EQUATION OF STATE OF REAL GASES

A. A. SABRY

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PIAZZA OBERDAN
TRIESTE
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A.A. Sabry**

TRIESTE
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** On leave of absence from the University of Assyout, U.A.R.
Extensive work has been done to calculate the virial coefficients which appear in the expansion of $\frac{PV}{RT}$ in powers of $\frac{1}{V}$.

In this work an expression of $\frac{PV}{RT}$ is obtained in a closed form and hence can be applied to very high densities of the gas. The value of $\frac{PV}{RT}$ at the critical point, as well as isothermals of the gas, agree remarkably with experimental results.
I. INTRODUCTION

A statistical study leading to the equation of state of a gas usually starts by considering the virial of Clausius

\[ P \cdot V = R \cdot T - \frac{1}{6} N \cdot V \int_0^\infty r^2 \ \rho_2(r) \cdot \varphi(r) \cdot 4 \pi r^2 \ dr \]  
(1)

where \( \rho_2(r) \) is the probability for two molecules to be at distance \( r \) apart, \( \varphi(r) \) the mutual potential between two molecules. The number \( N \) is the total number of molecules in one gram-mol of the gas.

The solving of the problem depends then in principle on a knowledge of \( \rho_2(r) \). For the evaluation of this function, one can refer to the work of BORN and GREEN \(^1\), in which they use a relation suggested by KIRKWOOD \(^2\), relating the probability of relative distribution \( \rho_{123}(\vec{x}_1, \vec{x}_2, \vec{x}_3) \) of three molecules to the probabilities of relative distribution of two molecules \( \rho_{12}, \rho_{31}, \rho_{13} \).

The Kirkwood relation was checked for the distribution of molecules in the solid state, where the functions \( \rho_{123}, \rho_{12} \) can be rigorously calculated on the assumption of small thermal vibrations \(^3\). The result was that the Kirkwood relation may be taken to be an approximate relation and in no way a rigorous one which can be reliable in all conditions.

It may be noted that the mean potential energy can be expressed, on use of the same function \( \rho_2(r) \), as

\[ \bar{E}_p = \frac{1}{2} N \int_0^\infty \rho_2(r) \ \varphi(r) \cdot 4 \pi r^2 \ dr \]  
(2)
There is a thermodynamic relation between the derivatives of $p$ and $\mathcal{E}_p$, namely,

$$\frac{\partial \mathcal{E}_p}{\partial V} = - \frac{3}{\partial (\frac{1}{T})} \left( \frac{p}{T} \right)$$  \hspace{1cm} (3)$$

This relation is generally not satisfied, if $p$, $\mathcal{E}_p$ are calculated from equations (1), (2). This is because $\rho_2(r)$ is not known rigorously.

In this paper, a different procedure is followed to obtain the equation of state, without the use of the function $\rho_2(r)$, and which conforms with the thermodynamic relations.

In the following, a short survey of the known equations of state of a gas will be given.

BOLTZMANN \textsuperscript{4)} obtained the following expansion of $\frac{pV}{RT}$, assuming the gas to consist of hard spheres

$$\frac{pV}{RT} = 1 + \frac{b}{V} + \frac{5}{8} \left( \frac{b}{V} \right)^2 + \cdots$$

where $b$ is four times the volume of the molecules. To obtain this equation, he took into consideration the possibility that two spheres of force surrounding the molecules intersect one another.

On adding to the above relation the Van der Waals term due to the cohesion forces, one obtains:

$$\frac{pV}{RT} = 1 + (b - \frac{\alpha}{RT}) \frac{1}{V} + \frac{5}{8} \left( \frac{b}{V} \right)^2 + \cdots$$  \hspace{1cm} (4)$$

This relation for small $\frac{b}{V}$ is, however, better than the Van der Waals equation. KAMMERLINGH ONNES \textsuperscript{5)} applied this relation to Helium and found that it agrees fairly well with experimental results over a temperature range from 100° up to -217°.

In order to obtain an expansion in density valid for all gases, Kammerlingh Onnes assumed an empirical equation of state
\[ \frac{pV}{RT} = 1 + \frac{A}{V} + \frac{B}{V^2} + \frac{C}{V^4} + \frac{D}{V^6} + \frac{E}{V^8} \]  

(5)

where the coefficients \( A, B, C, D, E \) depend on the temperature as an expansion in the form

\[ A = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} + \frac{a_3}{T^4} + \frac{a_4}{T^6} \]

(\( T, V \) being reduced temperature and volume)

On giving numerical values to the 25 constants, he succeeded in fitting observations of Amagat, Ramsay and Young on a number of gases (\( \text{H}_2, \text{O}_2, \text{N}_2, \text{C}_4\text{H}_{10}^0 \) and \( \text{C}_5\text{H}_{12} \)).

To obtain an equation of state correct for high values of the density, CLAUSIUS assumed the empirical equation

\[ \left( p + \frac{a'}{T(V+c)^n} \right)(V-b) = RT \]  

(6)

Although it fits the isothermals of \( \text{CO}_2 \) for high densities, it is found that for low densities the Van der Waals equation fitted the observations better. The equation, being partially successful with \( \text{CO}_2 \), was not equally successful with other gases. Clausius therefore suggested a more general formula

\[ \left[ p + \left( \frac{a''}{T^{n-1}} - \frac{a'''}{(V+c)^2} \right) \frac{1}{(V+c)^2} \right](V-b) = RT \]  

(7)

where \( n = 2 \) for \( \text{CO}_2 \) and has sometimes to be taken as a function of \( T \) to fit the observations.
There is no room to give all such empirical formula\(^7\). It is, however, obvious that there is no finality in any of these formulae and it is possible to go on extending them indefinitely without arriving at a fully satisfactory formula, as might be anticipated since they are purely empirical and not founded on any satisfactory theoretical basis.

II. GENERAL OUTLINE OF THE METHOD

The equation of state of the gas, namely the pressure as a function of \( T, V \), will be obtained from the free energy \( \Delta \)

\[
\rho = -\frac{2}{\delta V} A(V, T)
\]

It may be noted that the entropy \( S \) is also given

\[
S = -\frac{2}{\delta T} A(T, V)
\]

hence the thermodynamic relation (3) is automatically satisfied.

On the use of the Gibbs distribution for a fixed number of particles the free energy \( \Delta \) is obtained from

\[
\Delta = -kT \log \left[ \sum_n \bar{e}^{E_n/kT} \right]
\]

where the summation is over all quantum states of the system. If \( H_T \) be the Hamiltonian operator of the whole system, then we can express \( \bar{e}^{\beta E_n} \) as

\[
\bar{e}^{\beta E_n} = \int \left( \bar{e}^{\beta H_T} \nu_n \right) d\nu
\]
The wave functions \( \psi_n \) describing the whole system of molecules can be expressed as a product of a function \( u_j \) describing the motion of the centre of mass of molecules, multiplied by a function \( \prod \chi_i \) describing the internal structure of molecules. In a similar way we express the total Hamiltonian \( H_T \) as a sum of \( H + \sum H_i \), where \( H \) corresponds to the motion of the centre of masses of molecules. The expression (10) hence becomes

\[
\frac{1}{\beta} e^{-\beta E_n} = \prod_i \frac{1}{\beta} e^{-\beta \varepsilon_{n_i}} \left( \int (u^*_p \varepsilon^\beta_H u_p) \, d\nu \right) \tag{12}
\]

where \( \varepsilon_{n_i} \) are the eigenvalues corresponding to the internal states of a molecule \( i \).

For a weak interaction between the molecules we can assume \( u_j \) to be a plane wave

\[
u_p = \frac{1}{\sqrt{N^1}} \frac{1}{\sqrt{N^2}} \sum_P \varepsilon_p \varepsilon_+ (r_P) \tag{13}
\]

The summation is taken over all permutations (of number \( N! \)) of \( P_1, P_2, \ldots \), and \( \varepsilon_P = 1 \) for Bose statistics, \( \varepsilon_P = (-)^P \) for Fermi statistics.

Summing \( e^{\beta E_n} \) expressed by (12) over all states \( n \), we get for the partition function \( Z_T \) of the whole system

\[
\frac{Z_T}{Z_I} = \sum_n e^{\beta E_n} = Z_I \frac{Z}{Z_I} \tag{14}
\]
where
\[ Z = \sum_p \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} Z_p \]

is the partition function corresponding to one molecule. Also

\[ Z = \sum_p \int \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} Z_p \]

where the summation \( \sum_p \) over all momenta of the centre of mass of molecules is replaced by \( \sqrt{\frac{2}{\pi}} \int \frac{dp}{\hbar^3N} \). It may also be noted that the integration in (16) expressed by \( \int \) is taken only over regions in phase space corresponding to physical distinct states of the body. To extend the integral over all points of phase space, we have to divide it by the number of possible permutations of the \( N \) identical molecules, and hence we get

\[ Z = \frac{\sqrt{\frac{2}{\pi}}}{N!} \int \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} Z_p \int \frac{dp}{\hbar^3N} \]

where the integral now extends over all points in the phase space.

On substituting for \( Z_p \) from equation (13), we get for \( Z \)

\[ Z = \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]

\[ \frac{1}{N!} \sum_p \frac{e_p}{p} \int \left( \beta \right)^{\frac{3}{2}N} \left( \frac{\beta}{\pi} \right)^{\frac{3}{2}N} \int \frac{dp}{\hbar^3N} \]
The summation over the permutations $P$ of the momenta is taken only over the first $j^*$ in the exponential $e^\frac{i}{\hbar} (\vec{q}_1 \cdot \vec{p}_1)$. 

The Hamiltonian $H$ describing the motion of the centre of masses of molecules can be expressed as

$$H = -\frac{k}{2m} \frac{\vec{p}^2}{\vec{q}_1} + \Phi(\vec{q}_1, \ldots, \vec{q}_N). \tag{19}$$

where $\Phi$ is the mutual potential energy of the whole $N$ molecules of the gas.

It will be the aim in the following to compute the partition function $Z$ of the centre of mass motion from equation (18).

III. THE PARTITION FUNCTION OF TRANSLATIONAL MOTION

In order to compute the partition function $Z$ from (18), we first carry out the operation $e^{\Phi H} e^{\sum_k H_k}$, where $H$ is given by equation (19).

We start from the equation

$$H e^{\sum_k H_k} = E e^{\sum_k H_k} \tag{20}$$

where

$$E = \frac{1}{2m} \vec{p}^2 + \Phi \tag{21}$$

is the total energy of the centre of mass system.

Operating by $H$ on both sides of equation (20), we get

$$H e^{\sum_k H_k} = e^{\sum_k H_k} \sum E.$$

- 8 -
where
\[ S = - \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial \tilde{r}_i^2} + \frac{1}{k^2} \tilde{r}_i \right) + \Phi \]
\[ = E + \frac{k^2}{2m}(\tilde{p} \frac{\partial}{\partial \tilde{r}_i} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \tilde{r}_i^2}) \]
(22)

By successive applications of \( H \), we get
\[ H^n \frac{\hbar}{n} = \frac{\hbar}{n} \quad S^{-1} \]
Hence it easily follows
\[ \tilde{e}^\beta H \frac{\hbar}{n} = \frac{\hbar}{n} \left[ 1 + \frac{1}{\beta} \left( \tilde{e}^\beta S - 1 \right) E \right] \]
(23)

If we assume
\[ f(S) = \frac{1}{S} \left( \tilde{e}^\beta S - 1 \right) \]
(24)

Then the expression (23) can be written in the form
\[ \tilde{e}^\beta H \frac{\hbar}{n} = \frac{\hbar}{n} \left[ \tilde{e}^\beta E + \{ f(S) - f(E) \} E \right] \]
(25)

Substituting from this equation into the expression (18) for \( Z \), we get
\[ Z = \frac{1}{N!} \sum_{\tilde{r}_1, \ldots, \tilde{r}_N} \exp \left[ \frac{\hbar}{n} \left( \tilde{r}_1 \cdot \tilde{p}_1 + \cdots + \tilde{r}_N \cdot \tilde{p}_N \right) \right] \left[ \tilde{e}^\beta E + \{ f(S) - f(E) \} E \right] \]
(26)

where
\[ \tilde{\eta}_r = \tilde{q} \cdot \tilde{q}_r \]
(27)
and the summation is over all permutations of $\nu \alpha \gamma$.

We denote the quantity between brackets in the integrand of equation (26) by $I$, i.e.,

$$
I = 1 + \frac{1}{S} \left( e^{\beta S} - 1 \right) E
$$

$$
= e^{\beta S} + \sum_{f} \left( f(\alpha) - f(\gamma) \right)^{2} E
$$

We wish now to expand $I$ in powers of $\beta$. This can be done, either directly by expanding $f(\alpha)$ in (28), or by using the following way 8:

Differentiating (28) with respect to $\beta$, we get

$$
\frac{\partial I}{\partial \beta} = e^{\beta S} E
$$

and, operating on both sides of (28) by $S$, we get $S E = e^{\beta S} E$; hence

$$
\frac{\partial I}{\partial \beta} = -S I
$$

On expanding $I$ in powers of $\beta$, and using the above equation, we can easily find the coefficients of the expansion. The result can be written:

$$
I = e^{\beta S} + \frac{\beta}{2m} \sum_{\nu \alpha \gamma} \left( f_{\nu \gamma} e^{\beta S} \right)
$$

$$
- \frac{\beta^{2}}{2m} \sum_{\nu \alpha \gamma} \left( \frac{\partial^{2} E}{\partial \nu \partial \alpha} - \frac{1}{2} \frac{\beta^{2}}{m} \left( \frac{\partial E}{\partial \nu} \right)^{2} - \frac{1}{2} \frac{\beta^{2}}{m} \left( \frac{\partial E}{\partial \alpha} \right)^{2} \right) + \frac{\beta^{3}}{6m} \sum_{\nu \alpha \gamma} \left( \frac{\partial^{3} E}{\partial \nu \partial \alpha \partial \gamma} \right)
$$

$$
+ \cdots
$$

(30)

Substituting from this into (26), we get for $Z$

$$
Z = \frac{1}{N!} \int e^{\beta S} d\alpha \frac{d\beta}{h^{3N}} \left[ 1 - \frac{1}{4} \frac{\beta^{2}}{m} \frac{\partial^{2} E}{\partial \alpha^{2}} + \frac{1}{6m} \left( \frac{\partial E}{\partial \alpha} \right)^{2} \right] + \frac{\beta}{2m} \frac{\partial E}{\partial \alpha}
$$

$$
+ \left[ \frac{\beta^{2}}{6m} \frac{\partial E}{\partial \alpha} \frac{\partial E}{\partial \alpha} + \frac{\beta^{3}}{8m} \frac{\partial E}{\partial \alpha} \frac{\partial E}{\partial \alpha} \right]
$$

- 10 -
In this expression the term in the summation over all permutations of particles for which all $\eta_r = 0$ is separated from other terms. Hence the summation before the second integral in (31) is only over permutations for which all $\eta_r \neq 0$.

Integrating over all momenta $p$, the first part in equation (31) becomes

\[
Z_1 = \frac{1}{N!} \left( \frac{\pi m \hbar^2}{\beta} \right)^{\frac{3N}{2}} \int e^{i \Phi} d\eta \left[ 1 - \frac{k^2 \beta^2 \frac{\partial^2 \Phi}{\partial q_j^2}}{12m} + \frac{k^2 \beta^2 \frac{\partial^2 \Phi}{\partial q_j^2}}{24m} \right]
\]

(32)

Since $\beta \int e^{i \Phi} \left( \frac{\partial \Phi}{\partial q_j} \right)^2 d\eta = \int e^{i \Phi} \frac{\partial \Phi}{\partial q_j} d\eta$ the expression for $Z_1$, can be simplified to

\[
Z_1 = \frac{1}{N!} \left( \frac{\pi m \hbar^2}{\beta} \right)^{\frac{3N}{2}} \int e^{i \Phi} \left[ 1 - \frac{k^2 \beta^2 \frac{\partial^2 \Phi}{\partial q_j^2}}{24m} \right] d\eta
\]

(32 a)
For the integration over $\phi$ in the second integral, we have first to integrate over all directions in the $3N$ space and then over the magnitude $|\mathbf{p}|$ of the momentum. We set

$$d|\mathbf{p}| = |\mathbf{p}|^{3N-1} d|\mathbf{p}| d\mathcal{O}$$

and use the following results of the integration over the solid angle $d\mathcal{O}$ in the $3N$-dimensional momentum space (see Appendix I)

$$\int e^{i(\mathbf{k} \cdot \mathbf{p})} d\mathcal{O} = (2\pi)^{\frac{3N}{2}} J_{3N-1}(z)$$

$$\int e^{i(\mathbf{k} \cdot \mathbf{p})} d\mathcal{O} = (2\pi)^{\frac{3N}{2}} \frac{J_{3N}(z)}{2\pi^{\frac{3N}{2}}} |\mathbf{p}|^2 \frac{1}{\hbar} \gamma_c$$

$$\int e^{i(\mathbf{k} \cdot \mathbf{p})} d\mathcal{O} = (2\pi)^{\frac{3N}{2}} \left[ |\mathbf{p}|^2 \frac{J_{3N}(z)}{2\pi^{\frac{3N}{2}}} - \frac{1}{\hbar} \gamma_c \frac{1}{\hbar} \gamma_c \frac{J_{3N+1}(z)}{2\pi^{\frac{3N}{2}}} \right]$$

(34)

where the argument $z$ of the Bessel function is given by

$$z = \frac{|\mathbf{p}|}{\hbar} \sqrt{\frac{1}{\eta_1^2} + \frac{1}{\eta_2^2} + ...}$$

(35)

The results after the integration over all directions of $\phi$ in the second part of equation (31) then becomes

$$Z_2 = \frac{1}{N} \sum_\mathcal{O} e^{\frac{(2\pi)^{3N}}{\hbar}} \int d\mathcal{O} \mathcal{E}^2 |\mathbf{p}|^{3N-1} \left[ \gamma_1 - \frac{1}{2} \frac{k_1^2 \gamma_1}{m} \frac{x_1^2}{\hbar^2} + \frac{x_1^2 \gamma_1}{\hbar^2} \right]$$

$$\frac{J_{3N-1}(z)}{2\pi^{\frac{3N}{2}}} + \left\{ \frac{2}{2m} \frac{|\mathbf{p}|}{\hbar} \gamma_1 \frac{\gamma_1}{\beta_1} \frac{1}{\beta_1} \frac{\beta_1}{\hbar} \right\} \frac{J_{3N}(z)}{2\pi^{\frac{3N}{2}}}$$

(34)

- 12 -
For the integration over the magnitude $|\phi|$ of $\phi$, we use the general formula (see Appendix II)

$$\int_0^\infty J_n\left(\frac{\beta}{2\pi}\right) e^{-\frac{\beta^2}{2m} |\phi|^2} \frac{2^n}{\pi^{\frac{n}{2}}} \frac{1}{\sqrt{\pi}} \frac{1}{\left[\frac{\beta}{2\pi} + \frac{\left|\phi^2\right|}{2n} \right]^{\frac{n+1}{2}}}$$

(37)

The value of $\frac{\eta^2}{3N}$ fluctuates about $\frac{1}{5^2} \left(\frac{3V}{4\pi}\right)^3$, and for the least possible volume $V$ occupied by the hard spheres, the value of $\frac{G^2\eta^2}{m} \sim 10^{-15}$, and hence completely negligible, unless the temperature is extremely near the absolute zero. It follows then that the contribution $Z_2$ can be neglected compared to $Z_1$, and we finally have

$$Z = Z_1 = \frac{1}{N} \left(\frac{\eta^2}{3N}\right)^{3N} \int e^{\frac{2\pi \Phi}{m}} \left[1 - \frac{\beta^2}{8\pi} \frac{3^2}{m} \left(\frac{\Phi^2}{6\pi}\right)^2\right] \, dq$$

(38)
IV. CHOICE OF THE POTENTIAL

The evaluation of the $3N$-dimensional integral in the $q$-space for the partition function $Z$, given by equation (38), is a very difficult task. It is found possible to carry out the integration for a special choice of the mutual potential between the molecules. The mutual potential $\phi_{ij}(R_{ij})$ between any two molecules $i,j$ is supposed to be infinite within a sphere (of force) of radius $\sigma$, i.e.

$$\phi_{ij}(R_{ij}) = \infty \quad \sigma < R_{ij} < \sigma^- \quad (39)$$

For $R_{ij} > \sigma$, the potential is left unspecified but, as is well known, it tends to $-\frac{A}{R_{ij}}$ as $R_{ij}$ becomes large.

The total mutual potential energy $\Phi$, given by

$$\Phi = \frac{1}{2} \sum_{ij} \phi_{ij}(R_{ij}) \quad (40)$$

can then be expressed as a sum of two terms

$$\Phi = \Phi^{(0)} + \Phi^{(1)} \quad (41)$$

The part $\Phi^{(0)}$ is a hard sphere potential which is zero everywhere, except within the spheres of force where it is infinite. It may be noted that a molecule as a hard sphere is of radius $\frac{\sigma}{2}$, while the sphere of force around the same molecule is of radius $\sigma$; hence the spheres of force may overlap with each other.

On the other hand the part $\Phi^{(1)}$ is the cohesive potential between the molecules, which can be expressed as

$$\Phi^{(1)} = \frac{1}{2} \sum_{ij} \phi_{ij}^{(1)}(R_{ij}) \quad (42)$$
where the cohesive potentials \( \phi^{(1)}(R_{ij}) \) are only defined for \( R_{ij} > \sigma \).

We start now to evaluate the classical part of the partition function \( Z \), and postpone the quantum terms until later.

Substituting for \( \phi \) from equation (41), we find that the classical part of \( Z \) in (33) is

\[
Z_c = \frac{1}{N!} \left( \frac{\alpha}{\beta \hbar^2} \right)^N \int e^{\beta \phi^{(1)}(\Phi)} d\Phi \quad (43)
\]

The cohesive potential \( \Phi^{(1)} \) fluctuates about a mean value \( \overline{\Phi^{(1)}} \). Neglecting these fluctuations, we can take the part \( e^{\beta \Phi^{(1)}} \) outside the integral in equation (43), and we are left with the integral

\[
\int e^{\beta \Phi^{(1)}} d\Phi_1 d\Phi_2 \cdots d\Phi_N
\]

If we now denote by \( B_r \) the average volume occupied by \( r \) spheres of force, the above integral can easily be shown to be

\[
\int e^{\beta \Phi^{(1)}} d\Phi = (V-B_{N-1}) (V-B_{N-2}) \cdots (V-B_1) V
\]

Hence, the partition function \( Z_c \) in equation (43) can be expressed as

\[
Z_c = \frac{1}{N!} \left( \frac{\alpha}{\beta \hbar^2} \right)^N e^{\beta \overline{\Phi^{(1)}}} (V-B_{N-1}) (V-B_{N-2}) \cdots (V-B_1) V \quad (45)
\]

The average cohesive potential \( \overline{\Phi^{(1)}} \), and the average volume \( B_r \) occupied by \( r \) spheres of force, can both be expressed in terms of the radial distribution function \( P_2(R) \) as follows:
The average potential $\overline{\Phi}^{(1)}$ is given by

$$\overline{\Phi}^{(1)} = \frac{1}{2} \sum_{i,j} \int \Phi(R_{ij}) \rho_{ij}(R_{ij}) \, d^3 q_i \, d^3 q_j. \tag{46}$$

where $\rho_{ij}(\vec{q}_i, \vec{q}_j) \, d^3 q_i \, d^3 q_j$ is the probability that two specified molecules $i, j$ occupy the volume elements $d^3 q_i, d^3 q_j$ simultaneously.

Since $\rho_{ij}(\vec{q}_i, \vec{q}_j)$ depends only on the distance $R_{ij}$ between the molecules, we can integrate the integral in equation (46) over $d^3 q_j$ and get

$$\overline{\Phi}^{(1)} = \frac{1}{2} N^2 V \int_0^\infty \Phi(R) \rho_2(R) \cdot \frac{\pi}{4} R^2 \, dR. \tag{47}$$

For big values of $R$ the function $\rho_2(R)$ is constant and is given by

$$\rho_2(R) = \frac{1}{V^2} \tag{48}$$

but for small values of $R$, the function $\rho_2(R)$ is a complicated expression which depends also on the volume $V$ and temperature $T$. If we however assume $\rho_2(R) = \frac{1}{V^2}$ for all values of $R > 0$, we obtain from (47)

$$\overline{\Phi}^{(1)} = -\frac{\alpha}{V} \tag{49}$$

where

$$\alpha = \frac{-1}{2} N^2 \int_0^\infty \Phi(R) \cdot \frac{\pi}{4} R^2 \, dR \tag{50}$$
More rigorously, \( a \) is not a constant and is defined by

\[
a = - \frac{1}{4} N V \left[ \int_0^\infty \phi^{(1)}(R) \rho(R) \frac{4}{2} \pi R^2 dR \right]
\]

(51)

For small densities, the quantity \( a \) can be safely taken as a constant, but as the density becomes very high, \( a \) is no longer a constant and depends on \( V, T \).

In the following we shall regard \( a \) as a constant, and shall find that the results accordingly conform with observation up to densities as high as the critical point.

Next we attempt to calculate the quantity \( \mathcal{B}_r \), the average volume occupied by \( r \) spheres of force.

Assume \( \lambda_{ij}(R_{ij}) \) be the volume cut out by a sphere of force around a molecule \( j \) from the sphere around the molecule \( i \). This quantity is easily found to be

\[
\lambda_{ij}(R_{ij}) = \frac{4}{3} \pi \sigma - \frac{3}{2} \pi \sigma R_{ij} + \frac{1}{2} R_{ij}^2, \quad (\sigma < R_{ij} < 2\sigma)
\]

\[
= 0, \quad (R_{ij} > 2\sigma)
\]

(52)

Now, the total volume left from the sphere \( i \) is

\[
\mathcal{B}_i = \sum_j \lambda_{ij}(R_{ij})
\]

and the total volume of all \( r \) spheres of force is

\[
r \mathcal{B}_i = \frac{1}{2} \sum_j \lambda_{ij}(R_{ij})
\]
The average volume of \( r \) spheres is then given by

\[
\mathcal{B}_r = r \mathcal{B}_1 - \frac{1}{2} \int_{\sigma}^{\infty} \lambda(R) \cdot \rho_2(R) \cdot 4\pi R^2 \, dR
\]

(53)

For low densities, we can substitute for \( \rho_2(R) \) from equation (48), and obtain

\[
\mathcal{B}_r = r \mathcal{B}_1 - \frac{1}{2} \alpha \frac{R^2}{V} \]

(54)

where

\[
\alpha = \frac{1}{8} \int_{\sigma}^{\infty} \lambda(R) \cdot 4\pi R^2 \, dR
\]

(55)

when we substitute for \( \lambda(R) \) from (52).

In general, \( \alpha \) is a function of \( V, T \), especially for very high densities, and is given by

\[
\alpha = \frac{V}{B_1^2} \int_{\sigma}^{\infty} \lambda(R) \cdot \rho_2(R) \cdot 4\pi R^2 \, dR
\]

(56)

On substitution for \( \Phi_1 \) and \( B_r \) from equations (49), (54) into equation (45), we obtain the classical part of the partition function \( Z_c \) in its final form

\[
Z_c = \frac{1}{N} \left( \frac{2\pi m}{\beta k} \right)^{3N} e^{\frac{\beta A}{V}} \sum_{r=0}^{N-1} \prod_{r=0}^{N-1} \left[ 1 - r \frac{\beta_1}{V} + \frac{1}{2} \alpha \frac{R^2}{V^2} \right]
\]

(57)
V. THE EQUATION OF STATE

The free energy $A$, defined by equation (9), can now be expressed, on use of equations (14), (15) and (57), as

$$A = -\frac{1}{\beta} \left[ \sum_{r<0}^{N-1} \log \left( 1 - r \frac{B_1}{V} + \frac{1}{2} \alpha r^2 \frac{B_1^2}{V L} \right) \right]$$

plus another quantum term which we have so far not taken into account, $Z_1$ being the partition function for one molecule.

The last sum in this expression can be expressed as an integral, assuming the number $N$ to be very big,

$$\sum_{r<0}^{N-1} \log \left( 1 - r \frac{B_1}{V} + \frac{1}{2} \alpha r^2 \frac{B_1^2}{V L} \right) = \int_0^N \log \left( 1 - r \frac{B_1}{V} + \frac{1}{2} \alpha r^2 \frac{B_1^2}{V L} \right) dr$$

$$= -2N - \frac{V}{B_1} \left[ \lambda \left( 1 - \frac{N B_1}{\lambda V} \right) \log \left( 1 - \frac{N B_1}{\lambda V} \right) + \mu \left( 1 - \frac{N B_1}{\mu V} \right) \log \left( 1 - \frac{N B_1}{\mu V} \right) \right]$$

where $\lambda, \mu$ are constants given by

$$\frac{1}{\lambda} = \frac{1}{\beta} - \frac{1}{2} \sqrt{1 - 2\alpha}$$

$$\frac{1}{\mu} = \frac{1}{\beta} + \frac{1}{2} \sqrt{1 - 2\alpha}$$

(60)
On use of this expression for $\Lambda$, we can obtain the pressure $p$, on use of equation (6). It will however be more convenient to use the dimensionless quantity $\frac{PV}{RT}$, instead of $p$, and the equation for the pressure takes the form

$$\frac{PV}{RT} = -1 - \frac{a}{2bRT} \xi + \frac{1}{2} \left[ -\lambda \log \left(1 - \frac{\xi}{\lambda} \right) - \mu \log \left(1 - \frac{\xi}{\mu} \right) \right]$$

(61)

where we have used the constant $b$, already mentioned (equation (41)), and related to $B_1$ by

$$2b = B_1N$$

(62)

The dimensionless quantity $\xi$ is given by

$$\xi = \frac{NR^1}{V} = \frac{2b}{V}$$

(63)

The value of $\lambda = \frac{17}{32}$ when the function $\rho_2(R)$ is taken a constant $\frac{1}{V^2}$, but since $V^2 \rho_2$ tends to 1 as $R \to \infty$ and tends to zero as $R \to 0$, we expect $V^2 \rho_2$ to be bigger than 1 for $0 < R < 2\sigma^\circ$. Hence the value of $\lambda$ as defined by equation (56) must be greater than $\frac{17}{32}$. For the moment we shall leave $\lambda$ as an unspecified constant. However, we shall see later that there is a neat method for the numerical determination of the constant $\lambda$, as we study the critical data determination of the gas.

It may be noted that since $\lambda > \frac{1}{2}$, the constants $\lambda, \mu$ defined by equation (60) are complex. The expression for $\frac{PV}{RT}$ defined as a function of real variables, consequently takes the form

$$\frac{PV}{RT} = -1 - \frac{a}{2bRT} \xi + \frac{1}{2} \left[ -\lambda \log \left(1 - \frac{\xi}{\lambda} + \frac{1}{2} \alpha \frac{\xi^2}{\lambda^2} \right) + \frac{1}{2} \log 1 - \tan^1 \left( \frac{\xi \sqrt{2\alpha - 1}}{2 - \frac{\xi}{\lambda}} \right) \right]$$

(64)
When \( F > 2 \), we must replace \( \tan^{-1} \left( \frac{\sqrt{2 \alpha - 1}}{2 - \frac{b}{V}} \right) \) by the expression

\[ \Pi - \tan^{-1} \left( \frac{\sqrt{2 \alpha - 1}}{2 - \frac{b}{V}} \right) \] so that no discontinuity appears as \( G \) passes 2.

We now first examine the equation of state (61) when the density is small. Expanding in powers of \( \frac{\zeta}{\sqrt{2}} = \frac{2b}{V} \), we find

\[ \frac{pV}{RT} = 1 + \frac{b}{V} - \frac{a}{bRT} \frac{1}{V} + \frac{4}{5} (1 - \alpha) \frac{b^2}{V^2} + ... \] (65)

For \( \alpha = \frac{17}{32} \), the term in \( \frac{b^2}{V^2} \) becomes \( \frac{5}{8} \frac{b^2}{V^2} \), which is identical to the Boltzmann result 4).

We next examine the critical data. From equation (61), we find that \( \frac{dp}{dV} = 0 \) when \( \zeta \) satisfies the cubic equation

\[ \xi^3 + (\xi - \frac{a}{\alpha}) \xi^2 + \frac{2}{\alpha} \xi - \frac{2\alpha x}{\alpha} = 0 \] (66)

In this equation we have used a reduced temperature \( x \) defined by

\[ x = \frac{b}{a} \sqrt{\frac{RT}{\alpha}} \] (67)

For the critical isothermal, equation (66) has two repeated roots, the condition for which is

\[ y^4 - 6y^3 + 2(1 + 6\alpha) y^2 - 8(1 - 2\alpha) y + 2\alpha (1 - 2\alpha) = 0 \]

\[ y = \alpha x \] (68)

The roots of this algebraic equation define the critical temperature. It is clear that we must have only one physically allowed root of this equation.
If we substitute in equation (68) the value of \( \alpha = \frac{17}{32} \), we find that the four roots are

\[
\begin{align*}
y_1 &= 0.1864 \\
y_2 &= 0.1923 \\
y_3 &= 5.9334 \\
y_4 &= -0.3125
\end{align*}
\]

The critical \( y \) corresponding to \( y_3 \) is negative, hence the roots \( y_3, y_4 \) are not physically allowed, but still we have two physically allowed critical temperatures corresponding to \( y_1 \) and \( y_2 \).

To evade this unnatural situation, we try to fix the numerical value of \( \alpha \), such that equation (68) has two repeated roots.

To do this we consider equation (68) to be a quadratic equation in \( \alpha \). The condition that \( \alpha \) has two equal roots is found to be \( y = \frac{1}{5} \), and the two equal roots of \( \alpha \) are then

\[
\alpha = \frac{27}{50} \quad (69)
\]

For this value of \( \alpha \), equation (68) factorises to

\[
(y - \frac{1}{5})^2 (y - \frac{1}{5} + \sqrt{\frac{1}{5}}) (y - \frac{1}{5} - \sqrt{\frac{1}{5}}) = 0 \quad (70)
\]

which clearly shows that there is only one critical temperature corresponding to \( y_1 = y_2 = \frac{1}{5} \).

Substituting \( \alpha = \frac{27}{50} \) and \( y = \alpha x = \frac{1}{5} \) in equation (66), we find that it factorises to

\[
(\frac{y}{9} - \frac{10}{9})^3 = 0
\]

Hence there is one critical volume defined by

\[
\frac{V_c}{V_0} = \frac{2b}{V_0} = \frac{10}{9} \quad (71)
\]

The corresponding critical temperature is given from \( \alpha x_c = \frac{1}{5} \) or

\[
\frac{b}{a} \frac{RT_c}{T_0} = \frac{10}{27} \quad (72)
\]
To complete the critical data, we substitute in equation (64) for \( \alpha', \xi_c, T_o \) and obtain

\[
\frac{P_o V_c}{RT_o} = 0.3272
\] (73)

It may be noted that the modified value for \( \alpha = 0.54 \) given by (69) is a little greater than the value \( \alpha = \frac{17}{32} = 0.531 \), assuming constant \( \xi_2 \), a result which has already been anticipated.

A more elaborate investigation is furnished by the assumption that \( \alpha \) is a function of the temperature of the form

\[
\alpha = \alpha_o + \frac{\xi}{x}
\] (74)

where \( \xi \) is a small constant. Substituting for this value of \( \alpha \) in the condition (68) for equal roots of equation (66), we find that the critical temperature is obtained as a root of an equation of the fifth degree in the temperature. One finds that the condition that the equation for the critical temperature should have two equal roots is

\[
\alpha_o = \frac{27}{30} (1 - 5\xi)
\] (75)

and the two repeated roots are given

\[
y = \alpha x = \frac{1}{5},
\] (76)

From equations (74), (75), (76), one finds that the critical temperature
and the critical volume remain the same:

\[ x_c = \frac{10}{27}, \quad \xi_c = \frac{10}{9} \tag{77} \]

Also the corresponding value of \( \alpha \) at \( x_c \) is

\[ \alpha_c = \frac{27}{30} \tag{78} \]

Hence the critical isothermal is not affected by the assumption (74), but only the other isothermals are affected. The higher the temperature of the isothermal, the bigger the effect.

A good way to choose the parameter \( \xi \) for a certain gas is to consider its behaviour for small densities. On use of the expansion (65) for small density, and substituting for \( \alpha \) from (74), we get

\[ \frac{pV}{RT} = 1 + \frac{b}{V} - \frac{\alpha}{RT} \frac{1}{V} + \left( \frac{4\xi + 5\xi^2}{75} \xi - \frac{4\xi^3}{3825} \right) \frac{b^2}{V^2} + \ldots \tag{79} \]

We can then try to give a numerical value to \( \xi \) for a given gas, such that the above equation agrees with observation as closely as possible.

VI. QUANTUM EFFECT

We shall calculate the small quantum terms proportional to \( \frac{\hbar^2}{\kappa^2} \) in the partition function, which we have so far omitted.

From equation (32), the quantum contribution to
the partition function is given by

$$\mathcal{Z}_Q = \frac{1}{N!} \left( \frac{2\pi \hbar^2}{\beta m} \right)^\frac{3N}{2} \int \bar{\mathcal{E}}^\beta \mathcal{F} \frac{\partial}{\partial \mathcal{F}} \left[ \frac{1}{12m} \frac{\partial^2 \mathcal{F}}{\partial q^2} + \frac{1}{2\mu m} \frac{\partial^2 \mathcal{F}}{\partial J^2} \right]$$

(80)

This, added to the classical part \( \mathcal{Z}_0 \) defined by equation (57), gives the whole partition function of the translational motion of the molecules up to the second power in \( \hbar \).

On use of the expansion (40) for \( \phi \), we find that

$$\left( \frac{\partial \Phi}{\partial q} \right)^2 = \sum_j \frac{1}{2} \left[ \phi''(R_{ij}) \right]^2$$

(81)

$$\frac{\partial^2 \Phi}{\partial q^2} = \sum_j \frac{1}{R_{ij}^2} \frac{\partial}{\partial R_{ij}} \left( R_{ij}^2 \phi''(R_{ij}) \right)$$

(82)

Substituting from these into equation (80), and carrying out by the same procedure as for the classical part \( \mathcal{Z}_0 \), we obtain

$$\mathcal{Z}_Q = \frac{\mathcal{Z}_c}{c} \frac{N^2 \kappa^2}{\sqrt{m}} \int e^{-\frac{1}{2\kappa^2} \phi''(R)} \left[ -\frac{1}{R^2} \phi''(R) + \frac{\mu}{R^6} \right] \, dV \, d/\kappa$$

(83)

For simplicity we assume for \( \phi(R) \) (\( R > \sigma \)) a van der Waal potential

$$\phi(R) = \begin{cases} \frac{\mu}{R^6} & (R > \sigma) \end{cases}$$

(84)
The result of the integral is \( \frac{6 \mu}{\sigma^6} \), on neglecting \( \frac{\mu \beta}{\sigma^6} \) compared to 1. Hence

\[
Z_Q = \frac{Z}{\zeta} \frac{N^2}{V} \frac{k}{2\alpha \beta} \xi^2
\]  

(85)

On use of the approximate relation

\[
\frac{a}{b} = \frac{N}{Z} \frac{\mu}{\sigma^6}
\]  

(86)

we find that

\[
Z_Q = \frac{Z}{\zeta} \frac{3k^2 N^2}{8\pi m \sigma^2} \frac{Z}{\zeta} \frac{b}{\alpha} x \frac{\xi}{\chi}
\]  

(87)

where \( \frac{\xi}{\chi} \), \( x \) are given by (63), (67). Since \( \frac{Z_Q}{Z_c} \) is a small quantity, we get

\[
\log \left( Z_c + Z_Q \right) = \log Z_c + \frac{Z_Q}{Z_c}
\]

hence the quantum contribution to the free energy \( A \) given by equation (58) is

\[
A_Q = - \frac{1}{\beta} \frac{Z_Q}{Z_c}
\]  

(88)

Consequently the quantum contribution to the pressure is \( P_Q = - \frac{\partial A_Q}{\partial V} \), and hence we must add the following quantum correction to the equation of state (61):

\[
\frac{P_a V}{RT} = - \left( \frac{3k^2 N}{8\pi m \sigma^2} \frac{b}{\alpha} \right) \frac{\xi}{\chi^2}
\]  

(89)

\[= 26\]
For the gas nitrogen, the numerical value of the factor
\[ \frac{3 \frac{2}{5} \pi}{\gamma a} \times \frac{b}{a} \] is about \( 0.5 \times 10^{-4} \), and the quantum contribution

to \( \frac{pV}{RT} \) at the critical point \( \xi = \frac{10}{9}, \ x_c = \frac{10}{27} \) is roughly (for \( N_2 \))

\[ \frac{p q V}{RT_c} = -0.0004 \] (90)

which is of the order of experimental error. This is the reason that
the quantum terms were not included from the beginning in the
determination of the equation of state.

VII. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENT

The relation between \( \frac{pV}{RT} \) and \( \xi \) was computed numerically,
taking \( \alpha = .54 \).

The results are shown in Table I and Figure I, for ten
isothermals \( x = \frac{5}{27}, \frac{10}{27}, \ldots, \frac{50}{27} \). The argument \( \xi \) is taken
from zero to 2.0 with steps 0.2.

Theoretically, \( \xi \) can be as great as \( \frac{4 \ell - 2}{3} \pi = 5.9238 \),
a value corresponding to close packing of the hard spheres.
Experimentally, however, this is never achieved, for even subjecting
a gas (like \( CO_2 \)) at the critical temperature to a pressure up to
1000 atmospheres, the value of \( \xi \) is only about 2.

At first glance at the theoretical isothermals, one sees a
deviation to observations, starting at \( \xi \) about 1.5 and becoming
very strong as \( \xi \) increases to 2.

In fact the computed values of \( \frac{pV}{RT} \) tend to a very big negative
value as \( \xi \) increases beyond 2, while, according to observations,
the value of \( \frac{pV}{RT} \) tends instead steadily to a very big positive value.
The deviations for high density could be anticipated from the fact that the quantities $a$ and $\alpha$ are taken as constants in the formula (61) for $\frac{PV}{RT}$. For high densities the radial distribution function $\rho_2(r)$, as already mentioned, cannot be assumed as simply $\frac{1}{V^2}$, but must be some complicated function of $T, V$. Consequently the quantities $a, \alpha$ can no longer be regarded as constants for high values of $\xi$.

Nevertheless we find that for values of $\xi$ up to 1.5 there is a very remarkable agreement with observations. Thus at the critical point the value of $\frac{P_c V_c}{RT_c}$ was found near enough to the observed values, given in the ROWLINSON article 7).

We now try to illustrate the effect of the parameter $\xi$, introduced in equation (74), in the equation of state. Since this parameter does not affect the critical isothermal, and its effect increases as the temperature of the isothermal increases, we consider the case of a high temperature isothermal corresponding to $x = 1.851$ (five times the critical temperature). Taking extreme values for the parameters $\xi$, $\xi = \pm 0.1$, we find strong deviations at high densities of the isothermals corresponding to $\xi = \pm 0.1$ from the isothermal corresponding to $\xi = 0$. This is clearly shown in Table II and Figure II.

In fact, $\xi$ should be given a lower value to fit the isothermals of a given gas, in the way already described in the text.

A comparison between the theoretical and experimental critical isothermals of CO$_2$ is shown in Figure III. The observed values of $\frac{PV}{RT}$ for CO$_2$ are taken from the "International Critical Tables". For comparison with theory, the experimental values of $\frac{PV}{RT}$ are retabulated in Table III as a function of $\xi = 2bV$. Since the value of $b$ is difficult to determine experimentally, a value of $b$ consistent with the theory will be taken $b = \frac{3}{2} \xi c V_c = \frac{5}{9} V_c$. (according to viscosity measurement, the value of $b$ for CO$_2$ was found experimentally to be $\frac{V_c}{1.86}$)
ACKNOWLEDGMENT

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<td>$\xi = -0.1$</td>
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<tr>
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<td>0.63319</td>
</tr>
<tr>
<td>2.0</td>
<td>0.38947</td>
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TABLE III

Critical isothermal of carbon dioxide (experimental)

<table>
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<tr>
<th>( \xi )</th>
<th>( \frac{dV}{dT} )</th>
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<td>0.48890</td>
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<td>0.48548</td>
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<td>0.44750</td>
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<td>0.21480</td>
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<td>1.71985</td>
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<td>0.26150</td>
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<td>2.08392</td>
<td>0.29471</td>
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</table>
To carry out integrations over the solid angle in a space of 
\( n \leq 3 N \) dimensions, we use the spherical coordinates in \( n \) dimensions.

\[
p_1 = |p| \cos \theta_1 \cos \theta_2 \cdots \cos \theta_{n-1}
\]

\[
p_2 = |p| \sin \theta_1 \cos \theta_2 \cdots \cos \theta_{n-1}
\]

\[
p_3 = |p| \sin \theta_2 \cdots \cos \theta_{n-1}
\]

\[
p_{n-1} = |p| \sin \theta_{n-2} \cos \theta_{n-1}
\]

\[
p_n = |p| \sin \theta_{n-1}
\]

The element of volume \( dp \) is easily found, using the Jacobian of 
transformation,

\[
dp = |p|^{n-1} d|p| \cos \theta_2 \cos \theta_3 \cdots \cos \theta_{n-1} \ d\theta_1 d\theta_2 \cdots d\theta_{n-1}
\]

We first consider the integral

\[
\int e^{\frac{k}{\hbar} (p^2)} \ d\Omega
\]

On use of the above transformation,

\[
\int e^{\frac{k}{\hbar} (p^2)} \ d\Omega = \int \frac{d\theta_1}{2\pi} \int \frac{d\theta_2}{2\pi} \int \frac{d\theta_3}{2\pi} \cdots \int \frac{d\theta_{n-1}}{2\pi} \ \cos \theta_{n-1} d\theta_{n-1}
\]

\[
\frac{k}{\hbar} |p| \left[ \eta_1 (\cos \theta_1 \cdots \cos \theta_{n-1}) + \eta_2 (\sin \theta_1 \cos \theta_2 \cdots \cos \theta_{n-1}) + \cdots + \eta_n \sin \theta_{n-1} \right]
\]

Carrying out the integrations first over \( \theta_1 \) and then successively
over \( \theta_2, \theta_3, \ldots, \) up to \( \theta_{n-1} \), we find that the result is

\[
\int e^{\frac{k}{\hbar} (p^2)} \ d\Omega = \left( 2\pi \right)^{\frac{1}{2}} \frac{\Gamma(n/2) \ z}{\ z_{n-1}} \text{ where } z = \frac{p}{\hbar} \sqrt{\eta_1^2 + \eta_2^2 + \cdots + \eta_n^2}
\]
In the derivation of the successive integrals, use has been made of the relations
\[ \frac{d^n}{d(z^n)} J_\nu(z) = (-1)^n \frac{d^n}{d(z^n)} J_\nu(z) \]
\[ \frac{d^{n-1}}{d(z^{n-1})} J_{\nu+1}(z) = (-1)^n \sqrt{\frac{z}{\pi}} \frac{d^n}{d(z^n)} \left( \frac{\sin z}{z} \right) \]

In order to obtain the other two integrals in (34) we consider
\[ I = \int e^{i \rho \cdot \eta} \, d\Omega \]
and differentiating with respect to \( \eta_i \)
\[ \frac{\partial I}{\partial \eta_i} = \frac{2|p|^2}{k^2} \eta_i \frac{\partial}{\partial \eta_i} I = - \frac{|p|^2}{k^2} \eta_i (2\pi)^{1/n} \frac{J_{\nu+1}(z)}{z^{1/n}} \]
\[ = \frac{i}{k} \int e^{i \rho \cdot \eta} p_i \, d\Omega \]
\[ \int e^{i \rho \cdot \eta} p_i \, d\Omega = \frac{i}{k} |p|^2 \eta_i (2\pi)^{1/n} \frac{J_{\nu+1}(z)}{z^{1/n}} \]

In a similar way
\[ \frac{\partial^2 I}{\partial \eta_i \partial \eta_j} = \frac{3|p|^2}{k^2} \eta_i \eta_j \frac{\partial^2}{\partial \eta_i \partial \eta_j} I + \frac{3}{k^2} |p|^2 \delta_{ij} \frac{\partial I}{\partial \eta_i} = \frac{|p|^2}{k^2} \eta_i \eta_j (2\pi)^{1/n} \frac{J_{\nu+1}(z)}{z^{1/n+1}} \]
\[ - \frac{|p|^2}{k^2} \delta_{ij} (2\pi)^{1/n} \frac{J_{\nu+1}(z)}{z^{1/n+1}} \]
\[ = \left( \frac{i}{k} \right)^2 \int e^{i \rho \cdot \eta} p_i p_j \, d\Omega \]  
Hence
\[ \int e^{i \rho \cdot \eta} p_i p_j \, d\Omega = |p|^2 \delta_{ij} (2\pi)^{1/n} \frac{J_{\nu+1}(z)}{z^{1/n+1}} - \frac{|p|^2}{k^2} (2\pi)^{1/n} \eta_i \eta_j \frac{J_{\nu+1}(z)}{z^{1/n+1}} \]
APPENDIX II

On use of the asymptotic expression for $J_n(z)$ for large $n$

$$J_n(z) \sim \frac{1}{n!} \left( \frac{z}{2} \right)^n e^{-\frac{z^2}{2}}$$

one finds that ($z = \frac{1}{\sqrt{k}} \sqrt{\pi}$)

$$\int \frac{J_n(z)}{z^n} \frac{1}{e^{\frac{z^2}{2}}} \frac{p^2}{2m^2} p^{2n+1} dp = \int \frac{e^{-\frac{1}{4} \frac{p^2}{k^2} + \frac{\beta}{2m} p - \frac{\beta}{2m} p^2}}{m^1} \frac{2n+1}{p^2} dp$$

Integrating by parts successively, we easily arrive at the required result

$$\int \frac{J_n(z)}{z^n} \frac{1}{e^{\frac{z^2}{2}}} \frac{p^2}{2m^2} p^{2n+1} dp = \frac{1}{\left[ \frac{\beta}{m} + \frac{\beta^2}{2m^2} \right]^{2n+1}}$$
# REFERENCES


4. L. Boltzmann, Vorlesungen über Gastheorie - II, §51

5. Kammerlingh Onnes, Communications from the Physical Laboratory of Leiden, 102 a (1907)


\[ \frac{PV}{RT} \ (x = 1.851) \]

\[ \xi = \frac{2b}{V} \]

Fig. II

\( \epsilon = 0.1 \)

\( \epsilon = 0 \)

\( \epsilon = -0.1 \)