Recent Work

Title
STATISTICAL THEORY OF NONLINEAR EFFECTS IN THE POLARIZATION OF AN IMPERFECT GAS

Permalink
https://escholarship.org/uc/item/9gv1r7gg

Author
Klauder, Louis Thornton.

Publication Date
1964-07-24
Statistical Theory of Nonlinear Effects in the Polarization of an Imperfect Gas

Two-Week Loan Copy

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

STATISTICAL THEORY OF NONLINEAR EFFECTS
IN THE POLARIZATION OF AN IMPERFECT GAS

Louis Thornton Klauder, Jr.
(Ph. D. Thesis)

July 24, 1964

Reproduced by the
Technical Information Division
directly from author's copy
CONTENTS

Abstract, p. 3.

I. Introduction, p. 4.

II. Review of Basic Formulae:
   A. Formulae for ensemble averages, p. 8.
   B. The Kaufman - Watson approximation to the activity expansion for the log of the grand partition function, p. 11.
   C. Supplements to the Kaufman - Watson theory of the dielectric constant, p. 15.

III. Quadratic Electrostriction:
   A. The formula for the density in the cluster chain approximation, p. 17.
   B. Comparison with thermodynamics, p. 43.
   C. The physical significance of the chemical potential, p. 50.

IV. Cubic Polarization:
   A. The formula for the cubic polarization in the cluster cross approximation, p. 55.
   B. Physical interpretation of the one molecule contribution, p. 72.
   C. Formula for gas of fixed density in a uniform field, p. 78.

V. Summary, p. 81.

Acknowledgements, p. 83.
CONTENTS, Continued

Appendices:

A. Dielectric boundary effect, p. 84.
B. Nonlocal effect, p. 89.
C. Correction to intuitive approach, p. 94.
D. Hugenholtz theorem, p. 96.
F. Definition of the macroscopic electric field, p. 99.

References, p. 100.
This thesis presents relatively systematic derivations of useful formulae for the electrostriction and the nonlinear polarization in a gas of neutral molecules. The derivations begin with the definitions from quantum statistical mechanics for the grand ensemble averages of the two quantities in question, and the resulting formulae are obtained by means of a method devised by A. N. Kaufman and K. M. Watson.
I. INTRODUCTION

This thesis presents derivations of physically useful formulae for the electrostriction and the nonlinear polarization in an imperfect gas of neutral molecules. The derivations begin with the definitions from quantum statistical mechanics for averages with respect to the grand canonical ensemble, and the definitions are transformed into useful formulae by means of the method which was developed by A. N. Kaufman and K. M. Watson in two papers which will be referred to as K.W.I and K.W.II.

One feature of this method is that it begins with an expansion in powers of the chemical activity. T. L. Hill has also given a statistical treatment of polarization which is based on the grand ensemble and on an expansion in powers of the activity. The treatment in K.W.I and K.W.II differs from that of Hill by deriving a quantum mechanical prescription for each coefficient in the activity expansion and by going on from this prescription to evaluate explicitly the effect of the long range dipole - dipole interactions in the dielectric. The average effect of the long range interactions is that the field experienced by clusters of molecules in the interior of the dielectric is neither the field $E_0$ due to external charges, nor the average electric field, $E$. 
but rather the so-called effective field, \( \mathbf{E} = \mathbf{E} + \frac{4\pi}{3} \mathbf{P} \).

This fact has been known from an intuitive point of view for a long time; the treatment in K.W.II defines its validity in a systematic way. The definitions which are given by Hill for the coefficients of the activity expansion are the recursive ones which arise by simple mathematics from transformation of a certain power series. The recursive definitions do not lend themselves to any physical treatment of the clusters of molecules which they represent. Correspondingly, Hill does not sum up the effect of the long range interactions, so that his results picture the clusters as being acted on by \( E_0 \) rather than by \( \mathbf{E} \). Thus, while his results are mathematically correct, from a physical point of view they are inappropriate. (This objection does not apply to the thermodynamic part of Hill's treatment.)

There have been a number of attempts to describe the polarization of a gas on the assumption that each molecule has a moment equal to the polarizability of an isolated molecule times the field due to external charges and to the moments of the other molecules. However, the molecules of a gas are sometimes close together, and the polarizability of a close pair cannot be calculated from the polarizability of a single molecule. In order to take account of this fact within the framework of a description based on the concept of single molecule polarizability, Jansen and Mazur have proposed the point of view that the polarizability of a molecule is
modified by neighboring molecules and have tried to make the single molecule polarizability a function of density in such a way that this effect is properly incorporated. However, if in looking for the effective polarizability of a molecule one looks for its average with respect to all configurations of the molecules of the gas, then the effective polarizability can only be written down to the extent that the whole problem has been solved already. The approach taken by Jansen and Mazur was to look for the effective polarizability of one molecule with all the other molecules at definite positions. But the effect of the long range interactions can only be added up explicitly when there is an average over molecular configurations. Thus in the treatment of Jansen and Mazur, the effect of the long range interactions is spread out over an infinite series from which only a few terms can be incorporated into the calculation of the effective polarizability. It may be noted by way of contrast that the treatment in K.W.I and K.W.II includes this effect automatically and correctly.

There is a nice paper by Buckingham and Pople giving a result which is largely equivalent to that in K.W.II. However, the treatment is intuitive rather than deductive in that the role of the effective field is assumed rather than demonstrated.

The main way in which the treatment in K.W.I and K.W.II differs from earlier treatments is that it is based on a systematic method of treating grand ensemble averages for
gases in which dipole interactions are the dominant long range interactions. Because of this fact the method given in K.W.I and K.W.II is just as suitable for calculation of electrostriction, nonlinear polarization, pressure, force density, etc. as it is for the calculation of the linear polarization which was given in K.W.II. It may also be noted that these calculations should be done in a certain order and that one must use the result for the linear polarization in order to complete the treatment of the other effects.

The only other systematic statistical treatment of electrostriction of which the author is aware is that in the paper by Hill \(^3\), and Hill's treatment of electrostriction suffers from the same deficiency as was mentioned above regarding his treatment of polarization. The author is not aware of any other systematic statistical treatment of the part of the polarization which is proportional to the cube of the electric field.

Following the calculation of the electrostriction it is shown that the result is related to the result for the susceptibility in the manner which thermodynamics requires. Following the treatment of the part of the polarization which is proportional to the cube of the electric field it is shown that the result is physically reasonable.
II. REVIEW OF BASIC FORMULAE

A. Formulae for Ensemble Averages

The goal of the theory is to obtain useful formulae for ensemble averages of the electrical polarization, \( P(\sigma) \), the density of molecules, \( n(\bar{\sigma}) \), etc. The averages are based on the grand canonical ensemble in which it is the chemical potential, \( \mu \), rather than the average number of molecules, \( \langle N \rangle \), which is an independent variable. By definition,

\[
\langle P(\sigma) \rangle = \frac{1}{\beta} \sum_{N} \frac{e^{\beta \mu N}}{N!} \text{tr} \left[ P(\sigma) e^{-\beta H(N)} \right] \quad (II - 1)
\]

where

\[
\beta \equiv \sum_{N} \frac{e^{\beta \mu N}}{N!} \text{tr} \left[ e^{-\beta H(N)} \right] \quad (II - 2)
\]

\( H(N) \) is the total Hamiltonian for \( N \) molecules (all assumed to be of one kind) in a given volume, and the factor of \( N! \) is included because we consider the molecules to be distinguishable.

One of the terms in \( H(N) \) is the operator for the interaction of the \( N \) molecules with \( E_0(\sigma) \), the electric
field produced in the volume by charges extraneous to the
gas itself. Since each molecule is assumed to be neutral
and since \( \mathbf{E}_0(r) \) is assumed to be nearly constant in the
region occupied by a single molecule, this interaction may
be taken to be the dipole interaction,

\[
- \int d^3\mathbf{r}' \quad \mathbf{P}(\mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}')
\]  \hspace{1cm} (II - 3)

where

\[
\mathbf{P}(\mathbf{r}') \equiv \sum_{k=1}^N \mathbf{p}_k \delta(\mathbf{r}' - \mathbf{r}_k)
\]  \hspace{1cm} (II - 4)

is the operator for the polarization (dipole moment density)
in the gas and where \( \mathbf{p}_k \) is the operator for the dipole moment
of the \( k \) th molecule. The external field enters \( \mathcal{H}(\mathbf{N}) \) only
through the term (II - 3) so we consider this term as a
perturbation and write

\[
\mathcal{H}(\omega) = \mathcal{H}_0 - \int d^3\mathbf{r}' \quad \mathbf{P}(\mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}')
\]  \hspace{1cm} (II - 5)

We introduce \( \frac{\delta}{\delta \mathbf{E}_0(\mathbf{r})} \) as the symbol for functional differentiation
such that

\[
\frac{\delta}{\delta \mathbf{E}_0(\mathbf{r})} \int d^3\mathbf{r}' \quad \mathbf{P}(\mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}') = \mathbf{P}(\mathbf{r})
\]  \hspace{1cm} (II - 6)

Then
\[
\frac{\delta}{\delta E_0(R)} \left[ \ln \frac{1}{Z} \right] = \frac{1}{\beta} \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \left[ E_0 - \int dR' g(R') Q(R') \right]^k
\]

and although \( P \) and \( H_0 \) do not commute, the value of the trace is not altered by cyclic permutations of the operators so that in each term the free factor of \( P \) may be brought to one side. The series may then be resummed, and (II - 8) becomes

\[
\beta \left[ \frac{1}{\beta} \ln Z \right]
\]

From this it follows that

\[
\langle P(R) \rangle = \frac{1}{\beta} \frac{\delta}{\delta E_0(R)} \ln Z
\]

Suppose that we are interested in the average of some quantity, call it \( Q(R) \), which does not appear in the Hamiltonian. We then introduce the modified Hamiltonian,

\[
\mathcal{H}'(N) \equiv H(N) - \frac{1}{\beta} \int d^3R' Q(R') g(R')
\]

where \( g(R) \) is a function which we can vary at will, and the modified partition function
\[ \mathcal{Z} = \sum_{\mathcal{N}} \frac{e^{\beta \mu \mathcal{N}}}{\mathcal{N}!} \text{tr} \ e^{-\beta \mathcal{Z}(\mathcal{N})} \]  
(II – 12)

Then

\[ \langle Q(\mathcal{B}) \rangle = \lim_{\delta \to 0} \frac{\delta}{\delta q(\mathcal{B})} \ln \mathcal{Z}, \]  
(II – 13)

as the reader may verify.

B. The Kaufman-Watson Approximation to the Activity Expansion for the Log of the Grand Partition Function

K.W.I \(^1\) is devoted to the derivation of an expansion for the logarithm of the grand partition function. The result obtained there is that

\[ \ln \mathcal{Z} = \sum_{m=1}^{m} \frac{e^{\beta \mu \mathcal{L}_m}}{m!} \text{tr} \ e^{-\beta \mathcal{H}(m)} \]  
(II – 14)

where \( \text{tr} e^{-\beta \mathcal{H}(m)} \) stands for a certain limited part of \( \text{tr} e^{-\beta \mathcal{H}(m)} \), the trace being evaluated for a gas of \( m \) molecules in the given volume and subject to \( E_0(\mathcal{B}) \). Just what part this is can be stated after \( \text{tr} e^{-\beta \mathcal{H}(m)} \) has been reexpressed by means of the development which follows.

We assume the states \( \lambda_i \rangle \) as eigenstates of the free molecule Hamiltonian for molecule \( i \) and assume that they are antisymmetric in the electron variables and that they form
a complete set of states for molecule $i$. We then form the product states

$$|\Lambda\rangle \equiv \prod_{i=1}^{m} |\lambda_{i}\rangle$$  \hspace{1cm} (II - 15)

Since the product states are not antisymmetric with respect to the coordinates of electrons from different molecules, we imagine a unitary transformation to a basis which consists of a complete set of antisymmetric states for the $m$ molecules plus additional states which are not completely antisymmetric.

We then employ the projection operator,

$$A \equiv \frac{1}{(mZ)!} \sum_{\alpha} \delta_{\alpha} P_{\alpha}$$  \hspace{1cm} (II - 16)

where $Z$ is the number of electrons per molecule, $\sum_{\alpha}$ is over all permutations of the $mZ$ electrons, $P_{\alpha}$ is the operator which performs permutation $\alpha$, and $\delta_{\alpha} = 1$ if $\alpha$ is even and $-1$ if $\alpha$ is odd. The operator $A$ eliminates all $m$ molecule states which are not fully antisymmetric and leaves just the states which should appear in the trace. Thus,

$$\text{tr} e^{-\beta H^{(m)}} = \sum_{\Lambda} \langle \Lambda | A e^{-\beta H^{(m)}} A |\Lambda\rangle$$  \hspace{1cm} (II - 17)

Since $H^{(m)}$ is invariant under electron permutations we can bring one $A$ factor past $H^{(m)}$. We then have a factor $A^2$, but $A^2 = A$, as one may check from the definition. Thus,
where we have written $|\Lambda(o)\rangle$ to indicate the original labeling of the particle coordinates in $|\Lambda\rangle$ and where $|\Lambda(x)\rangle = P_{\alpha} |\Lambda(o)\rangle$.

Now for permutations $\alpha$ among the electrons within a single molecule,

$$\delta_\alpha |\Lambda(x)\rangle = \delta_\alpha^2 |\Lambda(o)\rangle = |\Lambda(o)\rangle \quad (II - 19)$$

Thus (II - 18) may be written

$$\text{Tr} e^{-\beta H(m)} = \frac{(Z!)^m}{(mZ)!} \sum \sum \delta_\alpha \langle \Lambda(x) | e^{-\beta H(m)} | \Lambda(o) \rangle \quad (II - 20)$$

where $\sum_\alpha$ is now only over assignments of coordinate labels to whole molecules and does not involve any permutations of coordinates within molecules.

It is necessary at this point to assume that the temperature is low enough so that the ensemble average number of molecules which are ionized is negligibly small. This assumption is needed so that the states $|\lambda_i\rangle$ in $|\Lambda\rangle$ may be restricted in (II - 20) to bound states only.

However, the preceding sentence is meant only figuratively. Namely, if we consider two molecules, a and b, there are combinations of continuum states for molecule a which localize one of its electrons about molecule b and vice
versa, and combinations of this sort give contributions which are equal to the normal bound state contributions. Thus, if we restrict the states \(|\lambda\rangle\) in \(|\Lambda\rangle\) to bound states only, we must also put in a factor \((mZ)!/(Z!)^m\) to compensate for loss of combinations of continuum states which have the effect of reassigning the electrons to molecules in all possible ways. Thus, \((II-20)\) becomes

\[ \text{tr} e^{-\beta H(m)} = \sum_{\Lambda} \sum_{\alpha} \sum_{\sigma} <\Lambda(\alpha)| e^{-\beta H(m)} |\Lambda(\sigma)> \quad (II - 21) \]

with \(|\Lambda\rangle\) now containing only bound states. This paragraph clarifies an aspect of K.W.I. which is somewhat obscure and misleading. The author does not know of any way to avoid the foregoing approximation or of any way to obtain a systematic improvement of it.

While the preceding approximation is frustrating because of its unsystematic nature, it does make it possible to introduce a perturbation expansion which would be divergent if the approximation had not been made, namely

\[ e^{-\beta H(m)} = \frac{1}{2\pi i} \int d\omega \ e^{-\beta \omega} \frac{1}{\omega-H(m)} \quad (II - 22) \]

\[ = \frac{1}{2\pi i} \int d\omega \ e^{-\beta \omega} \left\{ \frac{1}{\omega-H_0} + \frac{1}{\omega-H_0} \sqrt{\frac{1}{\omega-H_0}} + \cdots \right\} \quad (II - 23) \]

where

\[ H_0 \equiv \sum_{i=1}^{m} h_i \quad (II - 24) \]
is the sum of the free molecule Hamiltonians for the molecules of the gas and where

\[ V = \sum_{i,j, j < i} V_{ij} + \sum_i V_i \]  

(II - 25)

is the sum of the intermolecular interactions and the interactions of the molecules with the external field and where the complex variable \( w \) is integrated about a contour which encloses the spectrum of \( H(m) \) in the positive sense. Our final result is thus that

\[ \text{tr} e^{-\beta H(m)} = \sum_A \sum_\alpha \delta_\alpha \frac{1}{2\pi i} \int dw e^{\beta w} \cdot \cdot \cdot \]

\[ \cdot \langle \Lambda (\alpha) \mid \left\{ \frac{1}{w-H_0} + \frac{1}{w-H_0} V \frac{1}{w-H_0} + \cdots \right\} \Lambda (\alpha) \rangle. \]

(II - 26)

We may now state the result obtained in K.W.I; it is that

\[ \text{tr} e^{-\beta H(m)} \]

is equal to the sum of those terms on the right hand side of (II - 26) in which each molecule is linked to every other molecule either by a single interaction or exchange or by a sequence of interactions and or exchanges involving intermediate molecules.

C. Supplements to the Kaufman - Watson Theory of the Dielectric Constant

The derivation of the formula for the part of \( \langle \rho(R) \rangle \)
which is proportional to \( E_0(R) \) is explained in K.W.II .

However, the treatment in K.W.II is incomplete in that it does not indicate how the distance \( R_0 \) is to be chosen. (The interaction between two molecules is not treated as a dipole - dipole interaction unless the molecules are separated by at least \( R_0 \).) Appendix A of this thesis presents a calculation which indicates that \( R_0 \) should be made equal to the mean intermolecular distance. There are two other appendices which also present supplements to the work of Kaufman and Watson. Appendix B gives a derivation of the effect of field inhomogeneity on the cluster chain contribution to the polarization. Appendix C corrects the physical interpretation which was given in a third paper \(^6\) by Kaufman and Watson.
III. QUADRATIC ELECTROSTRICION

A. The Formula for the Density in the Cluster Chain Approximation

The ensemble average of the density, \( n(R) \), is defined by equations (II - 11), (II - 12), and (II - 13) with \( Q(R) \) replaced by \( n(R) \). Therefore, in order to obtain a formula for \( \langle n(R) \rangle \) we must first obtain an expression for

\[ \ln \mathcal{J} = \sum_{\mathcal{N}} \frac{e^{\beta \mathcal{J}_N}}{\mathcal{N}!} \mathcal{J}_N = \mathcal{J} \exp \left\{ -\beta \mathcal{H}(N) + \mathcal{S} d^3 R_n g(R) \right\} \]

(N - 1)

Now

\[ n(R) \equiv \sum_{i=1}^{\mathcal{N}} \delta (R - R_i) \]

(N - 2)

so that

\[ \mathcal{S} d^3 R' n(R') g(R') = \sum_i g(R_i) \]

(N - 3)

Since the terms which in this way are added to the Hamiltonian refer only to single molecules and do not link molecules together, we may group \( g(R_i) \) with the free molecule Hamiltonian for molecule \( i \). The derivation of the linked cluster expansion...
for \( \ln \gamma' \) may then be carried through exactly as was done in K.W.I for \( \ln \gamma \). We may thus write

\[
\ln \gamma' = \sum_m \frac{e^{\beta \mu_m}}{m!} \ln \gamma' \frac{-\beta \gamma' e^{\gamma'}}{m}
\]

(III - 4)

with the linked trace as explained in section B of Chapter II.

With this result, the definition (II - 13) takes the form

\[
\langle n(g) \rangle = \lim_{g \to 0} \frac{\delta}{\delta g(g)} \sum_m \frac{e^{\beta \mu_m}}{m!} \ln \gamma' \frac{-\beta \gamma' e^{\gamma'}}{m} \exp \left\{ -\beta H(m) + \int d^3 \gamma' n(\gamma') g(\gamma') \right\}
\]

(III - 5)

If the molecular center-of-mass motion were being treated classically, the functional differentiation could be performed directly in the usual way. Now, eventually we will assume that the molecular center-of-mass motion is classical, but it will be profitable at this point to forego that assumption and to proceed as follows. Introducing a Laplace transform and a Born expansion we write

\[
\ln \gamma' \exp \left\{ -\beta H(m) + \int d^3 \gamma' n(\gamma') g(\gamma') \right\}
\]

(III - 6)

\[
= \frac{1}{2\pi i} \int dw \ e^{\beta w} \ln \gamma' \frac{-\beta \gamma' e^{\gamma'}}{m} \left[ w - H(m) + \frac{1}{\beta} \int d^3 \gamma' n(\gamma') g(\gamma') \right]^{-1}
\]

(III - 7)

\[
= \frac{1}{2\pi i} \int dw \ e^{\beta w} \ln \gamma' \frac{-\beta \gamma' e^{\gamma'}}{m} \left[ \frac{1}{w - H(m)} - \frac{1}{w - H(m)} \frac{1}{\beta} \int d^3 \gamma' n(\gamma') g(\gamma') \frac{1}{w - H(m)} \right]
\]

(III - 8)

The first term of the Born series is eliminated by the
functional differentiation, and the third and higher terms are eliminated by the passage to the limit. The second term is left as

\[
\lim_{\delta \to 0} \frac{\delta}{\delta q(z)} \quad \text{tr} \quad \exp \left\{ -\beta H(m) + \int d^3 x' \eta(x') \delta(q) \right\} 
\]

(III - 9)

\[
= -\frac{1}{\beta} \frac{i}{2\pi i} \int dw e^{\beta w} \quad \text{tr} \quad \left[ \frac{i}{w-H(m)} n(q) \frac{1}{w-H(m)} \right] 
\]

(III - 10)

\[
= \frac{1}{\beta} \frac{i}{2\pi i} \int dw e^{\beta w} \quad \text{tr} \quad \frac{2}{\delta w} \left[ n(q) \frac{1}{w-H(m)} \right] 
\]

(III - 11)

\[
= \frac{1}{2\pi i} \int dw e^{\beta w} \quad \text{tr} \quad \left[ n(q) \frac{1}{w-H(m)} \right] 
\]

(III - 12)

\[
= \text{tr} \quad \left[ n(q) e^{-\beta H(m)} \right] 
\]

(III - 13)

the next to last step having been achieved through integration by parts. When we now put in the remaining factors from (III - 5) we get

\[
\langle n(q) \rangle = \sum_{m} \frac{e^{\beta H(m)}}{m!} \quad \text{tr} \quad \left[ n(q) e^{-\beta H(m)} \right] 
\]

(III - 14)

We may note that (III - 14) is exact except for the error which arises because continuum states are excluded from the trace (as explained in chapter II) and because we ignore the interaction of the molecules with the radiation field. In particular, (III - 14) includes contributions proportional to \((E_0)^0\), \((E_0)^2\), \((E_0)^4\), etc. The part of
\[ \langle n(R) \rangle \text{ which is independent of } E_0 \] is independent of position, and we will call it \( n_0 \). Our attention will be focused in this chapter on the part of \( \langle n(R) \rangle \) which is proportional to \( (E_0)^2 \), and we will call this part \( n_2(R) \).

For the discussion of any average involving long range electrical interactions we need to group the molecules into clusters exactly like those which were introduced in K.W.II for the treatment of \( \langle P(R) \rangle \). In order for this to be done it is necessary that each molecule have a definite position, and the position of (the center-of-mass of) each molecule is made definite when its center-of-mass motion is treated classically.

To make the transition one replaces the sum over center-of-mass states for molecule \( i \), \( (i = 1, 2, \ldots, m) \) by the factors \( \frac{1}{\hbar^3} \int d^3R_i \int d^3p_i \), where the center-of-mass position, \( R_i \), is integrated over the volume of the gas, and the center-of-mass momentum, \( p_i \), is integrated over all of momentum space. The momentum \( p_i \) occurs in the integrand only in the factor \( \exp[-\beta_{RI}^2/2m] \), so the \( p_i \) integration may be carried out and contributes a factor of \( (2\pi mkT)^{3/2} \).

Then introducing a thermal wave length,

\[ \lambda \equiv \frac{\hbar}{(2\pi mkT)^{1/2}} \quad \text{(III - 15)} \]

(III - 14) becomes
where we have introduced the symbol

\[ H(R^m) \equiv H(m) - \sum_{i=1}^{m} \frac{1}{2m} p_i^2. \]  

(III - 17)

We are now ready, following K.W. II, to group the molecules into clusters. It will be recalled from part B of the preceding chapter that the linked trace is a sum of linked terms and that a linked term can have any number of interactions and or exchanges as long as each molecule in the term can be connected in at least one way to every other molecule by an uninterrupted sequence of interactions and or exchanges. For any given linked term in the perturbation series (II - 26) we now define clusters by the rule that any two molecules which interact directly must be in the same cluster if they are separated spatially by a distance smaller than \( R_0 \). (The clusters are not to be any larger than this rule requires.)

So, given a particular linked term, the grouping into clusters is determined by the molecular configuration, and different parts of the integral \( \int d^3 R^m \) over molecular configurations will give rise to different groupings into clusters.

We assume some particular linked term of (II - 26) and some particular configuration of molecular positions so that the molecules are grouped into clusters in some definite way. Let the number of clusters be \( C \) and let the clusters be
labeled from 1 to C. Let us denote the free cluster Hamiltonian for cluster \( \delta \) by

\[
 k_\delta = \sum_i \left( h_i - \frac{1}{Z_m} E_i \right) + \sum_{i,j} V_{ij} \tag{III - 18}
\]

where \( \sum_i \) means that the index \( i \) is summed over the molecules in cluster \( \delta \), \( h_i \) is the free molecule Hamiltonian for molecule \( i \), and \( V_{ij} \) is the electrostatic interaction between molecules \( i \) and \( j \). Further, let

\[
 K \equiv \sum_\delta k_\delta \tag{III - 19}
\]

and let

\[
 V_{\delta \epsilon} \equiv \sum_\delta \sum_\epsilon V_{ij} \tag{III - 20}
\]

be the interaction between cluster \( \delta \) and cluster \( \epsilon \), and let

\[
 V_\delta \equiv \sum_i V_i \tag{III - 21}
\]

be the interaction of cluster \( \delta \) with \( E_0 \). The Hamiltonian for all \( m \) molecules may then be written

\[
 H(R^m) = K + \sum_{\delta < \epsilon} V_{\delta \epsilon} + \sum_\delta V_\delta \tag{III - 22}
\]
We may now shift our attention from the perturbation expansion of \( (II - 26) \), in which the individual molecules are the objects in view, to the expansion which comes from treating

\[
\sum_{\delta < \epsilon} V_{\delta \epsilon} + \sum_{\delta} V_{\delta} \quad (III - 23)
\]
as the perturbation and in which it is the clusters which are the objects in view. In order for a term in this new series to be linked, it is necessary that the \( C \) clusters be linked together. We will take care of this linkage, by considering only those terms of the new expansion which have the clusters linked together, and we will sometimes speak of those terms as linked terms. Since for the time being we are not expanding with respect to interactions and exchanges between molecules within individual clusters, we retain a linkage symbol, \( L \), as a reminder that eventually there must also be an expansion with respect to the interactions within a cluster and a retaining of only those terms in which all of the molecules of the cluster are linked together.

We next consider how the clusters should be linked together and how they should be linked to \( E_0 \).

First, the linkages between clusters must be electrical because we assume that the mean intermolecular distance \( R_0 \) is large enough so that exchange across the distance \( R_0 \) is negligible. (When the density is high enough so that
this assumption does not hold, then the basic activity expansion
does not converge quickly enough to be physically useful.)

Second, in each cluster, each electric multipole which
interacts at all must interact at least twice. Interaction via
one irreducible multipole moment does not orient a molecule
with respect to any of its other moments. Thus, the average,
over orientations, of an interaction via a moment will vanish
unless the average is weighted by at least one other interaction
via the same moment.

Third, we limit our attention to those linkage arrange-
ments which use as few linkages as possible to get the clusters
linked. In other words, for linking \( C \) clusters, we permit only
\( C-1 \) intercluster interactions. We will show by an estimate to
be given later that cluster figures having more than the minimum
number of intercluster linkages give a contribution which is
smaller than the ones which we are evaluating.

Fourth, we assume that the clusters interact only via
their dipole moments. The contribution involving quadrupole
moments depends on the inhomogeneity of the field, and we will
show by another later estimate that it is also smaller than the
contributions we are evaluating.

Fifth, we are interested in terms which have two inter-
actions with \( E_0 \) because these are the only ones which
contribute to \( n_2(H) \).

The foregoing five statements serve to determine the
kind of linkage arrangement which we need to work with. This
may be seen as follows. Take one of the two clusters with an
(blank)

(The numbers which follow were born by deleted equations.)

(III - 24)

(III - 25)

(III - 26)
$E_0$ interaction and call it number 1. Since the clusters must all be connected together, cluster 1 must be linked by a dipole-dipole interaction to at least one other cluster; pick a cluster which is linked to 1 and call it 2. Now 1 does not have to have any more interactions, but 2 must have at least one more. This leads to cluster 3, etc. One can go on like this until there are no more clusters, unless somewhere along the line one of the clusters is linked back to an earlier one. But that cannot happen because then more than $C - 1$ intercluster interactions would be required to get the clusters linked. When we run out of clusters, then the last one will have only one dipole interaction. We can provide it with its second dipole interaction by letting it interact with $E_0$. When we identified cluster 2, we left open the possibility that it might not have been the only cluster linked to cluster 1. If there had been another, we could have added further clusters onto it also, but then we would have eventually come to an end cluster for which we could not have supplied a second dipole interaction, and the result would accordingly have vanished. We see therefore that we are only to look at the arrangements in which the clusters are linked into a single linear chain with an $E_0$ interaction for each of the two end clusters. (If there is only one cluster, then it gets both $E_0$ interactions.) These are the cluster figures which were introduced in K.W.II and called cluster chains.

Our next task is to develop (III - 16) in accordance
with the procedure which has just been explained. We first convert the sum over number of molecules from its simple form in (III - 16) to a form which indicates the grouping of the molecules into clusters. Thus,

\[ \sum_{m_{s=1}}^{\infty} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^m \int d^3r^m \]  

(III - 27)

is converted to

\[ \sum_{c=1}^{\infty} \frac{c}{\xi_1} \left\{ \sum_{m_{s=1}}^{\infty} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^{m_{s}} \int d^3r^{m_{s}} \right\} \frac{1}{m_{1}} \]  

(III - 28)

where \( m_{s} \) is the number of molecules in cluster \( \xi \).

The procedure for taking account of the various positions which clusters can have in a chain and of the various ways that the molecules can be grouped into clusters is the following: we assign the cluster labels once and for all according to position in the chain starting with cluster 1 at the left hand end and going in order to cluster C at the right hand end, and then we sum over all the ways that the \( m \) molecules can be assigned to the clusters with \( m_{1} \) molecules going to cluster 1, \( m_{2} \) to 2, etc. When this procedure is followed, each physical chain is actually counted twice because given any one assignment of molecules to clusters, there is another assignment which produces a chain identical to the first one except that the clusters are assigned to positions in the reverse order. We put in a factor of \( 1/2 \) to compensate for
this. (In the one cluster case there is no need for this factor of $1/2$, but a little later, and for a different reason, a factor of $1/2$ will be needed for the one cluster case only.)

Next, we note that the contribution of a given chain depends only on how many molecules there are in each cluster and not on how the molecules are labeled. We therefore assume that the molecules have been assigned to the clusters in some definite way and then multiply the result by

$$\frac{m!}{\sum_{C \delta} \frac{C}{\delta^2} m_\delta!} \quad (III-29)$$

which is the number of different ways that the molecules could be assigned to the clusters. Thus, (III - 27) is now converted to

$$\frac{1}{2} \sum_{C \delta} \frac{C}{\delta^2} \left\{ \sum_{m_\delta \geq 1} \left( \frac{e^{\beta \mu}}{\lambda^2} \right)^m \int d^3 R^{m_\delta} \right\} \quad (III-30)$$

Because of this procedure, each integral, $\int d^3 R^{m_\delta}$, over configurations must be redefined in a manner which restricts it considerably. Cluster $\delta$ now consists of a definite group of $m_\delta$ labeled molecules. These molecules must stay near enough to one another so that they really do form a single cluster. The precise form of this restriction will be slightly different for different terms in the perturbation expansion which will eventually have to be done to take care of linkage between the $m_\delta$ molecules within the cluster. We will place the
symbol \( L_{m_0} \) in front of \( \int d^3 r \) as a reminder of the eventual need both to take only terms in which the molecules are linked and to restrict the integral \( \int d^3 R \) so that the linked molecules do form one cluster.

At the same time, if two clusters are neighbors in a chain, then there is one and only one interaction between them, the interaction being a dipole–dipole interaction between a molecule in one and a molecule in the other. If the two interacting molecules were to get too close together, then the two clusters would become one. Thus the integration is further restricted to regions of configuration space in which there is a separation of at least \( R_0 \) between the two molecules through which each pair of neighboring clusters interact. We will be able to incorporate this second restriction quite simply a little later on.

Taking account of the preceding discussion, introducing the expansion with respect to \( \sum_{\delta \epsilon \gamma} \mathcal{V}_\delta \mathcal{V}_\epsilon \mathcal{V}_\gamma \), and keeping only the cluster chain terms, (III–16) is replaced by

\[
\eta_2(\xi) = \frac{1}{2} \sum_{\xi' \eta} \sum_{\xi'' \eta'} \left\{ \sum_{\xi'' \eta''} \sum_{\xi'''} \sum_{\eta'''} \left( \frac{e^{i \epsilon R}}{\epsilon^2} \right)^{m_0} L_{m_0} \int d^3 R \right\} \eta(\xi')
\]

(III–31)

\[
= \frac{1}{2 \pi i} \int dw e^{-\beta w} \sum_{\xi'' \eta''} \sum_{\xi'''} \sum_{\eta'''} \left( \frac{e^{i \epsilon R}}{\epsilon^2} \right)^{m_0} L_{m_0} \int d^3 R \]

\[
\cdot \frac{1}{\omega - \xi} \mathcal{V}_1 \frac{1}{\omega - \xi} \mathcal{V}_{12} \cdots \mathcal{V}_c \frac{1}{\omega - \xi}
\]

where \( \sum_{\xi''} \) indicates summation over the \((C+1)!\) permutations of the order in which the operators \( \mathcal{V}_1 \), \( \mathcal{V}_{12} \), \( \cdots \), \( \mathcal{V}_c \)
occur. (The only $V$'s which occur in (III - 31) in the one cluster case are two factors of $V_1$, and in that case there is no $\sum_{o}$. However, to keep the one cluster chain from being a special case we consider the two factors of $V_1$ as distinguishable and sum over the two orders in which they can appear. As mentioned above, we have already put in the factor of $1/2$ which is needed to compensate.)

Next, we break $n(R)$ up into a sum of $C$ term according to the identity,

$$ n(R) \equiv \sum_{i=1}^{m} \delta(R-R_i) \quad (III - 32) $$

$$ = \sum_{\varepsilon=1}^{c} \left[ \sum_{i=1}^{\varepsilon} \delta(R-R_i) \right] \quad (III - 33) $$

With this separation, the $C$ cluster contribution to (III - 31) is replaced by a sum of $C$ contributions each of which corresponds to the presence of delta functions in a different one of the $C$ clusters. We will refer to the cluster which contains the delta functions as the central cluster, and we will let $C_{<}$ be the number of (delta-function-free) clusters to the left of the central cluster and $C_{>}$ the number of clusters to the right. We may now accomplish the sum in (III - 31) over number of clusters and the sum in (III - 33) over the location of the central cluster by starting with the central cluster and summing over the number of ordinary clusters on either side of
it. In doing this we will still number the clusters sequentially from the left end of the chain to the right end. We will refer to the central cluster as cluster $j$. Then (III - 31) becomes

$$n_j(x) = \frac{1}{2} \sum_{\delta = 1}^{\infty} \frac{1}{m_\delta^4} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^{m_\delta} L_{m_\delta} \int d^3 R m_\delta \sum_{\delta = 1}^{\infty} \delta (E - \hat{E})$$

$$+ \sum_{\xi = 0}^\infty \sum_{\xi = 1}^{\infty} \sigma \left( \frac{\beta \mu}{\lambda} \right)^{m_\xi} L_{m_\xi} \int d^3 R m_\xi$$

$$(III - 33)$$

$$+ \sum_{\xi = 0}^\infty \sum_{\xi = 1}^{\infty} \sigma \left( \frac{\beta \mu}{\lambda} \right)^{m_\xi} L_{m_\xi} \int d^3 R m_\xi$$

$$+ \frac{1}{2 \pi i} \int dw e^{-\beta \mu} \sum_{o} \left( \frac{1}{w-K} \right) \left( \frac{V_1 \ldots V_c}{w-K} \right)$$

Next we want to show that each arm represents a factor of the so-called effective field acting on the central cluster. The effective field is the field which exists at the center of a spherical cavity in a homogeneous dielectric in which there is an electric field which would be uniform if there were no cavity; it is equal to $E + \frac{4\pi}{3} \langle p \rangle$ (evaluated as if there were no cavity), and we denote it by the symbol $\hat{E}$. However, each arm is proportional to $E_0$ so that what we really want to show is that each arm represents a factor of $E_1 + \frac{4\pi}{3} p_1 \equiv \hat{E}_1$, where $E_1$, $p_1$, and $\hat{E}_1$ are the parts proportional to $E_0$ of $E$, $\langle p \rangle$, and $\hat{E}$ respectively. (The macroscopic electric field, $\hat{E}$, is defined in appendix F.)

To do this we need to separate those factors of
\[ \text{tr} \frac{1}{2\pi i} \int dw e^{-\beta w} \sum_{0} \frac{1}{w-K} V_{1} \ldots V_{C} \frac{1}{w-K} \quad (\text{III} - 34) \]

which refer to each arm from those factors which refer to the central cluster. The trace of a product of operators is not altered by cyclic permutation of the order of the operators so

\[ (\text{III} - 34) = -\frac{1}{2\pi i} \int dw e^{-\beta w} \frac{\partial}{\partial w} \text{tr} \sum V_{1} \frac{1}{w-K} V_{2} \ldots V_{C} \frac{1}{w-K} \quad (\text{III} - 35) \]

where \( \sum' \) indicates summation over noncyclic permutations in the order of the \( V \)'s. Integrating by parts we get

\[ (\text{III} - 34) = -\frac{\beta}{2\pi i} \int dw e^{-\beta w} \text{tr} \sum \sum' V_{1} \frac{1}{w-K} \ldots V_{C} \frac{1}{w-K} \quad (\text{III} - 36) \]

We will begin by separating the right arm in the case when the right arm contains one or more clusters. To save space we will write \( V_{\xi, \xi+1} \equiv V_{\xi} \) and (when the right arm has two or more clusters) \( V_{\xi+1, \xi+2} \equiv V_{\xi+1} \). We first note that

\[ \text{tr} \sum' \left( V_{1} \frac{1}{w-K} \ldots V_{C} \frac{1}{w-K} \right) = \text{tr} V_{\xi} \sum \left( \frac{1}{w-K} V_{1} \ldots V_{C} \frac{1}{w-K} \right) \quad (\text{III} - 37) \]

(The operators \( V_{1} \ldots V_{C} \) on the right side of \( (\text{III} - 37) \) no longer include \( V_{\xi} \).) We next appeal to the Hugenholtz theorem which is derived in appendix D and according to
where $K_>$ is the part of $K$ which refers to the clusters of the right arm, and $K_r$ is the rest of $K$. Each contour encloses the spectrum of the full Hamiltonian for the molecules of the corresponding part of the chain. This gives us

$$\langle \text{III-34} \rangle = -\beta \sum_{\omega_r} \frac{1}{2\pi i} \int dw_r e^{-\beta w_r} V_\omega \sum_0 \left( \frac{1}{w_r - K_r} V_\omega \cdots V_c \frac{1}{w_r - K_r} \right) \tag{\text{III - 39}}$$

We next make use of the expression

$$V_\omega = \int d^3 R' \sum_j p_j^R \delta(R' - R_j) \cdot \int d^3 \beta'' \Lambda(\beta'; \beta'') \cdot \sum_k p_k^R \delta(R'' - R_k) \tag{\text{III - 40}}$$

where the prime on $\int d^3 R''$ indicates that a sphere of radius $R_0$ about $R'' = R'$ is excluded from the region of integration. Here the intercluster interaction is between molecule $j$ of cluster $\mathfrak{f}$ and molecule $k$ of cluster $\mathfrak{f} + 1$ so that this limitation of the $R''$ integral takes
care of the restriction (mentioned on page 30) that there be a separation of at least \( R_0 \) between the two molecules through which neighboring clusters interact.

The only operator in (III - 39), which refers both to the right arm and to the rest of the chain is \( V_\gamma \). When we use (III - 40) the operators which refer to the right arm will be separated from the operators which refer to the rest of the chain. Because of this and because exchange between the right arm and the rest of the chain (i.e., between clusters \( \gamma \) and \( \gamma + 1 \)) is negligible, the trace for the chain as a whole may be factored into the trace for the right arm and the trace for the rest of the chain. Thus,

\[
(III - 34) = \beta \int d^3R' \frac{1}{2\pi i} \int dw e^{-\frac{\beta w}{\tau \rho}} \sum_{\gamma} \sum_{x} \delta(E_{\gamma} - E_{\gamma'})(\frac{1}{w - K}) \cdot \frac{1}{w - K}.
\]

\[
(III - 41)
\]

We look next at the case when \( C > 0 \), and the right arm consists just of \( E_0 \). We use (III - 36) as is, but in (III - 37) \( V_\gamma \) is replaced by

\[
V_\gamma = - \int d^3R' \sum_{j} \sum_{k} \delta(R' - R) \cdot E_0(R')
\]

which is the right hand interaction of the central cluster with \( E_0 \). Then
\[ (\text{III-34}) = \]

\[ \beta \int d^3 \mathbf{r}' \frac{i}{2\pi i} \int d \omega e^{-\beta \omega} \exp \left( \sum_{r} \frac{n(r)}{2} \sum_{j} \delta(\mathbf{r}' - \mathbf{r}_j) \sum_{o} \left( \frac{1}{\omega - \omega_o} \right) V_o \cdots \right) \cdot E_{o}(\mathbf{r}') \]

We note that the central cluster and left arm are represented by the same factors in \( (\text{III-43}) \) as they are in \( (\text{III-41}) \). When we put \( (\text{III-41}) \) and \( (\text{III-43}) \) back into \( (\text{III-33}) \) we get

\[ n_x(\mathbf{r}) = \frac{1}{2} \sum_{m_3} \sum_{m_5} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^{m_3} L_{m_3} \int d^3 R \delta(\mathbf{r} - \mathbf{r}_j) \cdot E_{o}(\mathbf{r}') \]

\[ \sum_{o = 0}^{\infty} \sum_{m_3} \sum_{m_5} \left( \frac{1}{\lambda^2} \right)^{m_3} L_{m_3} \int d^3 R \delta(\mathbf{r} - \mathbf{r}_j) \cdot E_{o}(\mathbf{r}') \]

\[ \beta \int d^3 \mathbf{r}' \frac{i}{2\pi i} \int d \omega e^{-\beta \omega} \exp \left( \sum_{r} \frac{n(r)}{2} \sum_{j} \delta(\mathbf{r}' - \mathbf{r}_j) \sum_{o} \left( \frac{1}{\omega - \omega_o} \right) V_o \cdots \right) \cdot E_{o}(\mathbf{r}') \]

\[ \left[ E_{o}(\mathbf{r}') - \sum_{o = 0}^{\infty} \sum_{m_3} \sum_{m_5} \left( \frac{1}{\lambda^2} \right)^{m_3} L_{m_3} \int d^3 R \delta(\mathbf{r} - \mathbf{r}_j) \cdot E_{o}(\mathbf{r}') \right] \]

\[ \int d^3 \mathbf{r} A(\mathbf{r}' - \mathbf{r}) \frac{i}{2\pi i} \int d \omega e^{-\beta \omega} \exp \left( \sum_{r} \frac{n(r)}{2} \sum_{j} \delta(\mathbf{r}' - \mathbf{r}_j) \sum_{o} \left( \frac{1}{\omega - \omega_o} \right) V_o \cdots \right) \cdot E_{o}(\mathbf{r}') \]

We now make use of the result obtained in \( \text{K.W.II} \) that
\[
\sum_{\ell=1}^{\ell_{\text{max}}} \frac{C}{\ell^2} \{ \sum_{m_{\ell}} \frac{1}{m_{\ell}!} \left( \frac{e^{i\beta}}{\ell^2} \right)^m \varepsilon \int d^4 R' \}
\]

\[
\frac{1}{2\pi} \int d\omega' e^{-i\omega' t} \sum_{k} \delta(R' - R_k) \sum_{0} \left( \frac{1}{\omega' - \omega'_k} \right) = P_1(R'')
\]

(Equation (III - 45) is derived in appendix E.) We see accordingly that the quantity in the square brackets in (III - 44) is

\[
E_0(R') - \int d^3 S'' \Delta(S : S'') \cdot P_1(R'')
\]

Furthermore, it is shown in appendix F that in our approximation which neglects quadrupole moments and field inhomogeneity,

\[
E_0(R') - \int d^3 S'' \Delta(S : S'') \cdot P_1(R'') = E_0(R') + \frac{4\pi}{3} P_1(R')
\]

Having completed the treatment of the factors in (III - 44) which represent the right arm, we proceed to the factors which represent the left arm. In order to separate the left arm from the central cluster we look first at the case that \( C_{<} \gg 1 \) and use
\[
\begin{align*}
&\text{III - 48} \\
&\tau r \frac{1}{2\pi i} \sum_j \delta (\mathbf{R} - \mathbf{R}_j) \left( \frac{1}{w_r - K_r} V_1 \cdots \frac{1}{w_r - K_r} V_{\infty} \right) \\
&\quad = \tau r V_\infty \frac{1}{2\pi i} \sum_j \delta (\mathbf{R} - \mathbf{R}_j) \frac{1}{w_r - K_r} V_1 \cdots \frac{1}{w_r - K_r} V_{\infty} \quad \text{(III - 49)} \\
\end{align*}
\]

Then we infer from the Hugenholtz theorem that

\[
\frac{1}{2\pi i} \int d\mathbf{w} e^{-\beta \mathbf{w}} \mathbf{z} \left( \frac{1}{w_r - K_r} \sum_j \delta (\mathbf{R} - \mathbf{R}_j) \frac{1}{w_r - K_r} V_1 \cdots \frac{1}{w_r - K_r} V_{\infty} \right) \\
\quad = \frac{1}{2\pi i} \int d\mathbf{w} e^{-\beta \mathbf{w}} \frac{1}{w_r - K_r} \sum_j \delta (\mathbf{R} - \mathbf{R}_j) \frac{1}{w_r - K_r} V_1 \cdots \frac{1}{w_r - K_r} V_{\infty} \quad \text{(III - 49)}
\]

Using (III - 48) and (III - 49) the third line of (III - 44) becomes

\[
\beta \int d^3 \mathbf{r} \tau r \frac{1}{2\pi i} \int d\mathbf{w} e^{-\beta \mathbf{w}} V_\infty \frac{1}{w_r - K_r} \sum_j \delta (\mathbf{R} - \mathbf{R}_j) \frac{1}{w_r - K_r} V_1 \cdots \frac{1}{w_r - K_r} V_{\infty} \quad \text{(III - 50)}
\]

\[
\frac{1}{2\pi i} \int d\mathbf{w} e^{-\beta \mathbf{w}} \sum_j \left( \frac{1}{w_r - K_r} V_1 \cdots \frac{1}{w_r - K_r} V_{\infty} \right)
\]

We now use

\[
V_\infty = \int d^3 \mathbf{r} \sum_j \delta (\mathbf{R} - \mathbf{R}_j) \cdot \int d^2 \mathbf{r} \Delta (\mathbf{R} : \mathbf{R}^\prime) \sum_j \delta (\mathbf{R}^\prime - \mathbf{R}_m) \quad \text{(III - 51)}
\]

and when this is put in (III - 50) the factors relating to
the left arm separate from those relating to the central cluster, and the trace factors into two parts as before. Thus (III - 50) becomes

\[-\beta \int d^3R' d^3R'' \frac{i}{2\pi i} \int dw e^{-\beta w} \frac{1}{\prod_{m} \delta (R''_m - R_m)} \sum_{j} \frac{1}{w - k_j} \delta (R' - R_j) \frac{1}{w - k_j} \cdot - \]

(III - 52)

\[-\int d^3R'' \sum_{m} \delta (R''_m - R_m) \cdot E_0 (R'') \]

(III - 53)

One can see using

\[V_{\xi} = - \int d^3R'' \sum_{m} \delta (R''_m - R_m) \cdot E_0 (R'') \]

that when \(C_\xi = 0\), the second line of (III - 52) is just \(E_0 (R'' \cdot)\).

We see therefore, that the second and third lines of (III - 44) are together equal to

\[-\beta \int d^3R' d^3R'' \frac{i}{2\pi i} \int dw e^{-\beta w} \frac{1}{\prod_{m} \delta (R''_m - R_m)} \sum_{j} \frac{1}{w - k_j} \delta (R' - R_j) \frac{1}{w - k_j} \cdot - \]

(III - 54)

\[\left[ E_0 (R') - \int d^3R'' \sum_{m} \frac{C_\xi}{\sum_{m} \delta (R''_m - R_m)} \frac{1}{\prod_{i = 1}^{m} \delta (E_i - E_{m+1})} \frac{1}{\prod_{i = 1}^{m+1} \delta (E_{m+2} - E_{m+1})} \right] \]

\[\cdot \frac{i}{2\pi i} \int d\omega \cdot e^{-\beta \omega} \frac{1}{\prod_{m} \delta (\omega - K_m)} \sum_{j} \frac{1}{\omega - K_j} \delta (\omega - R_j) \frac{1}{\omega - K_j} \cdot - \]

\[\left[ E_0 (R') - \int d^3R'' \sum_{m} \frac{C_\xi}{\sum_{m} \delta (R''_m - R_m)} \frac{1}{\prod_{i = 1}^{m} \delta (E_i - E_{m+1})} \frac{1}{\prod_{i = 1}^{m+1} \delta (E_{m+2} - E_{m+1})} \right] \]

\[\cdot \frac{i}{2\pi i} \int d\omega \cdot e^{-\beta \omega} \frac{1}{\prod_{m} \delta (\omega - K_m)} \sum_{j} \frac{1}{\omega - K_j} \delta (\omega - R_j) \frac{1}{\omega - K_j} \cdot - \]
and we again identify the quantity in the square brackets as the effective field, \( \xi_1(R') \).

Putting things together, (III - 44) becomes

\[
\mathcal{H}_2(R) = -\frac{1}{2} \beta \int d^3R' d^3R'' \left\{ \sum_{n=1}^{\infty} \frac{1}{n^3!} \left( \frac{e^{\beta R}}{\lambda^3} \right)^n L_m \int d^3R''' \sum_\xi \delta(R - B_\xi) \right\} \cdot \xi_1(R') \xi_1(R'') \tag{III - 55}
\]

and this is the basic result of the present chapter.

To be systematic, one would Taylor expand each \( \xi_1 \) factor about the point \( \xi \) and evaluate the effect of inhomogeneity in \( \xi_1 \). Appendix B shows how this is done, but it also shows that the effect of inhomogeneity will generally be smaller than other effects which have been neglected already. We therefore replace \( \xi_1(R') \) and \( \xi_1(R'') \) by \( \xi_1(R) \xi_1(R) \). The remaining factors of (III - 55) must constitute an isotropic tensor which we write as

\[
\mathcal{B}_2 \equiv -\frac{1}{2} \beta \int d^3R' d^3R'' \left\{ \sum_{n=1}^{\infty} \frac{1}{n^3!} \left( \frac{e^{\beta R}}{\lambda^3} \right)^n L_m \int d^3R''' \sum_\xi \delta(R - B_\xi) \right\} \cdot \xi_1(R) \xi_1(R) \tag{III - 56}
\]
The integrals $\int d^3R'$ and $\int d^3R''$ remove the corresponding delta functions. The remaining delta function, $\delta(R-R_i)$, removes $\int d^3R_i$ from $\int d^3R^m$ and locates molecule $i$ at $R$. The result does not depend on which molecule it is that is located at $R$, so we take it to be molecule 1 and replace $\sum i$ by a factor of $m$. It is also worth-while at this point to introduce the chemical activity, $z$, by the definition

$$z = \frac{\gamma}{\lambda^2} e^{\beta/\mu} \quad (\text{III - 57})$$

where $\gamma$ is the internal partition function for a single molecule in the volume of the gas and subject to $E_0(R)$. (One reason that $z$ is useful is that $z/n$ tends to unity as $n$ tends to zero.) We thus have

$$n_x(R) = B E_i^2(R) \quad (\text{III - 58})$$

with

$$B = \frac{\beta}{\alpha} \sum_{n=1}^{\infty} m z^m \alpha_m' \quad (\text{III - 59})$$

and

$$\alpha_m' = \frac{1}{3} S p \left( \frac{1}{m!} \gamma \right) \frac{1}{\lambda^2} \int d^3R_{m-1} \int d^3w \beta \frac{1}{2} - \int d^3h \frac{1}{2} \int d^3j \frac{1}{2} \int d^3k \frac{1}{2} \quad (\text{III - 60})$$

(The symbol $Sp$ means the trace for a second rank tensor in
The quantity $\alpha'_m$ was introduced in K.W.II., and it is characteristic of the $m$ molecule cluster with two dipole interactions. For the sake of comparison with (III - 59) we may recall from K.W.II. the formulae

$$P_1(r) = A \varepsilon_1(r) \quad \text{(III - 61)}$$

and

$$A = \sum_{m=1}^{\infty} z^m \alpha'_m \quad \text{(III - 62)}$$

which describe the linear part of the polarization of the gas.

A method is given in K.W.II. for converting activity expansions like (III - 62) into expansions in the zero field density. When that method is applied to (III - 59) the first two terms are

$$\mathcal{B}_1 = \frac{\beta}{2} \left[ \alpha_1 \mathbf{n} + \int d \mathbf{r} \left\{ e^{-\beta \phi_1(r)} (g_1(r) - 2z_1) + (e^{-\beta \phi_1(r)} - 1) z_1 \right\} \mathbf{n} \ldots \right] \quad \text{(III - 63)}$$

where $\alpha_1$ is the (field independent part of the) polarizability of a single molecule, $\alpha_2(r)$ is the polarizability of a system of two molecules displaced from one another by $r$, and $\phi(r)$ is the relative potential energy (in the adiabatic approximation) for two molecules separated by $r$. It may be noted for comparison that the first two terms of the corresponding expansion for $A$ are
\[ A \sim = \left[ \alpha_1 n + \int d^3 r \, e^{-\beta \phi(r)} (\frac{1}{2} \alpha_2 (r) - \alpha_1) n^2 \ldots \right]. \quad (III - 64) \]

We conclude this section with a discussion of the nature and relative magnitude of the contribution from diagrams with more than the minimum number of intercluster linkages and of the contribution from diagrams in which clusters interact via quadrupole moments.

The simplest diagram in which there are more than the minimum number of intercluster interactions is the one which is shown in figure 1. The diagram of figure 1 is typical of diagrams in which there are linkages forming a single loop which ends on the cluster with which it started. If one were to sum all diagrams which are like those with which we have dealt in this chapter but which have in addition one or more clusters linked in a loop which begins and ends on the central cluster (c.f. the example in figure 2), one would get for \( n_2 (\Pi) \) a contribution like \( (III - 58) \) but with a different coefficient. The new coefficient would then simply be added to the coefficient \( B \) as a higher order correction. Summing all diagrams which are like the cluster chains of K.W.II but which have in addition a linkage loop on one or more of the clusters of the chain would give a result which would just add a correction to the coefficient \( A \) of \( (III - 61) \).

The correction to \( A \) is of the same order as the correction to \( B \); we can estimate each one by comparing the magnitude
of the diagram in figure 1 with the magnitude of the diagram in figure 3. The extra cluster and the extra dipole interactions in figure 1 are represented in the perturbation expression by the factors

\[ \frac{Z}{\gamma} \sum d^3 R e^{-\beta w} \frac{1}{w-w'} V \frac{1}{w-w'} V. \]

where \( w \) and \( w' \) are molecular energies, and \( V \approx \langle 1|p_i|1\rangle|\lambda| \).

Now \( \frac{\langle 1|p_i|1\rangle^2}{w-w'} \) is of the order of the polarizability of a molecule; we will write it as \( a^3 \) with \( a \) equal to the molecular radius if the molecules are nonpolar. Making use of the three approximate relations, \( e^{-\beta w} \approx \gamma \), \( Z \approx \frac{1}{R_0^2} \), and \( \sum d^3 R \Delta \approx 1 \), we see that the correction is smaller than \( A \) or \( B \) by a factor of the order of \( (a/R_0)^6 \).

The next simplest type of diagram with more than the minimum number of intercluster linkages is illustrated in figure 4. One can see by the argument just given that this diagram is smaller than that in figure 3 by a factor of the order of \( (a/R_0)^9 \) so that it will generally be completely negligible.

Turning now to diagrams which contain quadrupole interactions, the simplest is that in which one cluster interacts twice via its quadrupole moment with \( \nabla E_0 \). The corresponding perturbation term is like that for the diagram in figure 3 except that factors \( \frac{\langle 1|p_i|1\rangle^2 E_0^2}{w-w'} \) are replaced by factors

\[ \frac{\langle 1|Q|1\rangle^2 E_0^2}{(w-w') L^2} \]

where \( L \) is the distance in which there is an appreciable change in \( E_0 \). The quantity \( \frac{\langle 1|Q|1\rangle^2}{w-w'} \) is of the
order of the quadrupole polarizibility, and so for spherical molecules the contribution will be smaller by a factor of \((a/L)^2\). Looking at the related diagrams in which a cluster with two quadrupole interactions has each one of them with the gradient of the dipole field of a neighboring cluster, one might think that the contribution would be smaller by only \((a/R_0)^2\), since the dipole field from a neighboring cluster can change in the distance \(R_0\). However, integration over the position of each neighbor and summation over the number of clusters in the arm on either side turns the field from the dipole moment of each neighbor into the field from the macroscopic polarization. Thus the distance of change is still really \(L\) and the estimate of \((a/L)^2\) still applies.
B. Comparison with Thermodynamics

Having derived a formula for the density from statistical mechanics, we may now check on whether or not the formula for the density and the formula for the polarization are related to one another in the manner which thermodynamics requires. We are not able in this way to test the correctness of the two formulae, but we can verify that they are consistent.

The treatment of electrostriction in thermodynamics is based on a consideration of the force density in the dielectric. The well known result for the force density in a gas of neutral molecules in equilibrium is that

$$ F(R) = -\nabla \left[ p_0 - \frac{1}{2} E^2 \nabla \cdot \frac{\partial \mathcal{V}}{\partial \mathcal{E}} \right] $$

where: "$p_0(R)$" is a quantity whose meaning may be explained as follows. Let $\langle n(R) \rangle$ be the density at $R$ when the field is present; then "$p_0(R)$" is the pressure the gas would have if its temperature were the same, its density were everywhere equal to $\langle n(R) \rangle$, and there were no electric field. The quantity "$p_0(R)$" is obtained by putting $\langle n(R) \rangle$ into the zero field
equation of state. Thus the term \( \nabla "p_0"(R) \) really involves the density of the gas rather than the pressure. The quotation marks are included as a reminder that "\( p_0 \)" is not the pressure in the gas when the field is turned off.

Because we are dealing with a gas in equilibrium, the force density is necessarily zero. Because the temperature is uniform, and we are dealing with a single species of molecule, we may write

\[
\nabla \chi = \frac{2\chi}{3n} \left|_T \nabla n \right. \tag{III-66}
\]

and

\[
\nabla "p_0" = \frac{\partial "p_0"}{\partial n} \left|_T \nabla n \right. \tag{III-67}
\]

Thus, what (III - 65) actually states for our system is that

\[
\frac{\partial "p_0"}{\partial n} \left|_T \nabla n \right. = \frac{n}{2} \nabla \left\{ \frac{2\chi}{3n} \left|_T E^2 \right. \right\} \tag{III-68}
\]

We may note that (III - 65) does contain an approximation. The approximation comes from the assumption that in a medium whose density is constrained to be independent of the electric field the free energy associated just with the field is

\[
\frac{1}{8\pi} \int d^3R \ K(R) E^2(R) \tag{III-69}
\]
But even when the density is made independent of \( E \), the
polarization will generally contain a contribution proportional
to \( E^3 \). Therefore the free energy will generally contain a
contribution proportional to \( E^4 \), and the same will be true
of \( \nabla "p_0" \). That contribution is not needed here because
there are no terms proportional to \( E^4 \) in \( \text{(III - 58)} \), the
statistical formula for density with which we want to make
comparison. In fact, since \( \text{(III - 58)} \) is proportional to
\( E_0^2 \), we will take only that part of \( \text{(III - 68)} \) which is
proportional to \( E_0^2 \). Thus, in \( \text{(III - 68)} \) we change \( E \) to
\( E_1 \), and we give \( \frac{\partial "p_0"}{\partial n} \bigg|_T \), \( n \), and \( \frac{\partial \chi}{\partial n} \bigg|_T \) the values which
correspond to \( n_0 \) rather than the values which correspond to
\( \langle n(n) \rangle \). (This means that "\( p_0 \)" is replaced by the pressure
\( p_0 \) which would actually exist with the field not present.)

Equation \( \text{(III - 68)} \) is still not comparable with
\( \text{(III - 58)} \) because it involves \( \chi \) and \( E_1 \) rather than \( A \)
and \( \xi_1 \), which are the natural quantities in the statistical
theory. One may check from \( \text{(III - 47)} \) and \( \text{(III - 61)} \) that

\[
E_1 = (1 - \frac{4\pi}{3} A) \xi_1
\]

(III - 70)

and that

\[
K \equiv (1 + 4\pi \chi) = 1 + \frac{4\pi A}{1 - \frac{4\pi}{3} A}
\]

(III - 71)

and therefore that
\[
\frac{1}{2 \pi} \mathcal{E}_1^2 \frac{\partial K}{\partial \eta} = \frac{1}{2} \mathcal{E}_1^2 \frac{\partial A}{\partial \eta}. \quad (III - 72)
\]

Thus, for our purpose the thermodynamic formula is

\[
\frac{\partial p_0}{\partial \eta} \nabla n_2(R) = \frac{1}{2} n_0 \frac{\partial A}{\partial \eta} \nabla \mathcal{E}_1^2(R). \quad (III - 73)
\]

or

\[
\nabla n_2(R) = \frac{n_0 \frac{\partial A}{\partial \eta}}{2 \frac{\partial p_0}{\partial \eta}} \nabla \mathcal{E}_1^2(R). \quad (III - 74)
\]

On the other hand, we see from \((III - 59)\) that the corresponding result in the statistical theory is

\[
\nabla n_2(R) = B \nabla \mathcal{E}_1^2(R). \quad (III - 75)
\]

Therefore, to show that the two results agree, we need to show that

\[
B = \frac{n_0 \frac{\partial A}{\partial \eta}}{2 \frac{\partial p_0}{\partial \eta}}. \quad (III - 76)
\]

or that

\[
2 B \frac{\partial p_0}{\partial \eta} = n_0 \frac{\partial A}{\partial \eta}. \quad (III - 77)
\]

The only expressions which are available for \(B\), \(p_0\), and
A are the expansions in powers of the activity which were derived, in K.W.I for \( p_0 \), and in K.W.II for \( A \), and in this chapter for \( B \). An activity expansion is given in K.W.I for \( n_0 \) also, so we can consider each quantity in (III - 77) as a function of the activity. Putting

\[
\frac{\partial p_0}{\partial n_0} = \frac{\partial p_0}{\partial z} \frac{\partial z}{\partial n_0} \quad (\text{III - 78})
\]

and

\[
\frac{\partial A}{\partial n_0} = \frac{\partial A}{\partial z} \frac{\partial z}{\partial n_0} \quad (\text{III - 79})
\]

we may drop a factor of \( \frac{\partial z}{\partial n_0} \) from each side, and (III - 77) becomes

\[
2B \frac{\partial p_0}{\partial z} = n_0 \frac{\partial A}{\partial z} \quad (\text{III - 80})
\]

The activity expansions for \( A \) and \( B \) are (III - 62) and (III - 59) respectively. The expansions from K.W.I are

\[
n_0 = \sum_{m=1}^{\infty} m Z^m b_m \quad (\text{III - 81})
\]

and

\[
p_0 = \frac{1}{\beta} \sum_{m=1}^{\infty} Z^m b_m \quad (\text{III - 82})
\]
where

\[ b_m = \frac{1}{m! \gamma^m} \int d^3 \mathbf{R}^{m-1} \frac{1}{2 \pi i} \int d \omega e^{-\beta \omega} \frac{1}{\omega - k} \]  

(III - 83)

is the analogue of \( \alpha'_m \) for a cluster with no dipole interactions.

Using these expansions, we see for the left side of (III - 80) that

\[ 2 \mathcal{B} \frac{\partial b_m}{\partial z} = 2 \left\{ \frac{\beta}{2} \sum_m m z^m \alpha'_m \right\} \left\{ \frac{1}{\beta} \sum_k k z^{k-1} b_k \right\} \]  

(III - 84)

\[ = \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} m \alpha'_m k b_k z^{m+k-1} \]

and for the right side of (III - 80) that

\[ \eta_0 \frac{\partial A}{\partial z} = \left\{ \sum_m m z^m b_m \right\} \left\{ \sum_k k z^{k-1} \alpha'_k \right\} \]  

(III - 85)

\[ = \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} m b_m k \alpha'_k z^{m+k-1} \]

This makes it manifest that the two sides of (III - 80) are equal and completes the proof that the statistical result is consistent with that from thermodynamics.
C. The Physical Significance of the Chemical Potential

This last part of the chapter is devoted to some comments on the relationship between (III - 38) and the two dielectric arrangements which are likely to be encountered in practice.

Equation (III - 38) gives \( n_2(R) \) as a function of \( \varepsilon_1, \beta, \) and \( \mu \). However, it is \( E_0 \) rather than \( \varepsilon_1 \) which is independent of \( \beta \) and \( \mu \). Now one can use (III - 61) to convert (III - 47) into a relation between \( \varepsilon_1 \) and \( E_0 \), and although it will not always be possible to obtain the solution for \( \varepsilon_1 \) in closed form, the iterated solution will converge quite quickly as long as the density is not too high. We will therefore think of (III - 58) as giving \( n_2(R) \) as a function of \( E_0, \beta, \) and \( \mu \).

We want to know what sort of experimental arrangement (III - 58) describes. The arrangements which are needed to control \( E_0 \) and \( \beta \) are common knowledge, so we need only look at the chemical potential, \( \mu \). Physically, \( \mu \) represents the increase in the Helmholtz free energy when the number of molecules in the volume is increased by one with no change in \( \beta \) or \( V \). It is shown in thermodynamics that \( \mu \) is independent of position in a gas in equilibrium. (If \( \mu \) depended on position, then the entropy would increase when a molecule went from a region of higher \( \mu \) to a region of lower \( \mu \).) Molecules which are in an electric field have a
negative potential energy of position relative to the field, and this potential energy diminishes the free energy which would be added to the gas if an additional molecule were placed in a region with a field. Thus, turning on an electric field tends to lower \( \mu \) where the field is. But because this happens, more molecules come into the electrified region until the increase in their positive free energy of compression just cancels their negative free energy relative to the field. Thus \( \mu \) can be controlled everywhere if it can be controlled anywhere. On the other hand, when \( \beta \) is fixed and there is no electric field, then \( \mu \) depends only on the density or, equivalently, on the pressure. Therefore, the value which \( \mu \) has in an experiment will actually be independent of \( E_0 \) if (by the use of a reservoir of molecules) the pressure is kept fixed in some region of the gas where there is never any electric field. Or, if it is not feasible to actually control \( \mu \), one can still measure the pressure in a region where there is no field and so find out what value \( \mu \) has.

We can also imagine an experimental situation in which there is a fixed amount of gas in a fixed volume in a uniform field. The variables which are actually independent in this sort of experiment are \( \beta \), \( E_0 \), and \( N \). One might think at first of trying to evaluate the desired averages with respect to a petit canonical ensemble, since then the results would automatically contain \( N \) as an independent variable. That approach does not work because the sort of treatment
given in K.W.I cannot be carried out for a petit ensemble. Instead, we may obtain the desired result from (III - 56) by making \( \mu \) depend on \( E_0 \) in such a way that for a gas in a uniform field the grand ensemble average of the density becomes independent of \( E_0 \). We will need to know the result in order to be able in the next chapter to write down the coefficient for the part of the cubic polarization which is present even when there is no electrostriction.

We assume that \( \mu = \mu(E_0) \) and require that

\[
\frac{d\langle N \rangle}{dE_0} = \frac{\partial \langle N \rangle}{\partial E_0} \bigg|_{\beta \mu E_0} + \frac{\partial \langle N \rangle}{\partial \mu} \bigg|_{\beta \mu E_0} \frac{d\mu}{dE_0} = 0 \quad (\text{III - 56})
\]

or that

\[
\frac{d\mu}{dE_0} = -\left[ \frac{\partial \langle N \rangle}{\partial E_0} \bigg|_{\beta \mu E_0} \right]^{-1} \left[ \frac{\partial \langle N \rangle}{\partial \mu} \bigg|_{\beta \mu E_0} \right] \quad (\text{III - 57})
\]

It follows from

\[
\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} \bigg|_{\beta \mu E_0} \quad (\text{III - 58})
\]

that

\[
\frac{\partial \langle N \rangle}{\partial E_0} \bigg|_{\beta \mu E_0} = \frac{1}{\beta} \frac{\partial^2}{\partial \mu \partial E_0} \ln \mathcal{Z} \quad (\text{III - 59})
\]

But when \( E_0 \) is uniform,
\[ \frac{1}{\beta} \frac{\partial}{\partial E_0} \ln \beta = \mathcal{V} \langle P \rangle \]  

so that

\[ \frac{\partial \langle N \rangle}{\partial E_0} \bigg|_{\beta \nu \mu} = \mathcal{V} \frac{\partial \langle P \rangle}{\partial \mu} \bigg|_{\beta \nu E_0} \]  

and (III - 87) becomes

\[ \frac{d\mu}{dE_0} = -\mathcal{V} \frac{\partial \langle P \rangle}{\partial \langle N \rangle} \bigg|_{\beta \nu E_0} \left[ \frac{\partial \langle N \rangle}{\partial \mu} \bigg|_{\beta \nu E_0} \right]^{-1} \]  

\[ = -\mathcal{V} \frac{\partial \langle P \rangle}{\partial \langle N \rangle} \bigg|_{\beta \nu E_0} \]  

\[ = -\frac{\partial \langle P \rangle}{\partial \langle n \rangle} \bigg|_{\beta \nu E_0} \]  

Thus

\[ \mu(E_0) = \mu_0 - \int_{E_0}^{E'} dE' \frac{\partial \langle P \rangle}{\partial \langle n \rangle} \bigg|_{\beta \nu E'} \]  

\[ = \mu_0 - \frac{\partial}{\partial \langle n \rangle} \int_{E_0}^{E'} dE' \langle P \rangle \]  

and since we will only need the constant and quadratic terms of the expansion of \( \mu(E_0) \) in powers of \( E_0 \), we may write.
\[ \mu(E_0) = \mu_o - \frac{1}{\pi} E_0 \frac{\partial P}{\partial \langle n \rangle} \]
IV. CUBIC POLARIZATION

A. The Formula for the Cubic Polarization in the Cluster Cross Approximation

Because of a parity consideration which will be introduced below, the coefficients which describe the response of a cluster to an electric field always have even rank. It is not possible to obtain a vector from two tensors of even rank, so that if the electric field is characterized by a single vector (i.e., is uniform), then the polarization cannot have any contribution proportional to $E_0^2$. But if the field is not uniform, then it can have among its characteristics tensors which are proportional to $E_0^2$ but are of odd rank, tensors such as $E_0 \nabla E_0$, $\nabla \left( \nabla E_0 E_0 \right)$, etc. These odd rank field tensors can be combined with even rank cluster tensors to give vectors. Thus when the field is nonuniform, the polarization can have a contribution proportional to $E_0^2$. This contribution corresponds to the divergence of the $|\nabla E_0|^2$ part of the macroscopic quadrupole density. Some remarks will be made later to indicate the cluster figures from which it comes and to show that it is much smaller than anything else which we consider.
The aim of this chapter is to obtain a formula for the part of the polarization which is proportional to the cube of the electric field. The procedure will be quite analogous to that which was developed in K. W. II and followed in the preceding chapter.

We begin with the perturbation expansion which was described in chapter III except that there is now no density operator. Since we again have long-range electrical interactions we again group the molecules of each linked term into clusters. As to the interactions between clusters, we again ignore exchanges, arrangements which use more than C-1 linkages to link C clusters, and interactions via quadrupole moments. (Estimates were given in chapter III for the magnitudes of the neglected terms.) But we must now look at terms which have four interactions with $E_0$ rather than just two. Because of the restriction to C-1 intercluster linkages, the clusters cannot be linked into any loops. This means that there must be two or more clusters which are linked to only one other cluster.

Since the terms must now have four interactions with $E_0$, there may be as many as four such "end" clusters. But the five statements of the preceding chapter do not rule out diagrams in which the clusters form a linear chain with two factors of $E_0$ at each end. Such diagrams are ruled out (except in the one cluster case) by the requirement that the number of dipole operators in each cluster be even.

This requirement holds for the following reasons. First,
the free-molecule Hamiltonian commutes with the parity operator so that the free-molecule states (which are used to compute the trace for a cluster) can be taken to have definite parity.

Second, each time a state occurs in the trace as a "bra", it occurs also as a "ket". This means that in each term of any trace the states have a net parity which is even. Therefore, the trace will vanish unless the net parity of its operators is even also. Last, the parity of the dipole operator is odd.

With this requirement added, the nature of the acceptable diagrams may be determined as follows. If there is only one cluster, then that cluster must obviously have all four $E_0$ interactions (c.f. figure 5). To see the nature of the diagrams with more than one cluster, we ask how additional clusters can be added to the one-cluster diagram. If there is a second cluster, it must have a dipole interaction with the first cluster, and this gives it one dipole operator. Since there cannot be another interaction between the two clusters, the second cluster must get one of the $E_0$ interactions in order that it have an even number of dipole operators. This keeps the number of dipole operators in the original cluster even also (c.f. figure 6). The ways in which third, fourth, and fifth clusters may be added are illustrated in figures 7, 8, and 9 respectively. It is clear from these examples that each acceptable diagram has the form of a cross made up of a central cluster and four arms. Each arm can consist of an $E_0$ interaction or of a chain of clusters which ends.
with an \( E_0 \) interaction. We will call these diagrams cluster crosses.

Having found the diagrams which give the main contribution to \( P_3 \), we may estimate the relative magnitude as follows. We continue to write the molecular polarizability as \( a^3 \) so that the dipole moment of the central cluster will be of the order of \( a^3 E \). For each additional interaction with the field, the Born series terms have an additional factor of the order of \( a^3 E^2 / w \), where \( w \) is a molecular energy. The field cannot be any larger than the breakdown field, which we estimate by assuming that an electron will receive an energy \( w \) if it is accelerated by \( E \) through a mean intermolecular distance \( R_0 \). So, \( E \approx w / e R_0 \). We also have \( w \approx e^2 / a \). The extra factor is thus of the order of \( (a / R_0)^2 \). Since the cluster crosses have two extra arms, \( P_3 \) will be smaller than \( P_1 \) by a factor of the order of \( (a / R_0)^4 \).

Before we go on with the crosses, we pause to complete our earlier discussion of the part of \( \langle P \rangle \) which is proportional to \( E_0^2 \). The simplest nonvanishing diagram with three \( E_0 \) interactions consists of a cluster interacting with \( \nabla E_0 \) three times via its quadrupole moment. This diagram does not contribute to the polarization. The simplest diagrams which do give a quadratic contribution to the polarization are those in which there are three arms and one central cluster which interacts via its quadrupole moment with the gradient of the field from each arm. Two of the arms are ordinary arms in which the
number of clusters is summed from zero to infinity. The third arm is special in that the number of its clusters is summed from one to infinity. Each of the regular arms represents a factor of $\nabla \mathcal{E}_1$ acting on the central cluster. The contribution to $P_2$ comes from the polarization of the cluster at the end of the special arm. We can compare the magnitude of the simplest of these diagrams with the magnitude of the simplest cluster cross as follows. There is one less electrical interaction, so we have a factor of $(R_0/a)^2$. The remaining three interactions have quadrupoles and gradients of macroscopic fields rather than dipoles and fields, so (for spherical molecules) we have a factor of $(a/L)^3$, where $L$ is the distance in which the macroscopic fields change appreciably. The preceding factors take account of the relative size of the field from the quadratic part of the quadrupole density. Finally, $P_3$ has a contribution from a diagram with a single cluster, whereas the first contribution to $P_2$ comes from a diagram with two clusters. The polarization of an extra cluster brings in a factor of $(a/R_0)^3$. So altogether $P_2$ is smaller than $P_3$ by roughly $(a/R_0)(a/L)^3$, and smaller than $P_1$ by a factor of the order of $(a/R_0)^5(a/L)^3$. From this estimate it seems that $P_2$ will always be completely negligible.

The procedure which we will use for summing over crosses is the following. We will regard the arms as having fixed orientations with arm 1 up, arm 2 to the right, arm 3 down, and arm 4 to the left. We denote the number of clusters
in arm \( i \) by \( C_i \). We assume that the clusters are numbered in some way or other. We let \( m_\xi \) be the number of molecules in cluster \( \xi \). The number of clusters in each arm is summed from zero to infinity, and the number of molecules in each cluster is summed from one to infinity.

For each specification of the sizes of the clusters, different linked terms in the perturbation series (II - 26) coupled with different parts of the integral over molecular configurations will give rise to all possible assignments of the molecules to clusters. As in the preceding chapter, we take care of the assignments of molecules to clusters by assuming some one fixed assignment and inserting a factor of

\[
\frac{m!}{\prod_{\xi=1}^{C} m_\xi!}
\]  

(IV - 1)

where \( C = \sum_{\xi=1}^{N} C_\xi + 1 \) is the number of clusters in the cross. But we must also put in a factor of \( 1/(4!) \) because, whereas all that the perturbation series cares about is which molecules are together in clusters in an arm, our procedure also sums over the \( 4! \) ways in which the physical arms (as identified by the molecules which they contain) can be labeled from 1 to 4. Actually our procedure counts each cross \( 4! \) times only if at least three of its arms have clusters. For instance, crosses with all four arms empty are counted only once. We take care of this by treating each of the four \( E_{0} \) interactions as distinguishable from the others even when the central cluster has more than one of them. Then when the
central cluster does have more than one, we include permutations in the order of the interactions of $E_0$ with the central cluster when we sum over the permutations of the order of the operators in the perturbation expansion we are about to write.

In the light of the foregoing, we write down the cluster cross contribution to the log of the partition function as

$$\frac{1}{4!} \sum_{C_s = 0}^\infty \sum_{m_\delta = 1} \left\{ \frac{C}{\delta^4} \right\} \sum_{m_\delta = 1} \left\{ \left( e^{\beta \mu} \right)^{m_\delta} \right\} \left\{ \delta^2 R^m \right\}$$

$$\text{(IV - 2)}$$

$$\text{tr} \left\{ \frac{1}{2\pi i} \oint_{w_K} e^{\beta w} \sum_{C_s} \left( \frac{1}{w-K} V_1 \cdots V_C \frac{1}{w-K} \right) \right\}$$

where the set $V_1 \cdots V_C$ includes the four interactions with $E_0$ and the $C - 1$ intercluster interactions which occur in the cross specified by the numbers $C_i$ and the numbers $m_\delta$.

Remembering (II - 10), we want next to multiply by $\frac{1}{\beta}$ and take the functional derivative with respect to $E_0(R)$. The result will be the leading contribution to the part of $\langle P(R) \rangle$ which is proportional to $E_0^3$, and we will denote it by the symbol $P_3(R)$.

For each term of (IV - 2) there would normally be a contribution from the differentiation of each of the four $E_0$ interactions. But the way that our procedure counts each physical cluster cross 4! times is that it assigns the first position to each of the four arms in turn and counts the cross 3! times for each such assignment. Therefore we may accomplish the differentiation by differentiating each
term of (IV - 2) with respect to the first $E_0$ interaction and replacing $1/(4!)$ by $1/(3!)$. We see from (III - 42) that when we differentiate $V_1$ it is replaced by

$$- \frac{1}{\mathbf{i}} \sum \mathbf{p}_i \delta(\mathbf{R} - \mathbf{R}_i)$$

(IV - 3)

where we call the cluster with the first $E_0$ interaction cluster 1 and where $\frac{1}{\mathbf{i}}$ means that the index $i$ is summed over the molecules of that cluster. Thus,

$$P_3(R) = \frac{-1}{3!} \mathbf{p}_z \sum_{\mathbf{C}_z} \left\{ \sum_{\mathbf{m}_z} \frac{1}{1!} \left\{ \sum_{\mathbf{w}_z} \frac{1}{1!} \left( \frac{e^{\beta \mu}}{N} \right)^{\mathbf{m}_z} L_{\mathbf{m}_z} \right\} \int d^3 R_m \right\} \cdot$$

(IV - 4)

$$\cdot \mathbf{h} \frac{1}{2\pi i} \int_{w-K} e^{-\beta \omega} \left\{ \sum_{\mathbf{w}-\mathbf{K}} \frac{1}{1!} \sum_{\mathbf{p}_i} \delta(\mathbf{R} - \mathbf{R}_i) \frac{1}{\mathbf{w}-\mathbf{K}} V_{1z} \cdots V_{c} \frac{1}{\mathbf{w}-\mathbf{K}} \right\}$$

Our next task is to separate cluster 1 from each cross in (IV - 4) and bring it outside the sum over crosses. We recall that cluster 1 may or may not be the central cluster. When $C_1 > 1$ then cluster 1 is separated from the cross in the same way that the arms were separated from the central cluster of each chain in chapter III. When we take the sum of all crosses for which $C_1 > 1$ and separate the first cluster, what is left is the first cluster being acted on by the field from all crosses with $C_1 > O$ or in other words, by the field from the cubic polarization itself. This contribution is
\[ \int d^3 R' \beta (R, R') \cdot \int d^3 R, \Delta (R', R), P_3 (R) \]  (IV - 5)

where

\[ \beta (R, R') \equiv \sum_{m} \left( \frac{e^{\beta \mu}}{\lambda^2} \right)^m L_m, \int d^3 R^m. \]  (IV - 6)

\[ \operatorname{tr} \frac{1}{2 \pi i} \int d \omega e^{-i \omega \beta} \sum_{i} \frac{1}{w - k_i} \sum_{j} \delta (R - R') \delta (\omega - \beta) \frac{1}{w - k_j} \]

is the quantity which represents the first cluster, \( \beta (R, R') \) was introduced and discussed in K.W., II, and \( \int d^3 R' \beta (R, R') \equiv A \) was mentioned in connection with equation (III - 61) and (III - 62) of the preceding chapter.

On the other hand, when \( C_1 = 0 \) we remove each arm from the central cluster (again exactly as was done in chapter III). As was the case in chapter III, each arm gives a factor of \( \mathcal{E}_i \) acting on the central cluster. Now, however, the central cluster has four dipole operators. The resulting contribution to \( P_3 (R) \) is

\[ -\int d^3 R' d^3 R'' d^3 R''' \mathcal{I}(g, R', g'', g''') \cdot \mathcal{E}_i (g') \mathcal{E}_j (g'') \mathcal{E}_k (g''') \]  (IV - 7)

where
\[ J(g; g' : g'', R'') = \frac{1}{3!} \sum_{m=1}^{\infty} \frac{1}{m!} \left( \frac{e^{\beta m}}{\lambda^3} \right)^m L_{m}, \int d^3R^m \operatorname{tr} \frac{1}{2\pi i} \int dw \, e^{-\beta w}. \]  

(IV - 8)

\[ \sum \delta(g - g') \sum \left( \frac{1}{w - k} \sum p \delta(r^2 - r^2_j) \frac{1}{w - k} \sum p \delta(r^2 - r^2_i) \right) \]

Collecting the two contributions we get

\[ P_3(g) = \int d^3R' \, \beta(g; g') \cdot \int d^3R_i \, \Delta(g' : g_i) \cdot P_3(g_i) \]  

(IV - 9)

\[ -\int d^3R' \, d^3R'' \int d^3R''' \, J(g; g', g'' : R''') \cdot E_i(g') E_i(g') E_i(g''') \]

The first term on the right of (IV - 9) represents the linear response of the molecules to the part of \( E \) which is proportional to \( E_0^3 \) rather than any nonlinearity in the way in which the molecules respond to \( E \). We may make this point more transparent by adding (IV - 9) to the result

\[ P_3(g) = -\int d^3R' \, \beta(g; g') \cdot \left[ E_0(g') - \int d^3R_i \, \Delta(g' : R_i) \cdot P_3(g_i) \right] \]  

(IV - 10)

which was derived in K.W.II. (IV - 10) is just a more detailed form of (III - 61). This gives
\[ P_1(R) + P_2(R) = - \int d^3 R' \int_2^\infty [E_2(R)^2 - \int d^3 R'' \Lambda (R' : R'') \cdot \{ P_1(R) + P_2(R) \}] \]

\[ - \int d^3 R' \int d^3 R'' J(R' : R'' : R') \cdot (R'' : R'' : R') \cdot E_1(R') E_1(R'') \]

We neglect the effect of inhomogeneity and write

\[ P_1(R) + P_2(R) = A \{ E_1(R) + E_3(R) \} + \mathcal{C} \cdot (E_1(R) E_2(R) E_2(R)) \]

where

\[ \mathcal{C} \equiv - \int d^3 R' \int d^3 R'' J(R' : R'' : R') \]

and where

\[ E_3(R) \equiv - \int d^3 R, \Lambda (R : R) \cdot P_2(R) \]

( and where analogous definitions will apply to \( E_5(R) \), etc.)

One might suspect from (IV - 12) that the expression for \( P_1(R) + P_3(R) + P_5(R) \) would contain the term

\[ A \{ E_1(R) + E_3(R) + E_5(R) \} \]

and similarly that the expression for \( \langle P(R) \rangle \) would contain
the term \( A \mathcal{E}(R) \) where

\[
\mathcal{E}(R) = \mathcal{E}_0(R) - \int \! d^3R_1 \, \mathcal{A}(R;R_1) \cdot \langle \mathcal{P}(R_1) \rangle.
\]  

(IV - 16)

As long as we consider the contribution from the diagrams in which only C-1 dipole-dipole interactions are allowed for linking C clusters, these suppositions are true. One may see this by noting that \( P_1, P_3 \), and all the other parts of \( \langle \mathcal{P}(R) \rangle \) are obtained by differentiating the \( E_0 \) interaction at the end of one arm of a diagram, and that the terms in which that arm starts with one or more clusters always add up to the integral of \( \mathcal{P} \) times the field from the part of \( \langle \mathcal{P} \rangle \) in question.

Likewise, every part of \( \langle \mathcal{P} \rangle \) from \( P_3 \) on will contain an integral of \( \int \) multiplied by three electric field factors, and when all the parts of \( \langle \mathcal{P} \rangle \) are put together, these terms will add up to

\[
- \int \! d^3R_1 \, d^3R_2 \, d^3R_3 \, \sum_{R_1:R_2:R_3} \mathcal{E}(R_1) \mathcal{E}(R_2) \mathcal{E}(R_3). 
\]  

(IV - 17)

This assertion is not as easy to prove as the preceding one, and the author has not found a general proof. But the pattern may be checked for the beginning terms as follows. In (IV - 17) we replace each factor of \( \mathcal{E} \) by its expansion in terms proportional to powers of \( E_0 \). We then multiply and rearrange the resulting terms according to their dependence on \( E_0 \). Thus
omitting the integral and the factor of \( J \), the beginning terms are

\[
\varepsilon_1 \varepsilon_2 \varepsilon_3 \\
+ 3 \varepsilon_1 \varepsilon_2 \varepsilon_3 \\
+ 3 \varepsilon_1 \varepsilon_2 \varepsilon_5 + 3 \varepsilon_1 \varepsilon_3 \varepsilon_5 \\
+ 3 \varepsilon_1 \varepsilon_2 \varepsilon_7 + 6 \varepsilon_2 \varepsilon_3 \varepsilon_5 + \varepsilon_3 \varepsilon_3 \varepsilon_3 
\]

(IV - 18)

We may now look at the diagrams corresponding to these terms to see if the numerical factors agree.

The only diagram which goes with \( \varepsilon_1 \varepsilon_2 \varepsilon_3 \) is the cluster cross which has already been discussed. This is illustrated in figure 10 where the circle represents the central cluster, arms 2, 3, and 4 represent the three factors of \( \varepsilon_1 \), and arm 1 represents the \( E_0 \) interaction which is differentiated away when the polarization of the central cluster is measured. It will be recalled from the earlier discussion that before differentiation the cross is counted 4! times and that after differentiation it is counted 3! times. The compensating factor of \( 1/(3!) \) is absorbed into \( J \).

The only diagram which goes with \( \varepsilon_1 \varepsilon_2 \varepsilon_3 \) is shown in figure 11 where the left hand circle represents the \( J \) of (IV - 15), arms 2 and 3 represent the two factors of \( \varepsilon_1 \), and the right hand circle and its four arms represent \( \varepsilon_3 \).
(Fig. 10)

(Fig. 11)
Our counting procedure counts each of these diagrams \(2)(3!)(3!)\) times before differentiation and \(2)(3!)\) times after differentiation. We may write the compensating factor as \(3/(3!)(3!)\). Each factor of \(1/(3!)\) is absorbed into the \(\mathcal{S}\) for one of the central clusters, and there is a factor of \(3\) left, in agreement with (IV - 18).

We note in passing that this diagram represents a contribution to \(P_5(R)\), the contribution being

\[
3\int d^3R_1 d^3R_2 d^3R_3 \mathcal{S}(R_1; R_2; R_3) \xi(R_1) \xi(R_2) \xi(R_3) (IV - 19)
\]

The other contribution to \(P_5\) comes from diagrams having a single central cluster with six arms attached to it. It does not contribute to the part of \(\langle P \rangle\) proportional to the cube of \(\xi\) but does contribute to the part proportional to the fifth power of \(\xi\). In the contribution from these diagrams, the central cluster is represented by a factor just like \(\mathcal{S}(R; R')\) and \(\mathcal{S}(R; R''; R'''\ldots)\) but having six arguments and six dipole operators.

The foregoing sketch makes the method clear. If the reader wishes to carry it a step further, he is reminded not to overlook factors like the factor of \(3\) in \((IV - 19)\).

In summary, we may write the expansion for \(\langle P(R) \rangle\) as

\[
\langle P(R) \rangle = \xi(R) + \xi(R)\xi(R)\xi(R)\xi(R) + \ldots \quad (IV - 20)
\]
It is clear from the preceding discussion how the subsequent coefficients are written.

It may be observed that $A, C, \text{ etc.}$ are expansions in powers of $z$, and that the coefficients are about as simple as such quantum mechanical expressions can be. It seems for this reason that (IV - 20) gives the natural and proper representation of gaseous polarization.

Now that we have found that $\langle P \rangle$ is represented more naturally by an expansion in powers of $\varepsilon$ than by an expansion in terms which are proportional to powers of $\varepsilon_0$, we may reexamine the treatment in the previous chapter to see if the same is true of $\langle \pi \rangle$. When we do so, we find that it is and that $B$ is really the coefficient of $\varepsilon^2$ rather than just of $\varepsilon^1$.

We want finally to notice that the coefficients in the expansion for $\langle \pi \rangle$ are related in a simple way to the corresponding coefficients in the expansion for $\langle P \rangle$. There are three differences, and we may see each one by comparing (III - 59) with (III - 62). The density and polarization coefficients will always have a factor of $z^m$ and a factor (generally a tensor) like $\alpha_m^\prime$ in common. The density coefficient will differ from the polarization coefficient by having the additional factors $\beta_m, \pi, m$, and one over the number of dipole operators.
B. Physical Interpretation of the One Molecule Contribution

We want to show here that the result for \( P_3(R) \) corresponds to the earlier result for \( n_2(R) \) in the way that common sense would lead us to expect. We are interested in the dependence on the electric field rather than in the dependence on the density so we will look just at the low density limit where things are relatively simple.

We denote the statistical average of the dipole moment of an isolated molecule in a uniform field \( \mathcal{E} \) by the symbol \( \overline{p} \). We denote the part of \( \overline{p} \) which is proportional to \( \mathcal{E} \) by \( \overline{p}_1 \) and the part proportional to \( \mathcal{E}^3 \) by \( \overline{p}_3 \). Then in the low density limit, we would expect that

\[
P_3 = n_0 \overline{p}_3 + n_2 \overline{p}_1 \quad \text{(IV - 21)}
\]

Expressions for \( \overline{p}_1 \) and \( \overline{p}_3 \) may be obtained as follows. By definition,

\[
\overline{p} = \frac{i}{\varepsilon} \sum_k \mathcal{F}^{\beta w_k} p_k \quad \text{(IV - 22)}
\]

where the index \( k \) labels the members of a complete set of eigenstates of the Hamiltonian, \( \mathcal{H} \), for a molecule fixed in space and acted on by the field \( \mathcal{E} \), \( w_k \) is the energy of the
kth state, \( \beta_k \) is the expectation value of the dipole moment for the \( k \)th state (The Hamiltonian for a molecule in a field is not invariant under coordinate reflection so that the energy eigenstates are not eigenstates of parity.), and

\[
\gamma = \sum_k e^{-\beta w_k} = \text{tr} e^{-\beta h} \tag{IV - 23}
\]

is the internal partition function for a molecule in the field. Using

\[
\beta_k = \left[ - \frac{\partial w_k}{\partial \epsilon} \right] \tag{IV - 24}
\]

we have

\[
\beta = \frac{1}{\beta \gamma} \frac{\partial}{\partial \epsilon} \text{tr} e^{-\beta h} \tag{IV - 25}
\]

We now use the fact that

\[
h = h_0 - \beta \cdot \epsilon \tag{IV - 26}
\]

where \( h_0 \) is the Hamiltonian for a free molecule (with center-of-mass fixed in space) and write

\[
\text{tr} e^{-\beta h} = \text{tr} \frac{1}{2\pi i} \int d\omega e^{-\beta \omega} \frac{1}{\omega - h} \tag{IV - 27}
\]
\[ = \text{tr} \frac{1}{2\pi i} \int dw \, e^{-\beta w} \]

\[ \left\{ \frac{1}{w-h_0} + \frac{1}{w-h_0} \left( p \frac{1}{w-h_0} \right)^2 \varphi^* + \frac{1}{w-h_0} \left( p \frac{1}{w-h_0} \right)^4 \varphi^4 + \ldots \right\} \]

where the terms with odd parity drop out because the trace in (IV - 28) is to be found using eigenstates of \( h_0 \) which may be taken to be eigenstates of parity, and where we use \( p \) to mean the component of the operator \( p \) which is along \( \xi \).

Using

\[ \text{tr} \frac{1}{w-h_0} \left( p \frac{1}{w-h_0} \right)^2 = -\frac{1}{\pi} \frac{d}{dw} \text{tr} \left( p \frac{1}{w-h_0} \right)^2 \]  

and

\[ \text{tr} \frac{1}{w-h_0} \left( p \frac{1}{w-h_0} \right)^4 = -\frac{1}{4} \frac{d}{dw} \text{tr} \left( p \frac{1}{w-h_0} \right)^4 \]  

and integrating by parts we get

\[ \text{tr} e^{-\beta h} = -\beta \text{tr} \frac{1}{2\pi i} \int dw e^{-\beta w} \left\{ \frac{-1}{w-h_0} + \frac{1}{\pi} \left( p \frac{1}{w-h_0} \right)^2 \varphi^* \right\} \]

and putting this back into (IV - 25) we have

\[ \tilde{p} = -\frac{1}{\beta} \text{tr} \frac{1}{2\pi i} \int dw e^{-\beta w} \left\{ \left( p \frac{1}{w-h_0} \right)^2 \varphi^* + \left( p \frac{1}{w-h_0} \right)^4 \varphi^4 \right\} \]
Next, we need to replace $\gamma$ by an expression which indicates its dependence on $\varepsilon$. We can write (IV - 25) in the form

$$\frac{1}{\varepsilon} = \frac{1}{\beta \gamma} \frac{\partial \gamma}{\partial \varepsilon} \quad (IV - 33)$$

and it follows from this that

$$\gamma = \gamma_0 e^{\beta \int_0^\varepsilon P(\varepsilon') d\varepsilon'} \quad (IV - 34)$$

and that we may write

$$\frac{1}{\varepsilon} = \frac{1}{\beta \gamma_0} \left(1 - \frac{1}{2} \beta \alpha_1 \varepsilon^2\right) + O(\varepsilon^4) \quad (IV - 35)$$

$\alpha_1$ being the coefficient such that

$$\frac{1}{\varepsilon} = \alpha_1 \varepsilon \quad (IV - 36)$$

Putting this into (IV - 32) we have

$$\frac{1}{\varepsilon} = -\frac{1}{\gamma_0} \frac{1}{2\pi i} \int dw \, e^{\beta w} \left( p \frac{1}{w - \omega_o} \right)^2 \varepsilon$$

$$+ \left[ -\frac{1}{\gamma_0} \frac{1}{2\pi i} \int dw \, e^{\beta w} \left( p \frac{1}{w - \omega_o} \right)^4 \right] \varepsilon^2 \varepsilon$$

$$+ \frac{1}{2} \beta \alpha_1 \frac{1}{\gamma_0} \frac{1}{2\pi i} \int dw \, e^{\beta w} \left( p \frac{1}{w - \omega_o} \right)^2 \varepsilon^2 \varepsilon \quad (IV - 37)$$
It is clear from (IV - 37) that

\[ \alpha_1 = \frac{1}{\gamma_0} \frac{1}{2\pi i} \int \frac{1}{w - h_0} \left( \frac{1}{p - h_0} \right)^2 \]  

(IV - 38)

and we may thus write

\[ \frac{p_3}{2} = \left[ -\frac{1}{\gamma_0} \frac{1}{2\pi i} \int d\omega e^{-\beta \omega} \left( \frac{1}{p - h_0} \right)^4 \right] \epsilon^2 \epsilon \]  

(IV - 39)

Referring back to (III - 63) and to the discussion at the end of part A of this chapter, we see that \( n_2 \) is given in the low density limit by

\[ n_2 = \frac{1}{2} \beta n_0 \alpha_1 \epsilon^2 \]  

(IV - 40)

Putting (IV - 36), (IV - 39), and (IV - 40) back into (IV - 21), two terms cancel and our intuitive expression becomes

\[ \frac{p_3}{2} = -\frac{n_0}{\gamma_0} \frac{1}{2\pi i} \int d\omega e^{-\beta \omega} \left( \frac{1}{p - h_0} \right)^4 \epsilon^2 \epsilon \]  

(IV - 41)

We return now to the statistical result obtained in part A of this chapter. We recall that we can choose between the statistical result in (IV - 9) for the part of \( \langle P \rangle \) proportional to the cube of \( E_0 \) and the statistical result in (IV - 20) for the part of \( \langle P \rangle \) proportional to the cube of \( \epsilon \). Since in our intuitive treatment we dealt with the field actually
experienced by the molecule, it is with (IV - 20) that
comparison should be made.

We see from (IV - 13) and (IV - 8) that in the low
density limit,

$$\mathcal{C} = - \frac{e^{\beta \mu}}{\lambda^3} \frac{1}{2\pi i} \int dw \ e^{-\beta w} \ \text{tr} \left( \frac{1}{w - h_0} \frac{1}{w - h_0} \frac{1}{w - h_0} \frac{1}{w - h_0} \right)$$  \quad \text{(IV - 42)}

and letting $\mathbf{p}$ again be the component of $\mathbf{p}$ along $\mathbf{e}$, the
statistical result for the part of $\langle P \rangle$ proportional to $E^3$ is

$$\mathcal{C} = - \frac{e^{\beta \mu}}{\lambda^3} \frac{1}{2\pi i} \int dw \ e^{-\beta w} \ \text{tr} \left( \frac{1}{w - h_0} \right)^4 \ E^2 E$$  \quad \text{(IV - 43)}

Now for the grand partition function we have

$$1 + \sum_{N=1}^{\infty} \frac{e^{\beta \mu N}}{N!} \ \text{tr} \ e^{-\beta H(\mathbf{w})} = e^{\beta \mathbf{p} \mathbf{V}}$$  \quad \text{(IV - 44)}

(where $\mathbf{p}$ here means the pressure) and in the limit of low
density this gives

$$\frac{\gamma V}{\lambda^3} \ e^{\beta \mu} = N$$  \quad \text{(IV - 45)}

or

$$\frac{e^{\beta \mu}}{\lambda^3} = \frac{\gamma}{\lambda}$$  \quad \text{(IV - 46)}

Since the left side of (IV - 46) is independent of $E_0$,
the right side is also and we may write
\[ \frac{e^{\beta \mu}}{\lambda^3} = \frac{n_o}{\gamma_o} \]  

(IV - 47)

which shows that (IV - 41) and (IV - 43) agree and completes the demonstration that the statistical result for \( P_3 \) corresponds in the way that we would expect to the statistical result for \( n_2 \).

C. Formula for Gas of Fixed Density in a Uniform Field

If we consider that part of the interior of a parallel plate condenser where the electric field is uniform and suppose that in that part there is a gas whose density is constrained to be independent of \( E_0 \), then it is the density rather than the chemical potential which is an independent variable. We may convert grand ensemble averages into expressions which describe such a system by making the chemical potential a function of \( E_0 \) as described in part C of chapter III. This part of the present chapter is devoted to obtaining from (IV - 11) and (III - 97) the formula for \( P_3 \) in such a system.

Formula (III - 97) is

\[ \mu(E_o) = \mu_o - \frac{1}{2} E_o \frac{\partial P}{\partial n} \]  

(IV - 48)

but for the terms of (IV - 11) which are proportional to \( E_0^3 \)
we use just the term $\mu_\phi$. Referring back to (III - 60) and
(III - 62) we find that when $\mu$ is replaced according to
(IV - 48), $A$ is replaced by

$$A = BE_0 \frac{\partial P}{\partial n} \quad (IV - 49)$$

so that (IV - 11) is changed to

$$P_1 + P_3 = A \left\{ E_0 - \int d^3 R' \Delta(R; R') \left[ P_1(R') + P_3(R') \right] \right\}$$

$$+ \zeta \cdot \epsilon_1 \cdot \epsilon_1 \cdot \epsilon_1 - BE_0 \frac{\partial P}{\partial n} \epsilon_1 \quad (IV - 50)$$

Subtracting $P_1$ from each side, we have

$$P_3 = - A \int d^3 R' \Delta(R; R') P_3(R')$$

$$+ \zeta \cdot \epsilon_1 \cdot \epsilon_1 \cdot \epsilon_1 - BE_0 \frac{\partial P}{\partial n} \epsilon_1 \quad (IV - 51)$$

Neglecting the small variation in $P_3$ near the condensor
plates (c.f. appendix A), we take $P_3$ out of the integral
and note that with $R'$ integrated over the interior of an
ideal parallel plate condensor,

$$\int d^3 R' \Delta(R; R') = \frac{4\pi}{3} \left( 3 \hat{z} \hat{z} - I \right) \quad (IV - 52)$$

where $\hat{z}$ is the unit vector normal to the plates. Thus
\[ P_3 = \frac{1}{1 + \frac{8\pi}{3} A} \left\{ -\frac{1}{z} \varrho \varphi \varphi \varphi - B E_0 \frac{\partial P}{\partial n} \varphi \right\} \] (IV - 53)

We note next that in the uniform field,

\[ B E_0 \frac{\partial P}{\partial n} \varphi = \frac{E_0}{\varepsilon_1} n \frac{\partial P}{\partial n} \] (IV - 54)

and

\[ E_0 = \varepsilon_1 + \int d^3\mathbf{R}' \Lambda (\mathbf{R}; \mathbf{R}') \cdot \varphi (\mathbf{R}') \]
\[ = \varepsilon_1 \left( 1 + \frac{8\pi}{3} A \right) \] (IV - 55)

so that (IV - 53) becomes

\[ P_3 = \frac{1}{1 + \frac{8\pi}{3} A} \left\{ -\frac{1}{z} \varrho \varphi \varphi \varphi - n \frac{\partial P}{\partial n} \right\} \] (IV - 56)

The physical meaning of the term \(-n \frac{\partial P}{\partial n}\) is obvious. Because this formula puts electrostriction in in one term and takes it out again in another, it does not give the most economical description of the fixed density case. The lack of economy is part of the price that must be paid for the mathematical convienience of the grand canonical ensemble.
V. Summary

The treatments of linear polarization in K.W.II and of electrostriction and cubic polarization in this thesis together demonstrate the adequacy and suitability of the method of Kaufman and Watson for the evaluation of the equilibrium properties of a gas of neutral molecules in an electric field.

The theory makes use of a number of approximations. Some of the approximations are introduced in such a way that they can be systematically improved and thus that their magnitudes are easy to estimate. The approximations of this type which have been used in the present work are: first, the neglect of diagrams with more than the necessary number of intercluster interactions; second, the neglect of diagrams with quadrupole interactions; and third, the neglect of inhomogeneity in the fields. Of these approximations, the first two are discussed at the end of part A of chapter III, and the third is discussed in appendix B. The author assumes that the approximation which comes from neglecting quantum effects in the molecular center-of-mass motion is also of this type, but he has not looked into the corresponding corrections.

There are other approximations which are intrinsic in the method and for whose systematic improvement the method is of no use. One of these approximations comes from the elimination
of the molecular continuum states. This approximation seem physically appropriate for gases in which the ratio of ions to neutrals is negligible. But the theory would be nicer if it could be made to include a description of ionization and of electrical shielding by ions and electrons near the electrodes.

Another neglected effect is that which arises from the interaction of the molecules with the electromagnetic field. This effect also increases with temperature, and inclusion of this effect would go hand in hand with inclusion of the effect of molecular continuum states.

The third approximation of this sort is that which comes from the neglect of exchange between molecules in different clusters. For most gas densities, this is hardly even an approximation. At densities which are high enough for this neglect to be appreciable, the quantum mechanical building blocks of the gas are so large that it is no longer appropriate to use the activity expansion on which the whole theory is based.
Acknowledgements

The research for this thesis was done at the Lawrence Radiation Laboratory of the University of California at Berkeley where the author was supported as a graduate student research assistant under the Laboratory's contract with the United States Atomic Energy Commission.

The author is deeply indebted to his research advisor, Dr. Alan N. Kaufman, for the latter's suggestion of this research and for advice and encouragement during the course of it. The author is also indebted to Professor Kenneth M. Watson for helpful discussions.
Appendix A

The following calculation of the dielectric boundary effect in an ideal parallel plate condensor affords a way of seeing how \( R_0 \) should be chosen. The calculation begins with (K.W.II - 3.5) (i.e., equation 3.5 of K.W.II) which is explained in appendix F and which is

\[
E(R) = E_0(R) - \int d^3k' \Delta(k; k') \cdot \langle p(k') \rangle - \frac{4\pi}{3} \langle p(R) \rangle.
\]  

(A - 1)

Here the prime on \( \int \) denotes exclusion from the region of integration of an infinitesimal sphere (\( \epsilon \)-sphere) about the point \( k' = k \). Equation (A - 1) is an immediate consequence of the definition used in K.W.II for the macroscopic electric field, \( E \). It is necessary for the development of the theory that the radius of the excluded sphere be changed to a distance \( R_0 \) which is at least large enough so that when two molecules are separated by \( R_0 \), the electron exchange between them may be neglected.

The integral

\[
\int d^3k' \Delta(k; k') \cdot \langle p(k') \rangle
\]

(A - 2)

over the region between the \( \epsilon \)-sphere and the \( R_0 \)-sphere vanishes if \( \langle p(R) \rangle \) is uniform so that this change in region...
of integration is permissible away from the condenser plates. However, if \( R \) is closer than \( R_0 \) to one of the plates, then (A - 2) does not vanish. We write
\[
\int d^3R' \Sigma (R; R') \cdot < P(R') > = \int d^3R' \Sigma (R; R') \cdot < P(R) > \quad \text{(A - 3)}
\]
where the triple prime indicates integration over that part of the region between the \( \epsilon \)-sphere and the \( R_0 \)-sphere which is occupied by the dielectric. We will see below that \( < P(R) > \) is not uniform near the condenser plates. The contribution to the integral from the next term in the Taylor expansion for \( < P(R') > \) is
\[
\int d^3R' \Sigma (R; R') \cdot (R - R') \cdot \nabla < P(R) > \quad \text{(A - 4)}
\]
This contribution turns out to be smaller than (A - 3) by a factor of the order of \( (a/R_0)^3 \) (\( a^3 \) being the molecular polarizability), and its inclusion would not alter the conclusion which we will reach.

Let the condenser plates be perpendicular to the \( z \) axis so that the external field and the polarization are both in the \( z \) direction. Let the distance from the point \( R \) to the closer condenser plate be \( R_1 \). Then (assuming the plates to be separated by more than \( 2R_0 \) and assuming \( R_1 > 0 \))
\[ \int d^3r' \hat{\Lambda}(\mathbf{r}'; \mathbf{p}') \cdot \langle \mathbf{P}(\mathbf{r}') \rangle = \eta(\mathbf{r}) \langle \mathbf{P}(\mathbf{r}) \rangle \]  \hspace{1cm} (A - 6)

where

\[ \eta(\mathbf{r}) = \begin{cases} 
+ 2\pi \left( \frac{R_o - R_i}{R_o} - \frac{R_o^3 - R_i^3}{3R_o^3} \right), & R_i < R_o \\
0, & R_i \geq R_o
\end{cases} \]  \hspace{1cm} (A - 7)

Equation (A - 1) then becomes

\[ \mathbf{E}_0(\mathbf{r}) - \int d^3r' \hat{\Lambda}(\mathbf{r}'; \mathbf{p}') \cdot \langle \mathbf{P}(\mathbf{r}') \rangle = \mathbf{E}(\mathbf{r}) + \left( \frac{4\pi}{3} + \eta(\mathbf{r}) \right) \langle \mathbf{P}(\mathbf{r}) \rangle \]  \hspace{1cm} (A - 8)

where the prime on \( \int \) now indicates exclusion of the \( R_0 \)-sphere.

This change in (K.W.II - 3.5) implies that (K.W.II - 6.19) should be changed (in the notation of this thesis) to

\[ P_1(\mathbf{r}) = A \left( E_1(\mathbf{r}) + \frac{4\pi}{3} P_1(\mathbf{r}) \right) + H(\mathbf{r}) P_1(\mathbf{r}) \]  \hspace{1cm} (A - 9)

where
\[ H(R) \equiv - \int d^3R' \beta \cdot (R; R') \cdot \eta (R'). \tag{A-10} \]

Now if \( R \) is far (i.e., many times \( R_0 \)) from either plate, \( H(R) = 0 \), and we have the ordinary relation between \( P_1 \) and \( E_1 \). Near the plate \( H(R) \neq 0 \), and the relationship between \( P_1 \) and \( E_1 \) is more complex.

To illustrate this we consider the case of a gas which is dilute enough so that we need include only the one molecule contribution to \( \beta (R; R') \). Then \( \beta (R; R') \) is local and (A - 9) becomes

\[ P_1 (R) = \frac{1}{2} (E_1 (R) + \frac{4 \pi}{3} \eta (R) \cdot P_1 (R)). \tag{A-11} \]

When \( R \) is at the wall, \( \eta (R) = + \frac{4 \pi}{3} \) so that

\[ P_{1, \text{wall}} = \frac{\frac{1}{2} \frac{1}{2} E_1}{1 - \frac{4 \pi}{3} \eta _1 \text{ wall}}. \tag{A-12} \]

whereas at interior points which are farther than \( R_0 \) from the wall,

\[ P_1 = \frac{\frac{1}{2} \frac{1}{2} E_1}{1 - \frac{4 \pi}{3} \eta _1}. \tag{A-13} \]

There is a gradual transition in the relationship as \( R \) moves out to a distance \( R_0 \) from the wall, and the nature of the transition is given approximately by (A - 11).
One may check using $(A-12)$ and $(A-13)$ and the relation $D = E_0 = E + 4\pi P$ that the theory indicates a slightly greater value of $P$ at the wall than in the interior. The thickness of the region of transition is roughly $R_0$. However, on physical grounds, we would expect the thickness of such a transition region to be of the order of the mean intermolecular distance, and we should therefore take that distance for the size of $R_0$. 
Appendix B

In this appendix we present an extension of the treatment in K.W.II, an extension aimed at including the effect produced by inhomogeneity in $E(R)$. We again begin with equation (A - 1). As explained in appendix A, the radius of the excluded sphere must be increased to $R_0$. This enlargement is based on Taylor expansion of $<P(R)>$ about the point $R' = R$. The contributions of the first two terms in the series vanish identically, so that increasing the size of the excluded sphere does not change the equation if, as in K.W.II, only the first two terms are kept. On the other hand, if the third term is kept, then (K.W.II - 3.5) is replaced by

$$E(R) = E_0(R) - \int d^3R' \Lambda(R; R') <P(R')> - \frac{4\pi}{3} <P(R)>$$

(B. - 1)

$$+ \frac{2\pi}{15} R_0^2 \left( 3\nabla \cdot \nabla + \nabla^2 \right) \cdot <P(R)>$$

Now (K.W.II - 3.5) (or rather, the part of it proportional to $E_0$) was used in K.W.II to eliminate the expression $E_0(R') - \int d^3R'' \Lambda(R'; R'') \cdot P(R'')$ from (K.W.II - 6.18) which (in our notation) is
\[ P_1(\mathbf{R}) = -\int d^3 \mathbf{R'} \beta_4(\mathbf{R'}; \mathbf{R}) \left[ \mathcal{E}_0(\mathbf{R'}) - \int d^3 \mathbf{R''} \lambda_4(\mathbf{R'}; \mathbf{R''}) \cdot P_1(\mathbf{R''}) \right] \quad (B - 2) \]

If for eliminating that expression we instead use (B - 1) then (K.W.II - 6.19) is replaced by

\[ P_1(\mathbf{R}) = -\int d^3 \mathbf{R'} \beta_4(\mathbf{R}; \mathbf{R'}) \left[ \mathcal{E}_1(\mathbf{R'}) - \frac{2\pi}{15} R_0^2 (3\mathbf{v'} \cdot \mathbf{v'} - (\mathbf{v'})^2 I) \cdot P_1(\mathbf{R'}) \right] \quad (B - 3) \]

where we have used the abbreviation

\[ \mathcal{E}_1(\mathbf{R}) \equiv \frac{4\pi}{3} P_1(\mathbf{R}) \quad (B - 4) \]

Equation (B - 3) is also evaluated by Taylor expansion of the quantity in braces. We let \( L \) be the distance in which there is a significant fractional change in \( P_1(\mathbf{R}) \) and assume that \( L \) is a good deal larger than \( R_0 \). Then \( R_0^2 (3\mathbf{v} \cdot \mathbf{v} - \mathbf{v}^2 I) \cdot P_1(\mathbf{R}) \) is smaller than \( P_1(\mathbf{R}) \) by a factor of \( (R_0 / L)^2 \). Therefore, in evaluating the integral in (B - 3), we keep the first and third terms in the Taylor expansion for \( \mathcal{E}_1(\mathbf{R'}) \), but only the first term in the expansion for \( \frac{2\pi}{15} R_0^2 (3\mathbf{v'} \cdot \mathbf{v'} - (\mathbf{v'})^2 I) \cdot P_1(\mathbf{R'}) \). As a result we obtain

\[ P_1(\mathbf{R}) = A \left\{ \mathcal{E}_1(\mathbf{R}) - \frac{2\pi}{15} R_0^2 (3\mathbf{v} \cdot \mathbf{v} - \mathbf{v}^2 I) \cdot P_1(\mathbf{R}) \right\} \]

\[ -\int d^3 \mathbf{R'} \beta_4(\mathbf{R}; \mathbf{R'}) \left( \frac{(\mathbf{R} - \mathbf{R'})^2}{2} \right) \mathbf{\nabla} \mathbf{\nabla} \mathcal{E}_1(\mathbf{R}) \quad (B - 5) \]
Since \( \beta(\mathbf{r}; \mathbf{g}') \) is a property of a gas in equilibrium in the absence of an applied electric field, it must be a combination of the tensor \( \frac{(\mathbf{r} - \mathbf{g})(\mathbf{r}' - \mathbf{g})}{|\mathbf{r} - \mathbf{g}|^2} \) and of the identity, 
\( \mathbf{I} = \hat{\mathbf{e}}_1 \hat{\mathbf{e}}_1 \) (where \( \hat{\mathbf{e}}_i \), \( i = 1, 2, 3 \) is one of three orthonormal vectors, and the repeated index is summed over).

Now
\[
\int d\Omega' \frac{(\mathbf{r} - \mathbf{g})(\mathbf{r}' - \mathbf{g})}{|\mathbf{r} - \mathbf{g}|^2} = \frac{4\pi}{3} \mathbf{I} \tag{B-6}
\]

and
\[
\int d\Omega' \frac{(\mathbf{r} - \mathbf{g})(\mathbf{r}' - \mathbf{g})(\mathbf{r} - \mathbf{g})}{|\mathbf{r} - \mathbf{g}|^4} = \frac{4\pi}{15} \left[ \mathbf{I} \mathbf{I} - \hat{\mathbf{e}}_i \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j \mathbf{e}_j \hat{\mathbf{e}}_j \right] \tag{B-7}
\]

Therefore \( \int d^3\mathbf{r}' \beta(\mathbf{r}; \mathbf{g}') (\mathbf{r}' - \mathbf{g})(\mathbf{r}' - \mathbf{g}) \) must be a combination of the tensors \( \mathbf{I} \mathbf{I} \), \( \hat{\mathbf{e}}_i \hat{\mathbf{e}}_i \mathbf{e}_j \hat{\mathbf{e}}_j \), and \( \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j \hat{\mathbf{e}}_j \hat{\mathbf{e}}_i \). We may thus assume that there are three numbers, \( \alpha, \gamma, \delta \) such that \( \alpha + \gamma + \delta = 1 \) and such that
\[
-\frac{1}{2} \int d^3\mathbf{r}' \beta(\mathbf{r}; \mathbf{g}') (\mathbf{r}' - \mathbf{g})(\mathbf{r}' - \mathbf{g}) = F (\alpha \mathbf{I} + \gamma \hat{\mathbf{e}}_i \hat{\mathbf{e}}_i \mathbf{e}_j \hat{\mathbf{e}}_j + \delta \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j \hat{\mathbf{e}}_j \hat{\mathbf{e}}_i) \tag{B-8}
\]

where \( F \) is some function of \( \beta \) and \( \mathbf{r}' \). Then \( (B-3) \) becomes
\[
P_i = A \hat{\mathbf{e}}_i - \frac{2\pi}{15} R_0^2 A (\mathbf{e} \mathbf{e} - \nabla^2 \mathbf{I}) \cdot \mathbf{P}_i + F [\alpha \nabla \hat{\mathbf{e}}_i + (\gamma + \delta) \nabla (\mathbf{e} \cdot \hat{\mathbf{e}}_i)] \tag{B-9}
\]
or substituting for $E_i$,

$$\mathbf{P}_i = \mathbf{A}E_i + \frac{2\pi}{3} \mathbf{A} \mathbf{P}_i - \frac{2\pi}{15} R_0^2 \mathbf{A} \left(3\mathbf{v} \cdot \mathbf{v} - \nabla^2 E_i\right) \mathbf{P}_i$$

$$+ F \left[ \kappa \nabla^2 E_i + (\chi + \delta) \nabla (\mathbf{v} \cdot \mathbf{E}_i) \right] + \frac{2\pi}{3} F \left[ \kappa \nabla^2 \mathbf{P}_i + (\chi + \delta) \nabla (\mathbf{v} \cdot \mathbf{P}_i) \right]$$

(E - 10)

Since the terms containing derivatives are relatively small, we may obtain a solution to the order of the small terms by iteration. Namely, we take $P_i = (P_i)^0 + (P_i)'$ with

$$\langle P_i \rangle_0 = \frac{\mathbf{A}}{1 - \frac{2\pi}{3} \mathbf{A}} E_i \equiv \chi E_i$$

(B - 11)

and neglect derivatives of $\langle P_i \rangle'$. Then using $\nabla (\mathbf{v} \cdot \mathbf{E}) = \nabla^2 \mathbf{E}$ we get

$$\mathbf{P}_i = \chi \mathbf{E}_i + \left[ - \frac{2\pi}{15} R_0^2 \frac{\kappa}{\chi} + \frac{F}{(1 - \frac{2\pi}{3} \mathbf{A})^2} \right] \nabla^2 E_i$$

(B - 12)

Of the two terms in the brackets in (B - 12) the first is smaller than $\chi E_i$ by a factor of the order of

$$\left(\frac{R_0}{L}\right)^2 \frac{\alpha}{R_0^3} = \left(\frac{a}{L}\right)^2 \frac{a}{R_0}$$

(B - 13)

where $\alpha$ is the polarizability of a molecule and is roughly equal (for nonpolar molecules) to the cube of the molecular radius. The second term in the brackets in (B - 12) is
smaller than \( \chi_E \) by a factor of the order of

\[
\frac{R_0^3}{\alpha} \frac{1}{L^2} \frac{d^5}{R_0^6} = \left( \frac{d}{L} \right)^2 \left( \frac{d}{R_0} \right)^3
\]

(B - 14)

where \( d^5 \) represents the factors \( \int d^5 R' (B' \cdot R') (B' \cdot R'') \) in (B - 8). The quantity \( d \) corresponds roughly to the range of the van der Waals force and so will be about 3 Å. Thus the first term will usually be larger than the second.

The nonlocal terms of (B - 12) give the leading effect of field inhomogeneity in the cluster chain approximation. That whole approximation neglects quadrupole contributions which may give to the effective field a contribution which is smaller than \( \chi_E \) by a factor of only \( (a/L)^2 \). But the resultant contribution to \( P_1 \) will be smaller than \( \chi_E \) by a factor of \( (a/L)^2 (a/R_0)^3 \). Thus, (B - 12) gives the leading nonlocal correction to \( P_1 \), but in order that the approximation be kept consistent, this nonlocal correction should only be used in conjunction with the leading contribution involving quadrupole moments and the macroscopic quadrupole density.
Appendix C

This appendix presents a correction to the physical interpretation given by Kaufman and Watson in a paper 6 which will be referred to here as K.W.III. The main result of K.W.II is the derivation of the form $P = A \cdot (E + \frac{4}{3}P)$ and of the formula for the coefficient $A$. The tensor $A$ is expressable as a power series in the density of the gas. The coefficient of $n$ is just $\alpha_1$, the polarizability of a single molecule. The coefficient $\alpha_2$ of $n^2$ is given by the formula

$$\alpha_2 = \int d^3r \ e^{-\beta \phi(R)} \left[ \frac{i}{2} \alpha_2(R) - \alpha_1 \right]$$

(C-1)

where $\phi(R)$ is the average potential energy of interaction of two molecules separated by the distance $R$, and $\alpha_2(R)$ is the polarizability of a two molecule system when one molecule is displaced by $R$ from the other.

K.W.III attempts an intuitive derivation of the preceding formula. The explanation given in K.W.III is based on the idea that a spherical volume $v$ in the gas is acted on by the effective field, $E = E + \frac{4}{3}P$ and that $vP$ can be found by adding the moment of a single molecule acted on by $E$ times the probability that the volume contains one and only one molecule, plus the average moment of a pair of molecules displaced by a given distance and acted on by $E$ times the probability that the volume contains two molecules displaced
by the given distance and then integrated with respect to the displacement, etc.

Now the formulae in K.V.III are all correct, but the quantities which they represent are not the ones mentioned above. The formulae actually have to do with the probability that there is a molecule in \( v \) and that at the same time, there is or is not a second molecule a given distance away from it. Whether the second molecule is or is not in \( v \) is immaterial. A molecule is considered to be acted on by the effective field as long as there is no other molecule within a distance \( R_0 \) of it. But when the molecule whose moment contributes to \( vP \) has a neighbor within the distance \( R_0 \), then the two molecules are to be treated as a single system subject to \( \mathcal{E} \), and the first molecule is then credited with half the moment of the system. If one wished to go on to obtain the part of \( A \) proportional to \( n^3 \), it would be necessary to include the probability of there being a third molecule within \( R_0 \) of one or both of the first two, etc. With this amendment, the intuitive approach gives an accurate picture of the physical content of the theory.
Appendix D

This appendix gives a simple derivation of the Buhrenholtz theorem in a form suitable for our purpose. Let \( K_a \) and \( V_a \) be operators for one arm of a cluster diagram, and let \( K_r \) and \( V_r \) be operators for the rest of the diagram. Then

\[
\text{tr} \ e^{-\beta (K_a + V_a + K_r + V_r)}
\]

\[
= \text{tr} \frac{1}{2\pi i} \int dw e^{-\beta w} \left\{ \frac{1}{w-K_a-K_r} + \frac{1}{w-K_a-K_r} \frac{1}{w-K_a-K_r} + \cdots \right\}
\]

\[
= \text{tr} \frac{1}{2\pi i} \int dw_r e^{-\beta w_r} \left\{ \frac{1}{w_r-K_r} + \frac{1}{w_r-K_r} V_r \frac{1}{w_r-K_r} + \cdots \right\}
\]

But since \( K_a + V_a \) commutes with \( K_r + V_r \), the exponential of (D - 1) can be factored and (D - 1) can be written as

\[
\text{tr} \frac{1}{2\pi i} \int dw_a e^{-\beta w_a} \left\{ \frac{1}{w_a-K_a} + \frac{1}{w_a-K_a} V_a \frac{1}{w_a-K_a} + \cdots \right\}
\]

We may consider the interactions of \( V_a \) and \( V_r \) as depending on variable parameters so that (D - 2) and (D - 3) have the nature of power series. We may then equate the terms of (D - 2) which contain each interaction a given number of times with the terms of (D - 3) which contain each interaction the same given number of times.
Appendix E

This appendix is devoted to a brief derivation of (III - 45). Molecules are grouped into clusters. The perturbation expansion with respect to \( \sum_{\delta < \epsilon} V_{\delta \epsilon} + \sum_{\delta} V_{\delta} \) is introduced, and only the cluster chain terms are retained. Then according to (II - 10)

\[
P_1(\mathcal{E}) = \frac{1}{\beta} \sum_{\mathcal{E} \in (\mathcal{E})} \frac{1}{\pi} \sum_{c = 1}^{\infty} \frac{1}{c!} \left( \frac{e^{\beta \mu}}{\beta^2} \right) m_{\epsilon} \int \sum_{d^m R^m} \left\{ \left( \frac{1}{w - \mu} \right) V_1 \ldots V_{\epsilon} \frac{1}{w - \mu} \right\}
\]

(E - 1)

The differentiation would normally apply to the \( E_0 \) at each end of each chain. But with our procedure for enumerating chains, each chain appears once with its cluster labels running in one direction and then a second time with its cluster labels running in the other direction. We may therefore accomplish differentiation with respect to the \( E_0 \) at each end of each chain by dropping the factor of 1/2 from (E - 1) and differentiating each term with respect to the \( E_0 \) in cluster 1. (This holds even for the one cluster case because we treat the two factors of \( V_1 \) as distinguishable.)

Recalling (III - 42) we have

\[
\frac{\delta}{\delta E_0(\mathcal{E})} V_1 = - \sum_k \frac{p_k}{2} \delta (R - R_k)
\]

(E - 2)

Finally we perform the operations corresponding to (III - 35)
and (III - 36) to obtain a factor of $-\beta$ and to get
\[ \sum_k \rho_k \delta(R-R_k) \text{ outside of the sum over orders. The result is} \]
\[ p_\nu(R) = \sum_{C=1}^{\infty} \prod_{\ell=1}^{C} \left\{ \sum_{m_\ell=1}^{\infty} \frac{1}{m_\ell!} \left( \frac{e^{\beta R}}{\lambda^3} \right)^{m_\ell} L_{m_\ell} \int d^3 R^m_\ell \right\} \]
\[ \left( E - 3 \right) \]
\[ \int \frac{1}{2\pi i} dw e^{-\beta w} + \sum_k \rho_k \delta(R-R_k) \sum \left( \frac{i}{w-K} V_2 \cdots V_c \frac{i}{w-K} \right) \]

and (III - 45) differs from this only in matters of labeling which are incidental.
Appendix F

This appendix deals with the definition of the macroscopic electric field. In a theory which ignores the effect of quadru-pole moments, it is defined as the sum of the field due to external charges and the field due to macroscopic polarization. Thus,

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) - \nabla \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \langle \mathbf{P}(\mathbf{r}') \rangle$$

(F - 1)

Since the integrand is not finite at the point \( \mathbf{R}' = \mathbf{R} \), there is a question as to the meaning of the gradient of the integral. However, we may exclude an infinitesimal sphere about the point \( \mathbf{R}' = \mathbf{R} \) from the region of integration without changing the value of the integral. The gradient then contains a contribution from differentiation of the integrand and a contribution from differentiation with respect to the location of the infinites-mal sphere. So

$$\mathbf{E}(\mathbf{R}) = \mathbf{E}_0(\mathbf{R}) - \int d^3\mathbf{r}' \mathbf{A}(\mathbf{R}; \mathbf{r}') \cdot \langle \mathbf{P}(\mathbf{r}') \rangle - \frac{4\pi}{3} \langle \mathbf{P}(\mathbf{R}) \rangle$$

(F - 2)

where the prime on \( \int d^3\mathbf{r}' \) indicates that an infinitesimal sphere about \( \mathbf{R}' = \mathbf{R} \) is excluded from the region of integration, and where

$$\mathbf{A}(\mathbf{R}; \mathbf{r}') \equiv \nabla \nabla' \frac{1}{|\mathbf{R} - \mathbf{R}'|}$$

(F - 3)
References

This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.