, \]

(b.114) \[ \left| \frac{\partial h(1,2,3)}{\partial x_1} \right| \sim \left| \frac{\partial h(1,2,3)}{\partial x_2} \right| \sim \left| \frac{\partial h(1,2,3)}{\partial x_3} \right| \sim \frac{h(1,2,3)}{\langle v \rangle}, \]

Finally, differentiating (B.8), (B.9) with respect to \( \mathbf{x} \) and using (A.20), and (B.6), we obtain
From these results, we may now estimate the orders of magnitude of the various terms in equation (I.17),

\[ \left[ \frac{\partial^2}{\partial t^2} + \frac{1}{2} (x_1 + x_2) \cdot \frac{2}{\partial x} + (y_1 - y_2) \cdot \frac{2}{\partial x} - \frac{1}{m} \frac{\partial^2}{\partial \xi^2} \cdot \partial_2 \right] g (t, x) \]

\[ = \frac{1}{m} \frac{\partial^2}{\partial \xi^2} \cdot 2 \cdot f_1 (t) f_2 (t) + \frac{1}{m} \int dx_1 dx_2 \left[ \frac{\partial^2}{\partial x_1} \cdot \partial_2 \right] [f_1 (t) g (x, 1, y)] \]

\[ + g (t, x) f_1 (t) + h (t, x, y)] \]

\[ - \frac{\partial^2}{\partial x_1} \cdot \frac{2}{\partial x_2} [f_1 (t) g (x, 1, y) + g (t, x) f_1 (t) + h (t, x, y)] \]

The left hand side may be estimated using (B.10), (B.11), (B.13), (B.14), (B.15) and (B.16). The integral term on the right hand side may be estimated from the results of (B.12), (A.27), (B.8) and (B.9). Thus the various terms in (I.17) bear the ratios

\[ (B.17) \quad \varepsilon : \varepsilon \frac{<v>T}{L} : \frac{\varepsilon}{\gamma_0} : \frac{\varepsilon}{\gamma_0} : \frac{\varepsilon}{\gamma_0} : \frac{\varepsilon}{\gamma_0} : \frac{\varepsilon}{\gamma_0} \]

This result will be used as a guide to solve equation (I.17) for $g$. 
Comparing (B.17) with (A.31), we see that they give exactly the same ratios. Thus Frieman's estimate given by (A.31) for the equation of \( f_2 \) (see (I.10)) actually gives the relative orders of magnitude of the terms in the equation of \( g \) (see I.17). It is therefore not surprising that he obtained the correct result in the calculation of \( g \) even though he had not made a similar estimate for the terms in the equation of \( g \).
APPENDIX C

GRAD'S THEOREM

In this appendix, we study Grad's theorem which states that if a distribution function is selected at random for a system of very many particles, it will in all likelihood satisfy the molecular chaos condition. We shall follow the proof due to H. Grad (1960).

I. The Coarse-graining

We consider the distribution function given in chapter I. For convenience, we introduce the following simplified notations

\[ x_i = (z_i, v_i) \]

\[ x = (z_1, \ldots, z_N, v_1, \ldots, v_N) \]

\[ f_N(x) = \frac{f_N(z_1, \ldots, z_N, v_1, \ldots, v_N)}{S} \]

The s-particle reduced distribution \( f_s \) defined in chapter I may now be written as (see I.5)

\[ f_s^{(w)}(x_1, \ldots, x_s) = \int (dx_1)^{N-s} (dx_s)^{N-s} f_N(x) \]

\[ S = 1, 2, \ldots, N-1, \]

where we have denoted \( f_s \) by \( f_s^{(N)} \) to emphasize the
dependence of $f_s$ on the number of particles $N$. We have omitted a factor $\mathcal{S}^s$ in (C.2) for convenience.

To investigate the behaviour of $f_s$ in the limit of large $N$, we study the sequence of functions $f_s^{(N)}$ with $N$ increasing towards infinity. However, one basic difficulty arises since we have to compare functions with different values of $N$ and hence different numbers of variables. It will be seen that such a difficulty is overcome if we use a coarse-grained distribution and make use of the symmetry of $f_N$.

We divide the 6-dimensional phase space of each particle into $r$ equal cells each of volume $\omega$. The cells in the phase space of the $i$th particle are labelled by the index $\xi_i$ which takes integral values $\xi_i = 1, 2, \ldots, r$, ($i = 1, 2, \ldots, N$), so that if the coordinates of the $i$th and $j$th particles are of the same values, they must fall in the cells $\xi_i$ and $\xi_j$ respectively with $\xi_i = \xi_j$. The 6N-dim. $\Gamma$-space for the $N$-particle system is therefore divided into $r^N$ cubes each having a volume $\omega^N$ of 6N-dimensions. We label such cubes by the set $\xi = (\xi_1, \ldots, \xi_N)$ and define the coarse-grained distribution

$$f_\xi = \int f(x) dx$$

(C.3)
where $\int_{\xi} (\ldots ) dx$ denotes the integration over the cube $\xi$. The normalization condition of $f_{\xi}$ is then given by

$$\sum_{\xi} f_{\xi} = \sum_{\xi} \int_{\xi} f_N(x) dx = \int f_N(x) dx = 1.$$  

Here $\sum_{\xi}$ is a summation over all cubes. For a given cube, we count the number $k_s$ of indices $\xi_1$ which are equal to $s$. $k_s$ therefore takes the integral values $k_s = 0, 1, 2, \ldots, N$ and

$$\sum_{s=1}^{t} k_s = N.$$  

By the symmetry of $f_N$, the value of the integral

$$\int_{\xi} f_N(x) dx$$  

is the same for all cubes $\xi$ which give the same set $k = (k_1, \ldots, k_r)$. We may therefore consider $f_{\xi}$ as a function of $k$. In fact, $f_{\xi}$ is the probability of finding $x_1, \ldots, x_N$ in the cell $\xi$ of the $\Gamma$-space. For convenience, we use the symbol $f(k)$ to represent such a function. We have therefore transformed the function $f_{\xi}$ of $N$ variables into the
function \( f(k) \) of \( r \) variables. It is then possible to investigate the limit of \( f_\xi \) as \( N \to \infty \) by studying the function \( f(k) \) in the \( k \)-space.

The transformation from the \( \xi \)-space into the \( k \)-space is not one-one. The number of points in the \( \xi \)-space which are mapped onto a given point in the \( k \)-space is

\[
(C.6) \quad \binom{N}{k} = \frac{N!}{k_1! k_2! \cdots k_r!}.
\]

From (C.4), we find

\[
(C.7) \quad \sum_\xi f_\xi = \sum_k \binom{N}{k} f(k) = 1.
\]

We now introduce the function

\[
(C.8) \quad F^{(N)}(k) = \binom{N}{k} f(k)
\]

which therefore obeys the normalization condition

\[
(C.9) \quad \sum_k F^{(N)}(k) = 1.
\]

The function \( F^{(N)}(k) \) may now be taken as the coarse-grained equivalent in \( k \)-space of the original distribution function \( f_N(x) \). Corresponding to the
transformation from the $\tilde{x}$-space into the k-space, there is a transformation mapping the $\Gamma$-space onto a single 6-dim. space which we shall call the $\mu$-space. The latter transformation is actually the result of mapping the 6-dim. spaces of all the N particles into the $\mu$-space. Thus for each point in the $\Gamma$-space, there are N points in the $\mu$-space each of which corresponds to the coordinates of an individual particle. We divide the $\mu$-space in exactly the same way as before into r equal cells of volume $\omega$. The function $P^{(N)}(k)$ may now be interpreted as the probability of obtaining $k_1, \ldots, k_r$ particles with coordinates in the cells 1, 2, \ldots, r respectively.

For a symmetric function $\overline{\Phi}(x)$, the mean value is given by

\begin{equation}
\langle \overline{\Phi} \rangle = \int \overline{\Phi}(x) f_N(x) \, dx.
\end{equation}

\text{(C.10)}

If we neglect the variation of $f(x)$ in each cube, we obtain the coarse-grained equivalent

\begin{equation}
\langle \overline{\Phi} \rangle = \sum_{\xi} \overline{\Phi}_{\xi} \int_{\xi} f(x) \, dx
\end{equation}

\text{(C.11)}

\begin{align*}
&= \sum_{\xi} \overline{\Phi}_{\xi} f_{\xi} \\
&= \sum_{k} \overline{\Phi}(k) F^{(N)}(k)
\end{align*}
where \( \overline{\varphi} \) stands for the volume average of \( \varphi(x) \) over the cube \( \xi \), that is

\[
\text{(C.12)} \quad \overline{\varphi}(k) = \overline{\varphi}_\xi = \omega^{-N} \int_\xi \varphi(x) \, dx.
\]

Consider the one-particle distribution

\[
\text{(C.13)} \quad f_1(x_1, t) = \int dx_2 \ldots dx_N \, f_N(x)
\]

\[
= \int dx'_1 dx_2 \ldots dx_N \, \delta(x'_1 - x_1) \, f_N(x)
\]

\[
= \int dx'_1 dx_2 \ldots dx_N \{N^{-l} \sum_{i=1}^N \delta(x'_i - x_i)\} \, f_N(x)
\]

\[
= \langle \overline{\varphi}_1 \rangle
\]

where

\[
\text{(C.14)} \quad \overline{\varphi}_1 = N^{-l} \sum_{i=1}^N \delta(x'_i - x_i).
\]

Thus \( f_1(x_1, t) = f_1(x_1, v_1, t) \) is just the mean value of \( \overline{\varphi}_1 \). The volume average of \( \overline{\varphi}_1 \) over the cube \( \xi \) is

\[
\text{(C.15)} \quad \overline{\varphi}(x) = \omega^{-N-l} \sum_{i=1}^N \int_\xi \delta(x'_i - x_i) \, dx'_1 dx'_2 \ldots dx'_N.
\]

If we assume that the coordinates \( x_1 = (x_1, v_1) \) lie in
the cell $\xi_1 = s$, we obtain

\begin{equation}
\int \delta(x_i' - x_1') \, dx' = \begin{cases} 
0 & \text{if } \xi_i \neq s, \\
\omega_n^s & \text{if } \xi_i = s.
\end{cases}
\end{equation}

Thus the expression $\sum_{i=1}^{N} \int \delta(x_i' - x_1') \, dx'$ merely counts the number $k_s$ of indices $\xi_i$ which are equal to $s$. (C.15) therefore gives:

\begin{equation}
\overline{\Phi}(x_i) = \overline{\Phi}(k, s) = \omega^s \left( \frac{k}{N} \right).
\end{equation}

The coarse-grained equivalent of $f_1(x_1, t)$ for $x_1$ lying in the cell $\xi_1 = s$ is

\begin{equation}
F_1(s) = \omega \sum_k \overline{\Phi}(k, s) f(k) = \left( \frac{k}{N} \right)
\end{equation}

which satisfies the normalization condition

\begin{equation}
\sum_{s=1}^{n} F_1(s) = 1.
\end{equation}

Here $\sum_{s=1}^{n}$ is a summation over all the cells of the 6-dim. phase space of the 1st particle. The function $F_1(s)$ may be interpreted as the probability of having the coordinates of a particle in the $s$th cell of the $\mu$-space.
Similarly, the two-particle distribution

\[
 f_2(x_1, x_2, t) = \int dx' f_N(x') \delta(x'_1 - x_1) \delta(x'_2 - x_2)
\]

is the mean value of the function

\[
 f_2 = \int dx' \left[ \omega^N \right]^{-1} \sum_{i \neq j} \delta(x'_1 - x_1) \delta(x'_2 - x_2) f_N(x')
\]

The volume average of \( f_2 \) is given by

\[
 \bar{f}_2 = \left[ \omega^N \right]^{-1} \sum_{i \neq j} \delta(x'_1 - x_1) \delta(x'_2 - x_2)
\]

\[
 \bar{f}_2 (k, s, t) = \left[ \omega^2 N(N-1) \right]^{-1} \left\{ \begin{array}{ll}
 k_s k_t, & \text{if } s \neq t;
 k_s (k_s - 1), & \text{if } s = t.
\end{array} \right.
\]

Here \( s \) is the cell containing \( x_1 \) and \( t \) is the cell containing \( x_2 \). The coarse-grained equivalent of \( f_2(x_1, x_2, t) \) is therefore given by

\[
 \bar{f}_2 (s, t) = \left[ N(N-1) \right]^{-1} \left\{ \begin{array}{ll}
 <k_s k_t>, & \text{if } s \neq t;
 <k_s (k_s - 1)>, & \text{if } s = t.
\end{array} \right.
\]

This is the probability of having \( k_s \) and \( k_t \) particles.
in the \( s \)-th and \( t \)-th cells respectively of the \( \mu \)-space. Similarly for \( f_3(x_1, x_2, x_3, t) \), we have

\[
\begin{align*}
(C.24) \quad f_3(x_1, x_2, x_3, t) &= \int dx'_1 \cdots dx'_N f_N(x'_1, x'_2, x'_3, x'_4, x'_5, \ldots, x'_N, t) \\
&= \int dx'_N(x') \delta(x'_1-x_1) \delta(x'_2-x_2) \delta(x'_3-x_3) \\
&= \int dx'_N(x') \left[ N(N-1)(N-2) \right]^2 \\
& \quad \times \sum_{i=1}^N \sum_{j \neq i} \sum_{k \neq i} \delta(x'_i-x_1) \delta(x'_j-x_2) \delta(x'_k-x_3).
\end{align*}
\]

and the corresponding quantity

\[
(C.25) \quad \overline{f_3}(s, t, u) = \left[ N(N-1)(N-2) \right]^{-1} \left\{ \begin{array}{ll}
k_s k_t k_u, & \text{if } s \neq t \neq u, \\
k_s (k_t-1) k_u, & \text{if } s = t \neq u, \\
k_s (k_t-1)(k_u-1) & \text{if } s = t = u.
\end{array} \right.
\]

Here \( s, t \) and \( u \) are the cells containing \( x_1, x_2 \) and \( x_3 \) respectively. The coarse-grained equivalent of \( f_3(x_1, x_2, x_3, t) \) is then given by
II. Molecular Chaos

We wish to show in this section that the molecular chaos condition is satisfied as $N$ becomes large, or more precisely,

$$F_2(s,t) - F_1(s)F_1(t) = O\left(\frac{1}{N}\right).$$

For convenience, we change the variables $k_s$ into $y_s = k_s/N$ and use the same symbol for $F_1^N(k)$ as a function of $y$. That is, we denote $F_1^N(ny) = F_1^N(k)$ by $F_1^N(y)$. From (C.18) and (C.23), and the assumption that $k_s/N = O(1)$, which means that the density is everywhere nonzero, we obtain for $s \neq t$,

$$F_2^N(s,t) - F_1^N(s)F_1^N(t) = \left[N(N-1)\right]^{-1}\left(\begin{array}{c} <k_s k_t k_u> \\ > \end{array}\right) \text{ if } s \neq t \neq u,
\left(\begin{array}{c} <k_s (k_{s-1}) k_u> \\ > \end{array}\right) \text{ if } s = t \neq u,
\left(\begin{array}{c} <k_s (k_{s-1}) (k_{s-2})> \\ > \end{array}\right) \text{ if } s = t = u.$$
and for $s = t$,

\[
\begin{align*}
(C.28) \quad F_2(s,s) - F_1(s)F_1(s) &= \left[ N(N-1) \right]^{-1} \left\{ k_s(k_s-1) \right\} - N^{-2} k_s^2 \\
&= N^{-2} \left\{ k_s^2 - k_s \right\} \left\{ 1 + O\left(\frac{1}{N}\right) \right\} - N^{-2} k_s^2 \\
&= N^{-2} \left\{ k_s^2 - k_s \right\} + N^{-2} k_s^2 \cdot O\left(\frac{1}{N}\right) \\
&\quad - N^{-2} k_s \cdot \left\{ 1 + O\left(\frac{1}{N}\right) \right\} \\
&= N^{-2} \left\{ k_s^2 - k_s^2 \right\} + O\left(\frac{1}{N}\right) \\
&= \left< y_s^2 \right> - \left< y_s \right>^2 + O\left(\frac{1}{N}\right).
\end{align*}
\]

Thus $F_2(s,t) - F_1(s)F_1(t)$ approaches zero if $\left< y_s y_t \right> - \left< y_s \right> \left< y_t \right>$ tends to zero in the limit of large $N$. The expression

\[
\sum_{s,t} = \left< y_s y_t \right> - \left< y_s \right> \left< y_t \right>
\]

is in fact the covariance matrix (see Anderson, 1958) of $F^{(N)}(y)$. That is
The right hand side of (C.29) approaches zero if \( F^{(N)}(y) \) becomes peaked and approaches a \( \delta \)-function in the limit of large \( N \). Thus if \( F^{(N)}(y) \) is a \( \delta \)-function which is peaked at \( y^0 = (y_1^0, y_2^0, \ldots, y_r^0) \), we have

(C.30) \[ \Sigma_{st} = y_s^0 y_t^0 - y_s^t y_t^0 = 0. \]

To study the properties of \( F_1(s) \), \( F_2(s,t) \), etc. for large \( N \), we investigate the properties of \( F^{(N)}(y) \) in the limit \( N \to \infty \) keeping \( r \) fixed. In doing so, we study \( F^{(N)}(y) \) as function of a fixed number of variables.

To agree with physical situations, we take the usual thermodynamic limit,

(C.31) \[
\begin{cases}
N \to \infty, \\
\Omega \to \infty, \\
\frac{N}{\Omega} = n \text{ a finite constant.}
\end{cases}
\]

Then in the coarse-graining procedure, we choose \( \omega \) of macroscopically small dimensions and yet large enough to be regarded infinite in the microscopic scale. For a system whose density is nonzero everywhere in the volume \( \Omega \), a spatial volume corresponding to a volume \( \omega \) in the \( \mu \)-space already contains a large
number of particles. This ensures that the numbers $k_1, k_2, \ldots, k_r$ of particles in the cells $1, 2, \ldots, r$ of the $\mu$-space are so large that approximate calculation based on large numbers, such as the Stirling's formula, may be used.

By definition, we have

$$F^{(w)}(y) = F^{(w)}(k) = \binom{N}{k} f(k).$$ \hfill (C.32)

This does not approach a limit as $N \to \infty$. To investigate $F^{(N)}(y)$ in such a limit, we first consider the distribution of a system of $N$ independent particles in a volume $\Omega$ having a finite density everywhere in $\Omega$. The distribution function may be written as $f_N(x) = f_1(x_1)f_1(x_2)\ldots f_1(x_N)$. Putting $f_1(x_1) = p_s$ where $s = \xi_i$, we find

$$f_\xi = \int f(x) \, dx$$

$$= \frac{k_1 k_2 \ldots k_r}{p_1 p_2 \ldots p_r}.$$ \hfill (C.33)

The values of $p_s$, $s = 1, 2, \ldots, r$, are finite if the cells $\xi_i$ have been chosen large enough. From (C.32) and (C.33), we obtain
\[ F^{(\omega)}(y) = \left( \begin{array}{c} N \\ k \end{array} \right) \prod_{s=1}^{r} p_s^{k_s} \]

which is obviously a coefficient of the multinomial expansion

\[ (p_1 + p_2 + \cdots + p_r)^N = \sum_{\sum k_s = N} \frac{N!}{k_1! k_2! \cdots k_r!} p_1^{k_1} p_2^{k_2} \cdots p_r^{k_r}. \]

This and the normalization condition of \( F^{(N)}(y) \) give

\[ \sum_{s=1}^{r} p_s = 1. \]

Differentiating (C.35), we obtain

\[ \langle k_s \rangle = N p_s, \]

\[ \langle k_s k_t \rangle = N(N-1) p_s p_t, \quad s, t = 1, \ldots, r. \]

Thus the covariance matrix defined in (C.29) is given by

\[ \sum_{st} = \langle y_s y_t \rangle - \langle y_s \rangle \langle y_t \rangle = \frac{N(N-1)}{N^2} p_s p_t - p_s p_t = p_s p_t O\left( \frac{1}{N} \right). \]
This tends to zero as \( N \to \infty \). The distribution (C.34) is therefore peaked at \( y_s = p_s \), \( s = 1,2, \ldots, r \) as \( N \to \infty \).

To obtain the limit of \( F^{(N)}(y) \), we first consider its maximum which is given by the maximum coefficient of the multinomial expansion (C.35) and satisfies the inequalities

(C.39) \[ N^{\frac{1}{s}} - 1 < k_s \leq (N + r - 1)^{\frac{1}{s}}, \quad i = 1, 2, \ldots, r, \]

(see W. Feller, 1957). Putting

(C.40) \[ k_s = N^{\frac{1}{s}} + l_s, \quad s = 1, 2, \ldots, r, \]

(C.39) gives

(C.41) \[ -1 < l_s \leq (r - 1)^{\frac{1}{s}}, \quad i = 1, 2, \ldots, r, \]

Also from (C.5) and (C.36), we obtain

(C.42) \[ \sum_{s=1}^{r} l_s = o. \]

Since \( r, p_s \) are finite, (C.40) and (C.41) ensure that the \( l_s \) are finite and the \( k_s \) become large as \( N \) tends to infinity. Using the Stirling's formula \( N! = \sqrt{2\pi N} \left(\frac{N}{e}\right)^N \), we obtain
(C.43) \[ k_s! = \sqrt{2\pi k_s} \left( \frac{k_s}{e} \right)^{k_s} \]

\[ \approx \sqrt{2\pi N k_s} \left( \frac{N k_s}{e} \right)^{N k_s + k_s} \]

Substituting (C.43) into (C.34), the maximum of \( F^{(N)}(y) \) gives

(C.44) \[ F^{(N)}(y) = \frac{N!}{\prod_{s} k_s!} \prod_{s} \frac{p_s^{k_s}}{k_s} \]

\[ = \frac{\sqrt{2\pi N}}{\prod_{s=1}^{r} \left( \sqrt{2\pi N k_s} \left( \frac{N k_s}{e} \right)^{N k_s + k_s} \right)} \]

\[ = \frac{\left( \sqrt{2\pi N} \right)^{-r}}{\prod_{s=1}^{r} \frac{1}{k_s^{\frac{1}{2}}} \frac{p_s^{k_s}}{k_s}} \]

We now consider another example in which the system has a uniform distribution. In this case, \( f(x) \) is a constant and

(C.45) \[ f_k = \int f(x) dx = (\frac{\omega}{t})^N = p^N \]

This and (C.32) give

(C.46) \[ F^{(\omega)}(y) = \binom{N}{k} p^k p_s^{k_s} \ldots p_r^{k_r} \]

Comparing (C.46) and (C.34), we find that the former may be obtained from the latter by putting \( p_s = p \), \( s = 1, 2, \ldots, r \). Thus the distribution (C.46) gives
results similar to the ones first discussed.

From the previous two examples, we expect that the limit \( \lim_{N \to \infty} \left[ F^{(N)}(y) \right]^{1/N} \) exists for a reasonable distribution \( f(x) \). For example, it is reasonable to assume that this is true for a distribution which is not too far from being uniform or a distribution in which the correlations between particles are not too large. We therefore consider distributions for which the function \( \left[ F^{(N)}(y) \right]^{1/N} \) approaches a limit uniformly

\[(C.47) \quad \lim_{N \to \infty} \left[ F^{(n)}(y) \right]^{1/N} = \psi(y)\]

Our aim is now to study the behaviour of \( F^{(N)}(y) \) when \( f(k) \) is "randomly" chosen among those which give definite limits for \( \left[ F^{(N)}(y) \right]^{1/N} \). To do so, we first prove the following theorem.

**Theorem.** If the function \( \psi(y) \), which is the limit of the sequence \( \left[ F^{(N)}(y) \right]^{1/N} \), attains its maximum at a single point \( y^0 \), then \( F^{(N)}(y) \) becomes peaked in the limit of large \( N \).

From \((C.32)\), we see that \( F^{(N)}(y) \) takes discrete values as the discrete variables \( y_1, y_2, \ldots, y_r \) assume values from \( 0, 1/N, 2/N, \ldots, (N-1)/N \). However, as \( N \to \infty \), it is convenient and reasonable to consider \( F^{(N)}(y) \) and hence \( \psi(y) \) as continuous functions of the continuous
variables $y_1, y_2, \ldots, y_r$. We may therefore integrate with respect to the $y_i$ rather than sum. In fact, the summation over consecutive values of $y_i$ may be written as

\[(c.48) \quad \sum_y N^r \int dy_1 \ldots dy_r = N^r \int dy\]

as $N \rightarrow \infty$.

We assume that $\psi(y)$ attains a maximum at

$y^0 = (y^0_1, y^0_2, \ldots, y^0_r)$ such that $\psi(y^0) - \psi(y) > 0$ for $y \neq y^0$. To show that $F(N)(y)$ is peaked at $y^0$, we choose an arbitrary region $R: |y - y^0| < \eta$. We wish to show that the integral of $F(N)(y)$ outside this region becomes arbitrarily small compared to the sum inside the region if $N$ is chosen sufficiently large.

In the region $R'$ which is the whole region outside $R$, we have $\psi(y) < \psi(y^0) (1 - \alpha)$ for some $\alpha$, $0 < \alpha < 1$. Within the region $R$, a small subregion of volume $V$ may be found such that $\psi(y) > (y^0) (1 - \tfrac{1}{2} \alpha)$. Thus we have

\[(c.49) \quad \int_R [\psi(y)]^N dy > (1 - \frac{\alpha}{2})^N [\psi(y^0)]^N V,
\]

and

\[(c.50) \quad \int_{R'} [\psi(y)]^N dy < (1 - \alpha)^N [\psi(y^0)]^N.
\]
By definition of uniform convergence, we have

\[(C.51) \quad \left| \left( F^{(n)} \right)^{1/N} - \gamma(y) \right| < \epsilon \]

for any $\epsilon > 0$ and all sufficiently large $N$. This gives

\[(C.52) \quad (1 - \epsilon)^N [\gamma(y)]^N < F^{(n)}(y) < (1 + \epsilon)^N [\gamma(y)]^N. \]

Choosing $\epsilon = \frac{1}{N}$, and using $(C.49)$, $(C.50)$ and $(C.52)$, we find

\[(C.53) \quad \sum_{y \in R} F^{(n)}(y) = N^T \int_{dy} F^{(n)}(y) > N^T (1 - \frac{\alpha}{N})^N \int_{R} dy [\gamma(y)]^N \geq N^T (1 - \frac{\alpha}{N} + \frac{1}{N} \alpha - 1) [\gamma(y)]^N. \]

Since $F^{(n)}(y)$ is positive definite and normalized, we have $N^T \int_{R} dy F^{(n)}(y) \leq 1$ and the right hand side of $(C.53)$ is bounded. For the region $R'$, we have

\[(C.54) \quad \sum_{y \in R'} F^{(n)}(y) = N^T \int_{R'} dy F^{(n)}(y) < N^T (1 + \frac{\alpha}{N})^N \int_{R'} dy [\gamma(y)]^N. \]
By inspection we see that the integration of \( F^{(N)}(y) \) over the outer region \( R' \) is arbitrarily small compared to that over the inner region \( R \) as \( N \) becomes large. We have therefore proved that \( F^{(N)}(y) \) is peaked and approaches a \( \delta \)-function at \( y^0 \) if \( \psi(y) \) attains a single maximum at the same point. We have thus proved the theorem.

Combining the previous results, we see that the molecular chaos condition is satisfied asymptotically if the function \( \psi(y) \) attains its maximum at a single point. We now show that this situation is very likely among functions chosen "at random". It is possible to study the situation from the theory of measure, but we shall be content to examine it on intuitive grounds. Since it is very difficult to draw conclusions on merely continuous functions, we shall examine smooth functions.

It is reasonable to assume that \( \psi(y) \), as the limit of \( [F^{(N)}(y)]^{1/N} \), is smooth and has continuous second derivatives. For simplicity in argument, we consider \( y \) as a single variable. First we argue that it is very unlikely that \( \psi(y) \) attains a maximum on a whole linear segment. If \( \psi(y) \) has maxima of equal
values at several points which are separated by small but finite segments, the maxima would give a maximum at which the first and second derivatives of $\psi(y)$ vanish. The same result is true if there is a point of accumulation of maxima. Finally, if $\psi(y)$ has a finite number of maxima, it would be unlikely, on intuitive grounds, that several of such maxima are equal. Thus it is reasonable to assume that $\psi(y)$ attains a maximum at a single point.
APPENDIX D

FURTHER DISCUSSION ON THE PERTURBATION METHOD

We have already obtained a kinetic equation using the perturbation technique. By removing the secular behaviour in the perturbation expansions, we have found that without initial correlations a weakly coupled gas approaches equilibrium through the interactions between the gas particles. However, it is important to ensure that the removal of secular behaviour does not eliminate the possibility of obtaining equations which do not give a final equilibrium state. The study in this aspect of the perturbation method has not been found in the literature. We shall content ourselves by considering a few examples.

We now attempt to solve the following equation

\[ \frac{d^2f}{dt^2} - k^2 f = \varepsilon R^2 f \]  

with the initial conditions

\[ f(t=0) = a, \]
\[ \frac{df}{dt} \bigg|_{t=0} = b, \]

where K, R, a, b are constants, K/R = O(1), and \( \varepsilon \ll 1 \) is
a dimensionless parameter. Equation (D.1) can be easily solved by ordinary methods and the solution is

\[ f(t) = \frac{1}{2} \left\{ a + \frac{b}{\sqrt{k^2 R^2}} \right\} e^{(k^2 R^2)^{1/2} t} + \frac{1}{2} \left\{ a - \frac{b}{\sqrt{k^2 R^2}} \right\} e^{-(k^2 R^2)^{1/2} t} = A e^{(k^2 R^2)^{1/2} t} + B e^{-(k^2 R^2)^{1/2} t} \]

We shall now solve (D.1) using the perturbation method described in chapter III. We obtain from (D.1)

\[ \frac{\partial^2 f^{(n)}}{\partial \theta_0^2} - k^2 f^{(n)} = 0, \]

\[ \{2 \frac{\partial^2 f^{(n)}}{\partial \theta_0^2 \partial \theta_1^2} + \frac{\partial^2 f^{(n)}}{\partial \theta_0^2} \} - k^2 f^{(n)} = R f^{(n)} \]

\[ \left\{ \frac{\partial^2 f^{(n)}}{\partial \theta_1^2} + 2 \frac{\partial^2 f^{(n)}}{\partial \theta_0 \partial \theta_1} + 2 \frac{\partial^2 f^{(n)}}{\partial \theta_0^2} \right\} - k^2 f^{(n)} = R f^{(n)} \]

for zeroth, first and second order in \( \epsilon \) respectively. They are therefore valid for times \( t \sim T, T/\epsilon, T/\epsilon^2 \) respectively where \( T \) is some finite characteristic time given by \( T = 1/K \). Thus for \( t \sim T \), we obtain from (D.4)

\[ f^{(0)} = A_0 e^{k \theta_0} + B_0 e^{-k \theta_0} \]

where \( A_0, B_0 \) are approximately constant in times \( t \sim T \). For longer times \( t \sim T/\epsilon \), \( A_0, B_0 \) are functions of \( \theta_1 \).
and we have to solve equation (D.5). Substituting (D.7) into (D.5), we find

\begin{equation}
(D.8) \quad \left( - \frac{\partial^2 f^{(4)}}{\partial \theta^2} - k^2 f^{(4)} \right) = R^2 f^{(4)} - 2 \left( \frac{\partial^2 f^{(3)}}{\partial \theta^2} \right) \frac{\partial f^{(3)}}{\partial \theta} \frac{\partial^2 f^{(3)}}{\partial \theta^2} \\
= R^2 \left[ A_0(q_1) e^{k_0} + B_1(q_1) e^{-k_0} \right] - 2k \left[ \frac{\partial A_0(q_1)}{\partial q_1} e^{k_0} - \frac{\partial B_1(q_1)}{\partial q_1} e^{-k_0} \right]
\end{equation}

This gives

\begin{equation}
(D.9) \quad f^{(4)} = A_0(q_1) e^{k_0} + B_1(q_1) e^{-k_0} \\
+ R^2 \left[ A_0(q_1) e^{k_0} B_1(q_1) e^{-k_0} \right] - 2k \left[ \frac{\partial A_0(q_1)}{\partial q_1} e^{k_0} + \frac{\partial B_1(q_1)}{\partial q_1} e^{-k_0} \right]
\end{equation}

In order that \( f^{(1)} \) and \( f^{(0)} \) should be of the same order in \( \epsilon \), \( f^{(1)} \) should not grow faster than \( e^{k \theta} \). Thus we must put

\begin{equation}
(D.10) \quad - \frac{\partial A_0(q_1)}{\partial q_1} + \frac{R^2}{2k} A_0(q_1) = 0,
\end{equation}

which gives

\begin{equation}
(D.11) \quad A_0(q_1) = A_0(q_1 = 0) e^{\frac{R^2}{2k} q_1}
\end{equation}

The coefficient \( B_0(q_1) \) needs not be restricted since
it does not give rise to secular behaviour. However, for convenience, we may arbitrarily put

$\frac{\partial B_{\phi}(\theta)}{\partial \theta} - \frac{R^2}{2k} B_{\phi}(\theta) = 0$

giving

$B_{\phi}(\theta) = B_{\phi}(\theta=0)e^{-\frac{R^2}{2k} \theta}$

which decays in time. Thus for times $t \sim T/\epsilon$, the solution of (D.1) is given by

$\phi(t) = \phi^{(0)}(\theta, \theta) + \epsilon \phi^{(1)}(\theta, \theta) + \cdots$

$= A e^{(k + \frac{er^2}{2k})t} + B e^{-(k + \frac{er^2}{2k})t}$

This is exactly the same as the result obtained from (D.3) after neglecting $O(\epsilon^2)$ in the exponents. To obtain the solution of $f(t)$ for longer times, we may continue the calculation up to higher orders in $\epsilon$.

The approximation of the perturbation method to this equation leads to the correct result in spite of the presence of terms that grow without bound with time.

In order to show that there are problems where the perturbation method is not applicable because it cannot remove the secular behaviour of some terms,
we consider the equation

(D.15) \[ \frac{df}{dt} - kf = \epsilon L^2 t f \]

where \( K, L \) are constants. It is easy to see that this gives a solution

(D.16) \[ f(t) = f(t=0) e^{kt + \epsilon \frac{L^2 t^2}{2}}. \]

Solving this with our perturbation method, we obtain

(D.17) \[ \frac{\partial f^{(0)}}{\partial \theta_0} - kf^{(0)} = 0, \]

(D.18) \[ \frac{\partial f^{(1)}}{\partial \theta_0} + \frac{\partial f^{(0)}}{\partial \theta_1} - kf^{(1)} = L^2 \theta_0 f^{(0)}, \]

(D.19) \[ \frac{\partial f^{(2)}}{\partial \theta_0} + \frac{\partial f^{(1)}}{\partial \theta_1} + \frac{\partial f^{(0)}}{\partial \theta_2} - kf^{(2)} = L^2 \theta_0 f^{(1)} \text{ etc.} \]

Thus (D.17) gives

(D.20) \[ f^{(0)}(\theta_0) = C_0 e^{k \theta_0}. \]

Substituting this into (D.18), we find

(D.21) \[ \frac{\partial f^{(1)}}{\partial \theta_0} - kf^{(1)} = (L^2 \theta_0 - k) C_0 e^{k \theta_0}. \]
This gives

\[(D.22) \quad f''(\theta) = C_1 e^{k\theta} + \left( \frac{1}{2} l^2 \theta^2 - k \theta \right) C_0 e^{k\theta} \]

\[= C_1 e^{k\theta} + \theta \left( \frac{1}{2} l^2 \theta - k \right) f'(\theta) \]

It is easy to see that \(f^{(1)}(\theta_0)\) cannot remain of the same order in \(\varepsilon\) as \(f^{(0)}(\theta_0)\) for times longer than \(T/\varepsilon\) where \(T = K/L^2\). In fact for \(t \sim K/\varepsilon L^2\), we have

\[(D.23) \quad f^{(0)}(\theta_0) \sim \varepsilon^{-1} f^{(0)}(\theta) \]

and we can no longer neglect higher order terms in the expansion of \(f(t)\).