THE RADIAL DISTRIBUTION FUNCTION AND ITS APPLICATION TO THE PROPERTIES OF FLUIDS.

Thesis

Submitted by

ALISTER GEORGE McLELLAN

B.Sc., M.Sc.,

(University of NEW ZEALAND).

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CONTENTS

CHAPTER 1.

THE RADIAL DISTRIBUTION FUNCTION AND ITS APPLICATION TO THE PROPERTIES OF FLUIDS

INTRODUCTION.

A general kinetic theory of fluids has recently been formulated by Professor Max Born and Dr. H.S. Green (1),(2),(3),(4)(5). As a result of this theory, they were able to derive an integral equation, the solution of which would give the well-known radial distribution function for liquids in their equilibrium state. This integral equation is not linear, but by an approximate treatment, Dr. Green gave a solution. From this solution he derived the qualitative properties of the equation of state of a fluid and Dr. Rodriguez (6),(7) made a more precise study of this method and obtained an equation of state for such fluids as those of the inert gases (Argon, Neon, etc.). The equation of state so obtained is satisfactory in that it exhibits the condensation phenomenon, substantially as a Van der Waal's curve. But it cannot be said to agree very well with the experimental data for liquid and vapour.

It is therefore the object of this work to discuss the approximations made by Dr. Green in the derivation of the original quadratic integral equation and in the linearised solution; and, further, to give another kind of solution, which can be made as close as possible to an exact solution of the integral equation. In this treatment the radial distribution function $n_2(r)$ is taken to be $n_1^2 e^{-\phi(r)/kT}\{1+f(r)\}$ where $\phi(r)$ is a potential function, for a single molecule, of a Lennard-Jones' type. This potential function has the advantage of giving good agreement with the second virial coefficient for many gases (8)(9) and its inverse 6th power attractive term has theoretical justification for neutral atoms (London (12)).

Condensation phenomena are so general to many kinds of molecules, symmetric and asymmetric, that the actual function chosen to represent the potential field of one molecule need not be exact, so long as it has the general characteristics of being attractive at large distances, repulsive near the molecule and has one potential minimum.

The correction function $f(r)$ is assumed to be a simple polynomial with arbitrary coefficients. The method of solution is to substitute this form for $n_2(r)$ into the integral equation and evaluate both sides of the equation for as many values of r as there are arbitrary coefficients in $f(r)$. Thus by equating both sides of the equation for these values of r , equations are obtained for the coefficients of the polynomial expression for $f(r)$.

In the work done here $f(r)$ was expressed as a cubic, with four coefficients therefore to be evaluated. This gives a reasonable solution for $f(r)$, nevertheless further work is desirable using perhaps a 5-order or 6-order polynomial. But sufficient results have been obtained to show the utility both of this method and also of the Kirkwood "superposition" approximation used in the derivation of the original integral equation. Calculations were completed for one temperature, to give an isotherm that passes through the vapour; Liquid-vapour; Liquid regions.

RESULTS.

The principal result of this method is that when quadratic terms in $f(r)$ are neglected, a form for $f(r)$ is obtained which has a divergence at exactly the density of the liquid when it first appears (at the Saturation Vapour Pressure). Taking into account the quadratic terms causes this divergence to vanish. This density of divergence, coincident with the experimental condensation density, differs by almost one order of magnitude from those densities where divergences occur in the theories of Drs. Green and Rodriguez and of J.E. Mayer (10). The result is therefore in agreement with the argument of Dr. Green (2) that divergence in the linear solution occurs at the point of condensation of the liquid, and not at the density of the saturated vapour.

When this linear solution for $f(r)$ is substituted in the equation of state, an equation in better agreement with experiment than previous theoretical derivations is obtained. Nevertheless when the more exact solution of $f(r)$ is used (i.e. taking the quadratic terms into account) the equation of state is not satisfactory, giving negative pressures in the liquid region. This is due to the inaccuracy of a cubic polynomial form for $f(r)$. It should be noted that the pressure is given by the small difference of two large quantities, the kinetic compnnent $n_1 kT$ and the potential part $\frac{1}{6}\int_0^\infty n_2(r)\, r\, \phi'(r)\, 4\pi r^2 dr$ For instance, at saturation vapour pressure which is 22 atmospheres at 130° K for Argon, the kinetic component of p is equal to approximately 300 atmospheres. That is, the actual pressure is only 7% of the two large parts. Such accuracy in $f(r)$ can not at present be claimed . The equation of state is a very stringent test of any solution for $f(r)$.

Many thermodynamic quantities can be expressed in terms of integrals of $n_2(r)$ associated with such factors as $\phi(r)$ and $\phi'(r)$. The internal energy, Surface Tension, Viscosity are given here. Derivations of the formulae for surface tension and another quantity of theroetical interest, the shear modulus of a fluid under an instantaneous strain are also given in the text.

Theory Leading to the Integral Equation for the Radial Distribution Function $n_2(r)$.

Since the original theory of Born and Green is by now well-known, it will be necessary only to reproduce enough to show the meaning of the notations used and to enable a discussion of the several approximations that were made.

An assembly of N molecules is considered confined within a volume V. The position of the r^{th} molecule is specified by the vector $\underline{X}^{(r)}$, its velocity by $\underline{\xi}^{(r)}$, its acceleration by $\underline{\eta}^{(r)}$, its rate of acceleration by $\underline{\zeta}^{(r)}$ etc.

By $n_h(t, \underline{X}^{(1)}, \underline{X}^{(2)}, \cdots X^{(h)}) \prod_{i=1}^{h} d\underline{X}^{(i)}$ is denoted the probability that h distinct molecules, numbered from $1, 2, \cdots h$, occupy volume elements $d\underline{X}^{(1)}$, $d\underline{X}^{(2)}, \cdots d\underline{X}^{(h)}$ located at $\underline{X}^{(1)}, \underline{X}^{(2)}, \cdots \underline{X}^{(h)}$ respectively at time t. $n_h(t, X^{(1)}, X^{(2)}, \cdots X^{(h)})$ is often abbreviated to $n_h(t, \underline{X})$ or even n_h, the variables being sufficiently indicated by the suffix h. In this notation n_1 is simply the number density and n_2 the radial distribution function of the molecular assembly in isotropic conditions. Similarly by $f_h(t, \underline{X}^{(1)}, \underline{X}^{(2)}, \cdots \underline{X}^{(h)}; \underline{\xi}^{(1)}, \underline{\xi}^{(2)}, \cdots \underline{\xi}^{(h)}) \prod_{i=1}^{h} d\underline{X}^{(i)} d\underline{\xi}^{(i)}$

is denoted the probability that h distinct molecules with their velocities in the ranges $\underline{\xi}^{(i)}$, $d\underline{\xi}^{(i)}$, $i = 1, 2, \cdots h$, occupy the volume elements

$\underline{X}^{(i)}, d\underline{X}^{(i)}; \ i=1,2,\cdots h$ at time t. Then f_1 is the velocity distribution function employed in the kinetic theory of gases. The f_h satisfy

$$(1.1) \quad \int\overset{(h)}{\cdots}\int f_h(t,\underline{X},\underline{\xi}) \prod_{i=1}^{h} d\underline{\xi}^{(i)} = n_h(t,\underline{X})$$

Similarly an acceleration distribution function $g_h(t,\underline{X},\underline{\xi},\underline{\eta})$ may be defined satisfying,

$$(1.2) \quad \int\overset{(h)}{\cdots}\int g_h(t,\underline{X},\underline{\xi},\underline{\eta}) \prod_{i=1}^{h} d\underline{\eta}^{(i)} = f_h(t,\underline{X},\underline{\xi})$$

and, further, a rate-of-acceleration distribution function satisfying an analogous equation etc.

There exist also normalising formulae connecting distribution functions of the same kind but with different values of h. It is seen easily, for example, from the definitions, that

$$(1.3) \quad \int n_{h+1}(t,\underline{X})\, d\underline{X}^{(h+1)} = (N-h)\, n_h(t,\underline{X})$$

$$(1.4) \quad \iint f_{h+1}(t,\underline{X},\underline{\xi})\, d\underline{X}^{(h+1)} d\underline{\xi}^{(h+1)} = (N-h) f_h(t,\underline{X},\underline{\xi})$$

and similar relations must hold between the g_h's and higher distribution functions.

From these definitions, equations of continuity are simply and rigorously derived.

$$(1.5) \quad \frac{\partial n_h}{\partial t} + \sum_{i=1}^{h} \frac{\partial}{\partial \underline{X}^{(i)}}\left(n_h \overline{\underline{\xi}^{(i)}}\right) = 0,$$

where

$$(1.6) \quad \overline{\underline{\xi}^{(i)}} = \frac{1}{n_h}\int\overset{(h)}{\cdots}\int f_h\, \underline{\xi}^{(i)} \prod_{i=1}^{h} d\underline{\xi}^{(i)}$$

is the average velocity of the i^{th} molecule in a group of h molecules whose positions are specified. Similarly, there follows the analogous equation for f_h

$$(1.7)\quad \frac{\partial f_h}{\partial t} + \sum_{i=1}^{h} \frac{\partial f_h}{\partial \underline{x}^{(i)}} \underline{\xi}^{(i)} + \sum_{i=1}^{h} \frac{\partial}{\partial \underline{\xi}^{(i)}} \left(f_h \overline{\underline{\eta}^{(i)}} \right) = 0,$$

where

$$(1.8)\quad \overline{\underline{\eta}^{(i)}} = \frac{1}{f_h} \int \overset{(h)}{\cdots} \int g_h \, \underline{\eta}^{(i)} \prod_{i=1}^{h} d\underline{\eta}^{(i)}$$

is the average acceleration of the i-th molecule in a group of h molecules with specified positions and velocities.

It is now assumed that the potential function Φ can be expressed in the form

$$(1.9)\quad \Phi = \frac{1}{2} \sum_{i,j=1}^{N} \phi^{(ij)}$$

where $\phi^{(ij)} = \phi(\underline{x}^{(i)}, \underline{x}^{(j)})$ is the mutual potential energy of two molecules at $\underline{x}^{(i)}$ and $\underline{x}^{(j)}$. In what follows it will be assumed that the inter-molecular forces are central, i.e. $\phi^{(ij)}$ will depend only on the distance $|\underline{x}^{(i)} - \underline{x}^{(j)}|$ between the two molecules.

Since the acceleration of a molecule at a point $\underline{x}^{(i)}$ is given by

$$(1.10)\quad \underline{\eta}^{(i)} = -\frac{1}{m} \sum_{j=1}^{N} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}}$$

it follows that an alternative expression to (1.8) for the mean acceleration is

$$(1.11)\quad \overline{\underline{\eta}^{(i)}} = -\frac{1}{m}\sum_{j=1}^{h} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} - \frac{1}{mf_h}\iint \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}^{(i)}}\, d\underline{x}^{(h+1)}\, d\underline{\xi}^{(h+1)}$$

If this expression is inserted in (1.7) the fundamental equation of the classical theory is obtained.

$$(1.12)\quad \frac{\partial f_h}{\partial t} + \sum_{i=1}^{h} \frac{\partial f_h}{\partial \underline{x}^{(i)}}\, \underline{\xi}^{(i)}$$
$$= \frac{1}{m}\sum_{i,j=1}^{h} \frac{\partial f_h}{\partial \underline{\xi}^{(i)}}\, \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} + \frac{1}{m}\iint \sum_{i=1}^{h} \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}^{(i)}}\, \frac{\partial f_{h+1}}{\partial \underline{\xi}^{(i)}}\, d\underline{x}^{(h+1)}\, d\underline{\xi}^{(h+1)}$$

In this work, the case of equilibrium only is studied, where

$$(1.13)\quad \frac{\partial f_h}{\partial t} = 0.$$

The solution of (1.12) is of the form

$$(1.14)\quad f_h = n_h \left(\frac{m}{2\pi k T}\right)^{3h/2} e^{-\frac{m}{2kT}\sum_{i=1}^{h} \xi^{(i)2}}$$

provided n_h satisfies the equation.

$$(1.15)\quad \frac{\partial n_h}{\partial \underline{x}^{(i)}} + \sum_{j=1}^{h} \frac{n_h}{kT}\, \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} + \int \frac{n_{h+1}}{kT}\, \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}^{(i)}}\, d\underline{x}^{(h+1)} = 0.$$

This equation (1.15) is now the fundamental equation for the state of equilibrium. It can be solved formally by putting $h = N$ and observing that $n_{h+1} = 0$ (since total number of molecules is N). This gives

$$(1.16)\quad Q\, n_N = e^{-\Phi/kT},$$

where

(1.17) $$Q = \frac{1}{N!}\int^{(N)}\!\!\cdots\!\!\int e^{-\Phi/kT}\prod_{i=1}^{N} d\underline{X}^{(i)}$$

(1.17) is obtained easily by repeated use of the normalising equation (1.3).

One then has as the formal solution of (1.15)

(1.18) $$n_h = \frac{N!}{(N-h)!}\,\frac{\int^{(N-h)}\!\!\cdots\!\!\int e^{-\Phi/kT}\prod_{i=h+1}^{N} d\underline{X}^{(i)}}{\int^{(N)}\!\!\cdots\!\!\int e^{-\Phi/kT}\prod_{i=1}^{N} d\underline{X}^{(i)}}$$

This is a solution that agrees with the usual statistical mechanical derivations, but is not susceptible of computation.

In practice a second procedure is preferable since one is usually interested only in obtaining solutions for h small. In particular the case $h=2$ is the most important, yielding as it does the radial distribution function.

If the equation (1.15) is taken with the value $h=2$ inserted and is divided by $n_2^{(12)}$ the following equation is obtained

(1.19) $$\frac{1}{n_2^{(12)}}\frac{\partial n_2^{(12)}}{\partial \underline{X}^{(2)}} + \frac{1}{kT}\frac{\partial \phi^{(12)}}{\partial \underline{X}^{(2)}} = \frac{1}{kT}\int \frac{n_3^{(123)}}{n_2^{(12)}}\,\frac{\partial \phi^{(23)}}{\partial \underline{X}^{(3)}}\, d\underline{X}^{(3)}$$

This equation has a plain physical meaning. Compare it with the formula for $n_2^{(12)}$ in equilibrium obtained from ordinary statistical mechanics,

(1.20) $$\log_e n_2^{(12)} = \frac{-1}{kT}\left(\phi^{(12)} + W_c\right) + \text{Constant}.$$

where W_c is the free energy of the molecular configurations about the two fixed molecules 1 and 2 . If we take the gradient of (1.20) w.r.t. $\underline{X}^{(2)}$ and compare this with (1.19) we see that

$$(1.21)\quad \frac{\partial W_c}{\partial \underline{X}^{(2)}} = \frac{1}{kT}\int \frac{n_3^{(123)}}{n_2^{(12)}} \frac{\partial \phi^{(23)}}{\partial \underline{X}^{(2)}}\, d\underline{X}^{(3)} = -\frac{1}{kT}\int \frac{n_3^{(123)}}{n_2^{(12)}} \frac{\partial \phi^{(23)}}{\partial \underline{X}^{(3)}}\, d\underline{X}^{(3)}$$

$n_3^{(123)}/n_2^{(12)}$ is the number density of molecules about the arbitrarily fixed molecules 1 and 2. Hence we can express (1.19) in words, viz. kT times the gradient of the $\log_e n_2^{(12)}$ w.r.t. $\underline{X}^{(2)}$ is equal to the force on the molecule 2 due to molecule 1 $\left(-\frac{\partial \phi^{(12)}}{\partial \underline{X}^{(2)}}\right)$ and due to the configuration of molecules around 1 and 2 (The integral term.).

THE KIRKWOOD APPROXIMATION .

In view of the presence of $n_3^{(123)}$ in the integral of (1.19), it is obvious that an assumption must be made as to its form. The most suitable assumption is that of the Kirkwood "Superposition" approximation, namely

$$(1.22)\quad n_3(\underline{X}^{(1)}, \underline{X}^{(2)}, \underline{X}^{(3)}) = \frac{n_2(\underline{X}^{(3)}, \underline{X}^{(2)})\, n_2(\underline{X}^{(1)}, \underline{X}^{(3)})\, n_2(\underline{X}^{(2)}, \underline{X}^{(1)})}{n_1(\underline{X}^{(1)})\, n_1(\underline{X}^{(2)})\, n_1(\underline{X}^{(3)})}$$

This approximation was first used with some success by Kirkwood and Boggs(11) in 1942. Its validity can only be judged at present by its utility in giving results that will agree with experiment. It is obviously the more accurate the lower the density. (1.22) expresses that the relative probability $n_3/n_1^{(3)}\, n_2^{(12)}$ of the occurrence of a molecule at $\underline{X}^{(3)}$ in conjunction with two others 1 and 2 should be equal to the product of the relative probabilities $n_2^{(31)}/n_1^{(3)}\, n_1^{(1)}$, and $n_2^{(3,2)}/n_1^{(3)}\, n_1^{(2)}$ of the occurrence of the same molecule in conjunction with each of the others separately.

(1.22) gives n_3 as a cubic form in the n_2's , simpler forms of n_3 as quadratic in the n_2's have been proposed but these cannot satisfy the very important criterion that any form for $n_3^{(123)}$ should tend to zero as any two of the molecules 1, 2 and 3 approach each other and coincide.

It can be seen that the Kirkwood approximation does satisfy this criterion.

This approximation can also be discussed for rigid molecules of the type usually imagined as billiard-balls. Such molecules are surrounded by a volume 'b' , into which the centre of any other molecule cannot penetrate. n_3 for an assembly of these molecules is

$$(1.23)\quad n_3 = \frac{N(N-1)(N-2)}{V(V-b)(V-2b)} = \frac{N^3}{V^3}\cdot\frac{1-\frac{3}{N}+\frac{2}{N^2}}{1-3\left(\frac{b}{V}\right)+2\left(\frac{b}{V}\right)^2} = \frac{N^3}{V^3}\left(1+3\,\frac{b}{V}+7\left(\frac{b}{V}\right)^2+15\left(\frac{b}{V}\right)^3+\cdots\right)$$

Here N is the total number of molecules occupying a volume V. Whereas the right hand side of (1.22) becomes

since $n_2 = \frac{N(N-1)}{V(V-b)}$ and $n_1 = \frac{N}{V}$

$$(1.24)\quad \frac{N^3}{V^3}\frac{(1-\frac{1}{N})^3}{(1-\frac{b}{V})^3} = \frac{N^3}{V^3}\left(1+3\left(\frac{b}{V}\right)+6\left(\frac{b}{V}\right)^2+10\left(\frac{b}{V}\right)^3+\cdots\right)$$

Hence in this case it can be seen that (1.23) and (1.24) agree up to first-order terms in $1/N$ and b/V. So that as long as b/V remains small the approximation will be very good in this case. The last forms in (1.23) and (1.24) are obtained by neglecting $1/N$ etc., and show that the approximation is good to the terms in $\left(\frac{b}{V}\right)^2$, but at high densities an appreciable error through $\left(\frac{b}{V}\right)^3$ may occur.

Furthermore in calculations on the integral equation which will be derived from (1.19), one is continually impressed by the great importance of the repulsive force in regions close to a particular molecule. Since these repulsive forces are so important relative to the attractive forces at larger distances, and since a "billiard-ball" molecule has no attractive force but an infinite repulsive force at its circumference, then it is felt that the above considerations, although applied to these idealised molecules, can be applied reasonably safely to other types of molecules.

If then the Kirkwood approximation is substituted in (1.19), the following equation is obtained:-

$$(1.25)\quad \frac{1}{n_2^{(12)}}\frac{\partial n_2^{(12)}}{\partial \underline{x}^{(2)}} + \frac{1}{kT}\frac{\partial \phi^{(12)}}{\partial \underline{x}^{(2)}} = \frac{1}{kT}\int \frac{n_2^{(23)}\,n_2^{(31)}}{n_1^3}\,\frac{\partial \phi^{(23)}}{\partial \underline{x}^{(3)}}\,d\underline{X}^{(3)}$$

As was explained before the right hand integral represents the force on molecule 2 exerted by the molecular configuration about 1 and 2. Thus one can see more clearly the meaning of the Kirkwood approximation. It assumes that the configuration about 1 and 2 is the product of the configurations $n_2^{(23)}$, $n_2^{(31)}$ that would be about 1 and 2 were they infinitely separated, such an assumption will become doubtful when the short-range structure becomes very pronounced, at high densities and low temperatures.

After reduction (1.25) becomes

$$(1.26)\quad \frac{n_2'(r)}{n_2(r)} + \frac{\phi'(r)}{kT} = \frac{2\pi}{n_1^3}\int_0^\infty\int_{|r-s|}^{|r+s|} n_2(t)\,t(t^2-r^2-s^2)\,dt\; n_2(s)\,\frac{\phi'(s)}{kT}\,ds.$$

Then if $n_2(r)$ and $\phi(r)$ are defined for negative r by $n_2(r) = n_2(-r)$, $\phi(r) = \phi(-r)$, (1.26) can be integrated giving finally the integral equation which must be solved.

$$(1.27)\quad \log\frac{n_2(r)}{n_1^2} + \frac{\phi(r)}{kT}$$
$$= \frac{\pi}{n_1^3}\int_0^\infty\int_{-s}^{s}(s^2-t^2)\,\frac{t+r}{r}\left\{n_2(t+r)-n_1^2\right\}dt\; n_2(s)\,\frac{\phi'(s)}{kT}\,ds.$$

CHAPTER II.

THE RADIAL DISTRIBUTION FUNCTION AND ITS CONNECTION WITH THE PROPERTIES OF FLUIDS.

Since the object of this work is to obtain a solution for $n_2(r)$ which will give some agreement with experiment, a short account will be given of those properties of a fluid which the radial distribution function principally determines. Such properties are mainly descriptive of the equilibrium state or are, otherwise, descriptive of states which represent only a small disturbance from equilibrium. In the latter category is the coefficient of viscosity.

Section I.

X-RAY DIFFRACTION

The X-ray diffraction by liquids and vapours is of great importance since it shows as directly as possible the radial distribution function. By measuring the X-ray diffraction of Argon, which gives several maxima of X-ray diffracted intensity, and by performing a Fourier transformation on the experimental results, Eisenstein and Gingrich(13) were able to obtain the radial distribution function.

Their results showed that $n_2(r)$ has a principal maximum and smaller maxima and minima at larger values of r . Gingrich has given an interesting review of their work and others in "The Review of Modern Physics"$^{(14)}$. The theory of this diffraction phenomenon is also given.

This experimental work, instructive though it is, cannot show accurately the important part of $n_2(r)$, that part, for instance, which principally determines the equation of state.

$$(2.1) \quad p = n_1 kT - \tfrac{1}{6}\int_0^\infty n_2(r)\, r\, \phi'(r)\, 4\pi r^2\, dr$$

In order that p will be positive in the liquid state the integral in (2.1) must be decreased with increasing density. Simple calculations show that the production of minima after the principal maximum of $n_2(r)$ ~~are~~ is not sufficient, the principle change in $n_2(r)$ as the density increases must be a relative increase in $n_2(r)$ for values of r where $\phi'(r)$ is large and negative, i.e., where $n_2(r)$ tends to zero as r tends to zero. Hence the important quantity in $n_2(r)$ as the density increases is the rate at which $n_2(r)$ tends to zero. Since $n_2(r)$ even at low densities tends to zero very quickly because of the factor $e^{-\phi(r)/kT}$ it will be very difficult to display experimentally any change of this rate of going to zero.

However the $n_2(r)$ obtained experimentally in this

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way ~~does~~ enable one to criticise the assumptions made by Lennard-Jones and Devonshire (15)(16) in their ~~liquid~~ theory of liquids and to suggest different assumptions more consistent with experiment. Since this theory starting with a simple physical model gives a critical isotherm at the correct temperature, although the critical volume and pressure do not agree so well, it is worthwhile to add some refinement to it. A further discussion of it will be given in the next chapter.

Eisenstein and Gingrich found that the position of the first maximum of the radial distribution function always remained very near the position of the potential minimum of $\phi(r)$, but that the number of nearest neighbours was approximately proportional to the density. This is in contradiction to the theory of Lennard-Jones and Devonshire who assumed that each molecule moved in a cell surrounded by a number of nearest neighbours remaining constant with change in density. The parameter they took as varying principally with density was the distance of the nearest neighbours from the centre of the cell; if this is a, they assumed $n_1 = \gamma/a^3$ which gives the density of a crystal when a is the lattice constant (γ is a constant for a certain lattice type, e.g., $\gamma = \sqrt{2}$ for a face-centred cubic lattice.)

Section II.

THE EQUATION OF STATE

A direct derivation of formula (2.1) for the pressure has been given by Dr. Green(2) . The densities of liquid argon and its vapour at S.V.P. have been measured for many temperatures. Fig. I. shows a schematic equation of state for argon at 130° K, with which is compared the equation of state derived by Dr. Rodriguez. Volumes or densities are in this work always presented in terms of v/v_0 and n_1/n_0 , where v is the volume occupied per molecule. v_0 is the volume occupied by one molecule when in the crystal state, $n_0 = 1/v_0$. For the case of Argon which crystallises to a face-centred cubic lattice, and where r_0 is the position of the potential minimum of the molecular field then

$n_0 = \sqrt{2}/r_0^3$.

Section III

INTERNAL ENERGY E.

A derivation of the formula for E is also given by Dr. Green(2) , it is

$$(2.2) \quad E/N = \frac{3}{2}kT + \frac{1}{2}\int_0^\infty \frac{n_2(r)}{n_1}\phi(r)4\pi r^2 dr,$$

where E/N is the internal energy per molecule. From this the specific heats could be derived were $n_2(r)$ known as a function of density and temperature.

Section IV

SURFACE TENSION γ .

(2.3) $$\gamma = -\frac{\pi}{2}\int_0^\infty n_2(r)\,\phi(r)\,r^3\,dr.$$

This formula can be derived if it is assumed that near the surface of a fluid, $n_2(r)$ is not appreciably different from the $n_2(r)$ which is obtained under isotropic conditions.

Consider a system consisting of two domains A and B, the liquid occupying A, and B is unoccupied. The surface of the fluid is the surface between A and B. The potential energy of the liquid is

(2.4) $$\frac{1}{2}\int_A\int_A n_2(\underline{r})\,\phi(r)\,d\underline{X}^{(1)}d\underline{X}^{(2)}$$

which is equal to

(2.5) $$\frac{1}{2}\int_A\int_{A+B} n_2(\underline{r})\,\phi(r)\,d\underline{X}^{(1)}d\underline{X}^{(2)} - \frac{1}{2}\int_A\int_B n_2(\underline{r})\,\phi(r)\,d\underline{X}^{(1)}d\underline{X}^{(2)}$$

$=$

(2.6) $$\frac{1}{2}V_A\int_0^\infty n_2(r)\,\phi(r)\,4\pi r^2\,dr - \frac{1}{2}\int_A\int_B n_2(\underline{r})\,\phi(r)\,d\underline{X}^{(1)}d\underline{X}^{(2)}$$

The first term of (2.6) is proportional to the volume and may be identified with the potential part of the internal energy. The second part is proportional to the surface area S and is the surface energy.

First we find $\int_{\mathcal{B}} n_2(\underline{r})\phi(r)\,d\underline{X}^{(2)}$ where $\underline{X}^{(2)}$ is in $\mathcal{B}$ and $\underline{X}^{(1)}$ in A .
This is (See Fig. II.)

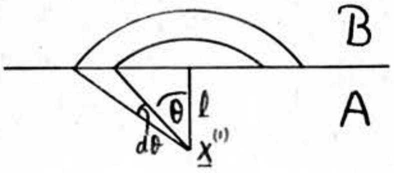

FIG. II.

$$(2.7)\quad \int_{\mathcal{B}} n_2(\underline{r})\phi(r)\,d\underline{X}^{(2)} = \int_0^{\frac{\pi}{2}}\int_{l\sec\theta}^{\infty} n_2(r)\phi(r)\,r^2\,dr\,2\pi\sin\theta\,d\theta$$

On integrating by parts the R.H.S. of (2.7) becomes

$$2\pi\left\{\left[-\cos\theta\int_{l\sec\theta}^{\infty} n_2(r)\,\phi(r)\,r^2\,dr\right]_{\theta=0}^{\theta=\frac{\pi}{2}}\right\}$$

$$(2.8)\quad -2\pi\int_0^{\frac{\pi}{2}}(-\cos\theta)\left[-n_2(l\sec\theta)\phi(l\sec\theta)(l\sec\theta)^2\right](-l\sec\theta\tan\theta)\,d\theta$$

$$= 2\pi\left\{\int_l^{\infty} n_2(r)\,\phi(r)\,r^2\,dr - l\int_l^{\infty} n_2(s)\,\phi(s)\,s\,ds,\right.$$

after putting $s = l\sec\theta$ in the second integral.

Therefore the surface energy,

$$-\frac{1}{2}\int_A\int_{\mathcal{B}} n_2(\underline{r})\,\phi(r)\,d\underline{X}^{(1)}\,d\underline{X}^{(2)}$$

becomes

$$(2.9)\quad -\pi S\int_0^\infty\left\{\int_l^\infty n_2(s)\,\phi(s)\,s^2\,ds - l\int_l^\infty n_2(s)\,\phi(s)\,s\,ds\right\}dl.$$

The factor S (surface area) arises from the integration over the two components of $\underline{X}^{(1)}$ at right angles to the direction of l.

Integrating each integral in (2.9) by parts gives finally

$$(2.10)\quad \text{Surface energy} = -\tfrac{1}{2}\pi S\int_0^\infty n_2(l)\,\phi(l)\,l^3\,dl$$

Thus the surface tension γ is given by (2.3).

Not very many experimental values of the surface tension for Argon have been determined. In fact, only one value has been found for liquid Argon at 87.3° K, which is very near the triple point, there $\gamma = 12.5$ dyne cm^{-1}.

Section V.

VISCOSITY

Professor Born and Dr. Green (3) have derived a formula for the viscosity η which is

$$(2.11)\quad \eta = \tfrac{1}{30}\left(\frac{m}{kT}\right)^{\frac{1}{2}}\int_0^\infty n_2(r)\,\phi'(r)\,r^2\,d\underline{r}.$$

It should be mentioned that some objections have been raised to this formula by Mr. Yang of this department, who will discuss this in his thesis. This point will not be discussed here, since at present no experimental values have been found for the viscosity of liquid argon or the liquids of the other inert gases (except Helium, which has to be treated as a quantum fluid).

(2.11) is included for completeness.

Section VI.

THE SHEAR MODULUS μ FOR A LIQUID SUBJECTED TO AN INSTANTANEOUS STRAIN (NO CHANGE IN VOLUME).

If a liquid is subjected to a strain, the effect produced depends very much on the time of application of the strain. For strains applied slowly the viscous properties of the liquid will determine the effect; whereas if the strain is applied almost instantaneously, the fluid will behave as a solid temporarily. A development of the theory of this effect would be of great importance in the theory of plastics. Such a quantity, then, as μ the modulus under instantaneous strain will be of considerable use.

Born and Green (3) have shown that the pressure tensor for a liquid is made up of two parts, a kinetic term and a potential term, the latter being the predominant term for liquids. The potential pressure tensor they give as

$$(2.12) \quad \underline{\underline{\ell}} = -\tfrac{1}{2}\int n_2(\underline{r})\,\frac{\phi'(r)}{r}\,\underline{r}\,\underline{r}\,d\underline{r} .$$

We seek the change in $\underline{\underline{\ell}}$, $\delta\underline{\underline{\ell}}$ when an instantaneous strain $S(\underline{x})$ is applied. Under such a strain the spherically symmetric $n_2(\underline{r})$ changes to $n_2(|\underline{r} - \delta\underline{s}|)$, since the strain has been applied so quickly that the distribution of molecules is merely distorted from spherical symmetry about each molecule to an ellipsoidal distribution. No time has, therefore, been allowed for any re-distribution of molecules. Here

$$(2.13) \quad \underline{\delta s} = \underline{r}\,\frac{\partial}{\underline{\partial x}}\,\underline{s}$$

and

$$(2.14) \quad \delta n_2(\underline{r}) = n_2(|\underline{r} - \underline{\delta s}|) - n_2(\underline{r}) = -\underline{\delta s}\cdot\underline{r}\,\frac{n_2'(r)}{r}$$

Therefore using (2.13)

$$(2.15) \quad \delta n_2(\underline{r}) = -\underline{r}\,\frac{\partial}{\underline{\partial x}}\,\underline{s}\cdot\underline{r}\,\frac{n_2'(r)}{r}$$

Therefore

$$(2.16) \quad \delta\underline{\underline{\ell}} = -\tfrac{1}{2}\int -\underline{r}\,\frac{\partial}{\underline{\partial x}}\,\underline{s}\cdot\underline{r}\,\frac{n_2'(r)}{r}\,\frac{\phi'(r)}{r}\,\underline{r}\,\underline{r}\,d\underline{r}$$

and the strain tensor $\underline{\underline{e}} = \frac{\partial}{\partial \underline{x}} \underline{S}$

(2.17) $\therefore \; \delta \underline{\underline{\ell}} = \frac{1}{2} \int \underline{r} \cdot \underline{\underline{e}} \cdot \underline{r} \; \frac{n_2'(r)\, \phi'(r)}{r} \; \underline{r}\, \underline{r}\, d\underline{r}$

This integral is evaluated by Chapman and Cowling(17) giving

(2.18) $\delta \underline{\underline{\ell}} = \frac{1}{15} \underline{\underline{e}} \int n_2'(r)\, \phi'(r)\, r^2 \, d\underline{r}$

and

(2.19) $\delta \underline{\underline{\ell}} = -2\mu \, \underline{\underline{e}}$

Therefore

(2.20) $\mu = -\frac{2\pi}{15} \int_0^\infty n_2'(r)\, \phi'(r)\, r^4 \, dr.$

CHAPTER III.

THE LIQUID THEORY OF LENNARD-JONES AND DEVONSHIRE.

Lennard-Jones and Devonshire(15)(16) have given an equilibrium theory of liquids by considering a physical model of the liquid which has, as its basis, ideas drawn from the crystalline state rather than the vapour state. Such a method is of importance in equilibrium theory, since for this the work of Born and Green requires the assumption of the Kirkwood approximation, and from the simple considerations given in Chapter I, it is quite likely that this will break down at high compressions and low liquid temperatures.

The experimental results of Eisenstein and Gingrich are in better agreement with the assumptions that (a) the number of nearest neighbours is proportional to the density and (b) the cell radius is nearly independent of the density.

The liquid is compared with a crystal where only a certain proportion γ of the lattice sites is occupied. If $\gamma = 1$ i.e., all sites occupied, the number density $n_1 = \sqrt{2}/a^3$ where a is the shortest distance between molecules. In the case $\gamma < 1$ one will have obviously $n_1 = \gamma\sqrt{2}/a^3$. For a close packed (face-centred) cubic lattice the number of nearest neighbours is 12. Hence the average number of nearest neighbours is $z = 12\gamma$.

Therefore one has

$$n_1 = \frac{Z}{12}\frac{\sqrt{2}}{a^3} \text{ and } n_0 = \frac{\sqrt{2}}{r_0^3}$$

(3.1) $$\text{i.e. } \frac{n_1}{n_0} = \frac{Z}{12}\left(\frac{r_0}{a}\right)^3$$

Table 1 shows the experimental results obtained from the work of Eisenstein and Gingrich (13) on Argon.

TABLE 1.

$\frac{n_1}{n_0}$	Temperature °K.	Z	a/r_0	$\left(\frac{n_1}{n_0}\right)\Big/\frac{Z}{12}\left(\frac{r_0}{a}\right)^3$
(Crystal) 1	—	12	1	1
0·848	84·35	10·2–10·9	1·00	0·97 (mean)
0·818	93	6·8–7·2	1·00	1·37 (")
0·655	127	5·9–6·2	1·00	1·31 (")
0·527	144	3·9–4·6	1·00	1·49 (")
0·455	150	6	1·18	1·51

The values in the last column would be all equal to 1 if (3.1) were exact. The agreement with (3.1) is fair, and certainly better than with the original assumptions of Lennard-Jones and Devonshire

(3.2) $$\begin{cases} n_1 = \sqrt{2}/a^3 \quad \text{i.e. } \frac{n_1}{n_0} = \left(\frac{r_0}{a}\right)^3 \\ Z = 12 \end{cases}$$

since as shown in the table $\frac{r_0}{a} \sim 1$ as $\frac{n_1}{n_0}$ varies from 1 to ·45.

In order to discuss another assumption made it is necessary to outline their theory.

Occasional migrations of a molecule out of its cell are neglected. One has to determine the partition function of a particle moving in the field of a number Z of other particles symmetrically arranged. As the immediate neighbours are fairly closely packed, the field within the cell will have a high degree of symmetry and can be, with sufficient accuracy, considered as due to a constant density covering the surface of a sphere of radius a.

If r is measured from the centre of the sphere, the atom in the cell can then be thought of as moving in a potential field $\psi\left(\frac{r}{a}\right)$. The corresponding contribution to the partition function is

$$(3.3)\quad 2\pi a^3 \int_0^1 \left(\frac{r}{a}\right)^2 e^{-\psi(\frac{r}{a})/kT}\, d\left(\frac{r}{a}\right) = 2\pi a^3 g,$$

using their notation.

If by $-N\chi_0$ is denoted the energy of the assembly when each molecule is at the centre of its cell, referred to an energy zero at infinite separation of the molecules, then referred to this zero the partition function for the motion of each molecule in a given cell becomes

$$(3.4)\quad \frac{(2\pi m kT)^{3/2}}{h^3}\, e^{\chi_0/kT}\, 2\pi a^3 g$$

But since all the N cells are available (through migration) for each molecule, the complete partition function for the motion of each molecule through the assembly is

$$(3.5)\quad \frac{(2\pi m k T)^{3/2}}{h^3}\, e^{\chi_0/kT}\, N\, 2\pi a^3 g\, .$$

The partition function for the whole assembly is then (3.5) raised to the Nth power and divided by $N!$. Then finally the free energy of the whole assembly is obtained by taking $-kT$ times the logarithm of the partition function. Then if $f =$ the free energy per molecule (F/N), one obtains finally

$$(3.6)\quad f = C(T) - \chi_0 - kT \log_e (2\pi a^3 g),$$

($C(T)$) being the contribution due to kinetic motion and internal degrees of freedom. χ_0 is evidently closely related to the energy at the centre of the cell, and here $-\chi_0$ is taken equal to $\frac{1}{2}\psi(0)$, the factor ½ being required so as not to count the interaction between each pair of neighbours twice.

$$(3.7)\quad \psi(0) = z|\phi_0| \left\{ -2\left(\frac{r_0}{a}\right)^6 + \left(\frac{r_0}{a}\right)^{12} \right\}$$

The Lennard-Jones potential function for a molecule being

$$(3.8)\quad \phi(r) = |\phi_0| \left\{ -2\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12} \right\}$$

Here a very convenient convention for units of energy and length will be introduced, which is used throughout this work. Since the only natural reference of energy occurring in this work is $|\phi_0|$, this quantity is taken as the unit of energy. For instance with argon, $|\phi_0| = kT$ at a temperature of $T = 120^\circ K$. Therefore with $|\phi_0|$ as unit, at this temperature $kT = 1$. This saves a lot of writing, when working at $T = 120^\circ K$ for argon. Again, since r_0, the position of the potential minimum, is the only natural reference of length, it is taken as the unit of length. For instance the number density of the crystal is then $n_0 \left(= \frac{\sqrt{2}}{r_0^3}\right) = \sqrt{2}$. These conventions lead to no confusions as results are always presented in dimensionless form, e.g., if $n_1 =$ the number density using r_0 as the unit of length, then $\frac{n_1}{n_0}$ is simply $\frac{n_1}{\sqrt{2}}$. Using these we can re-write (3.7) and (3.8):-

$$(3.7)' \quad \psi(0) = z\left(-\frac{2}{a^6} + \frac{1}{a^{12}}\right)$$

$$(3.8)' \quad \phi(r) = -\frac{2}{r^6} + \frac{1}{r^{12}}$$

Referring back, now, to equation (3.3)

$$(3.3) \quad 2\pi a^3 g = 2\pi a^3 \int_0^1 \left(\frac{r}{a}\right)^2 e^{-\psi\left(\frac{r}{a}\right)/kT} d\left(\frac{r}{a}\right).$$

Physically $2\pi a^3 g$ gives the average volume of the cell in which the central molecule moves. If this is divided by $\frac{4}{3}\pi a^3$, then the average proportion of the volume of the cell in which the molecule is free to move $= \frac{3}{2} g$.

g is a very small quantity varying from $1/12$ at very high temperatures to about ·002 at $T = 150^{0}K$ for Argon, when 12 neighbours are assumed.

In the density relationship (3.1), an extra parameter has been introduced and this could be evaluated by minimising the free energy w.r.t. it. This is legitimate at constant density and tempera-ture. However, using this value for g it was impossible to find a minimum value for the free energy with respect to a or z.

Let us, therefore, consider more closely this quantity $\frac{3}{2} g$ which is the average proportion of the cell volume in which the central molecule can move. This will necessarily be a crude improvement.

$\frac{3}{2} g$ is obtained considering all the lattice sites next to the central molecule as occupied. Here the crystal analogy is being pursued. However, a most important effect in the liquid is the vacation of such sites. In the region of these empty sites, then, the central molecule will be free to move in a practically potential-free region. Therefore it is plausible to add to $\frac{3}{2} g$ a term $\frac{12-z}{12}$ representing the proportion of empty neighbouring sites. This concept will bring in the effect which allows the molecule to escape its environment, by first moving into a vacant site.

This assumption, then, is made that $\frac{3}{2}g$. is replaced by $\frac{3}{2}g + \frac{12-z}{12}$. $\frac{3}{2}g$. can be considered as the residual proportion of the cell volume, occupied on the average by the central molecule when all the sites are occupied. It can be seen that with $z \leq 10$, the extra term is much greater than $\frac{3}{2}g$. Thus altering g as described, and using (3.1), the equation for the free energy per molecule (3.6) is obtained in terms of a parameter $x = \frac{1}{a^3}$. It should be mentioned that in $-\chi_0 = \frac{1}{2}z\left(-\frac{2}{r^6} + \frac{1}{r^{12}}\right)$ Lennard-Jones and Devonshire empirically increased the coefficient of the attractive term ($-\frac{2}{r^6}$) to $-2 \cdot 4$ to allow for the effect of neighbours more remote than the nearest. Thus (3.6) becomes

$$(3.9)\ f = C(T) - 12\frac{n_1}{n_0}\left(1 \cdot 2x - 1 \cdot 5x^3\right) + kT\log x - kT\log\left(1 - \frac{n_1}{n_0} \cdot \frac{1}{x}\right)$$

$$x = \frac{1}{a^3}.$$

Since $\frac{3}{2}g$ is, at liquid temperature and densities, very much smaller than $\frac{12-z}{12}$, in (3.9) it is completely neglected. Of course when $z = 12$, $\frac{3}{2}g$ will be the residual term that prevents f from becoming infinite. It can be seen, quite simply, that f has a minimum value for $x \backsim 1$.

Taking $\frac{\partial f}{\partial x} = 0$, one obtains a quartic equation for x,

viz.,

$$(3.10) \quad -12\,\frac{n_1}{n_0}\left(1{\cdot}2x - 1{\cdot}5x^3\right) + kT - kT\,\frac{n_1/n_0}{x - \frac{n_1}{n_0}} = 0$$

This can be solved reasonably accurately since $x = 1$ is an approximate solution. If x is taken equal to $1 - \delta$ where δ is small, then neglecting higher powers of δ than the first, a solution is obtained for δ,

$$(3.11) \quad \delta = \frac{3{\cdot}6\left(1 - \frac{n_1}{n_0}\right)^2 + kT\left(\frac{n_0}{n_1} - 2\right)\left(1 - \frac{n_1}{n_0}\right)}{39{\cdot}6\left(1 - \frac{n_1}{n_0}\right)^2 + kT} \;;$$

since $x = 1 - \delta = 1/a^3$, and $\frac{n_1}{n_0} = \frac{Z}{12} \cdot \frac{1}{a^3}$

(3.12) then $\frac{Z}{12} = \frac{n_1}{n_0}(1 + \delta)$

From (3.11) it is seen that $\delta \to 0$ when $\frac{n_1}{n_0} \to 1$: δ can also be zero for a value of $\frac{n_1}{n_0}$ given by

$$\left(\frac{n_1}{n_0}\right)_0 = \frac{1}{2}\left\{1 - \frac{kT}{1{\cdot}8} + \sqrt{1 + \left(\frac{kT}{1{\cdot}8}\right)^2}\right\}$$

E.g.,

for

$$kT = 0 \,;\; \left(\frac{n_1}{n_0}\right)_0 = 1 \,;$$

$$kT = 1{\cdot}8 \,;\; \left(\frac{n_1}{n_0}\right)_0 = 1/\sqrt{2} \,;$$

$$kT \to \infty \,;\; \left(\frac{n_1}{n_0}\right)_0 \to \frac{1}{2} \,.$$

Thus $\left(\frac{n_1}{n_0}\right)_0$ always occurs either in the liquid or highly compressed vapour regions. Therefore at a given temperature, for densities less than $\left(\frac{n_1}{n_0}\right)_0$, $\delta > 0$ i.e. $a > 1$ (r_0 in ordinary units); for densities greater than $\left(\frac{n_1}{n_0}\right)_0$, $\delta < 0$ i.e. $a < 1$.

Table 11 gives the values of δ and Z calculated from (3.11) and (3.12), Z is compared with the experimental values given in Table 1.

TABLE II.

n_1/n_0	T°K.	$\frac{kT}{\lvert\phi_0\rvert}$	δ(3.11)	Z(3.12)	Z(Expt^{l}.)
Crystal 1	—	—	0	12	12
0·848	84·35	0·703	-0·005	10·2	10·2 – 10·9
0·818	93	0·775	+0·005	9·9	6·8 – 7·2
0·655	127	1·058	+0·044	8·2	5·9 – 6·2
0·527	144	1·200	+0·074	6·8	3·9 – 4·6
0·455	150	1·250	+0·093	6·0	6·0
0·333	150	1·250	+0·129	4·5	(Critical Point) —

The agreement is fair, but considering the method used by Eisenstein and Gingrich of integrating $n_2(r)\,4\pi r^2$ to an arbitrary point in finding the number of nearest neighbours, very good agreement could not be expected.

Using the value of x obtained from (3.11) and (3.12), and substituting this into the equation for the free energy (3.9), f is given then as a function of density and temperature. Thus an equation of state and other thermodynamical quantities could be derived. This has not been done, since it is rather laborious, but straightforward. Sufficient has been done to show that this theory can be modified to give better accord with experiment, as far as the radial distribution function is concerned; and to show that further work, e.g., evaluation of an equation of state is worthwhile.

CHAPTER IV.

THE ORIGINAL SOLUTION OF THE INTEGRAL EQUATION FOR $n_2(r)$.

The solution of this equation (1.27) was first obtained by Dr. Green(2), who by making one assumption obtained a linear equation, which could be solved by means of Fourier transforms in the usual way. Since it is necessary to indicate why another and more laborious method must be used to obtain better agreement with experiment, Dr. Green's method is repeated here together with some criticism.

In the equation

(1.27)

$$\log \frac{n_2(r)}{n_1^2} + \frac{\phi(r)}{kT} = \frac{\pi}{n_1^3}\int_0^\infty \int_{-s}^{s} (s^2-t^2)\frac{(t+r)}{r}\left\{n_2(t+r)-n_1^2\right\} dt \; n_2(s)\,\frac{\phi'(s)}{kT}\,ds$$

$n_2(r)$ was taken as $n_1^2\, e^{-\phi(r)/kT}\left\{1+f(r)\right\}$ where squares and higher powers of $f(r)$ are neglected. This procedure will be justified only when the right-hand side of (1.27) is small compared with 1.

There then results,

(4.1)

$$r f(r) = -\pi n_1 \int_0^\infty \int_{-s}^{s} (s^2-t^2)(t+r)\, f(t+r)\left\{1+\alpha(t+r)\right\} dt\, \alpha'(s)\left\{1+f(s)\right\} ds$$

$$-\pi n_1 \int_0^\infty \int_{-s}^{s} (s^2-t^2)(t+r)\,\alpha(t+r)\, dt\; \alpha'(s)\left\{1+f(s)\right\} ds\,,$$

where

(4.2) $$\alpha(r) = e^{-\phi(r)/kT} - 1$$

At this point, since $\alpha(r)$ and $\alpha'(r)$ are small except for small r, the assumption is made that when $f(r)$ is multiplied by either of these two functions, it may be replaced by $\epsilon - 1$ its average value in the neighbourhood of the origin. Then after integration by parts,

(4.3)
$$r f(r) = 2\pi n_1 \int_0^{\infty} \int_{-s}^{s} (t+r)\left\{ f(t+r) + \epsilon\,\alpha(t+r) \right\} dt \, \epsilon\, \alpha(s)\, ds .$$

This equation can be solved by Fourier transforms; writing

(4.4)
$$\left\{ \begin{aligned} r\, g(r) &= \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} s\, f(s) \sin(rs)\, ds . \\ r\, \beta(r) &= \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} s\, \alpha(s) \sin(rs)\, ds . \end{aligned} \right.$$

Then (4.3) becomes

(4.5) $$\lambda\, g(r) = \left[g(r) + \epsilon\, \beta(r) \right] \epsilon\, \beta(r)$$

where $\lambda^{-1} = (2\pi)^{3/2} n_1$, so that

(4.6) $$r\, f(r) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{\epsilon^2 s \{\beta(s)\}^2 \sin(rs)\, ds}{\lambda - \epsilon\, \beta(s)} .$$

It was supposed that there is an analytic function $\beta(z)$ which reduces to $\beta(r)$ when $z = r$ is real. The most general solution of (4.3) is then given by (4.6) where the path of integration may follow any course from negative to positive infinity in the complex plane. There are different solutions for $r f(r)$ obtained from (4.6) depending on the roots of the denominator of the integrand i.e. $\lambda - \epsilon \beta(z) = 0$. When the density is small, in the gas phase, this has complex roots. As the density increases, first of all an equal pair of real roots occur and with further increase of density this equal pair splits up into two real equal and opposite roots.

Thus the case of the gaseous phase was identified with densities for which $\lambda - \epsilon \beta(z) = 0$ has complex roots only; the case of the liquid phase with densities for which $\lambda - \epsilon \beta(z) = 0$ has two real roots. This identification will be discussed in greater detail in a later section of this chapter.

It should be pointed out that in this method of solution, two of the linear terms in $f(r)$ of equation (4.1) have been replaced by a mean value. This probably accounts for the lack of agreement with the results of this work. For the terms of the right-hand side of (4.1) which are first order or less in $f(r)$ are given by:-

$$(4.7)\qquad \begin{aligned} &-\pi n_1 \int_0^\infty \int_{-s}^{s} (s^2-t^2)(t+r)\, f(t+r)\{1+\alpha(t+r)\}\,dt\,\alpha'(s)\,ds \\ &-\pi n_1 \int_0^\infty \int_{-s}^{s} (s^2-t^2)(t+r)\,\alpha(t+r)\,dt\,\alpha'(s)\{1+f(s)\}\,ds. \end{aligned}$$

In the first integral of (4.7) $f(t+r)\alpha(t+r)$ was replaced by $(\epsilon-1)\alpha(t+r)$ and in the second integral $\alpha'(s)\{1+f(s)\}$ by $\epsilon\,\alpha'(s)$. If in equation (4.1) a solution were attempted using only these linear terms (4.7), this could not be done using Fourier transforms, because of the occurrence of the product $f(t+r)\alpha(t+r)$. This approximation of the linear terms is almost certainly the cause of the indifferent quantitative agreement with experimental results, and with the method shown later.

However, if this method is accepted, it is also possible that the interpretation of the gas phase and liquid phase that has been given, is incorrect.

For, if the equation of state obtained thus is examined (this is shown in Fig. 1 for T = 130°K), it is seen that at higher densities than those of the condensation "dip," the equation of state droops downwards, i.e. $\frac{dp}{dV} = +ve$. This effect also occurs in the equation of state for T = 150°K.

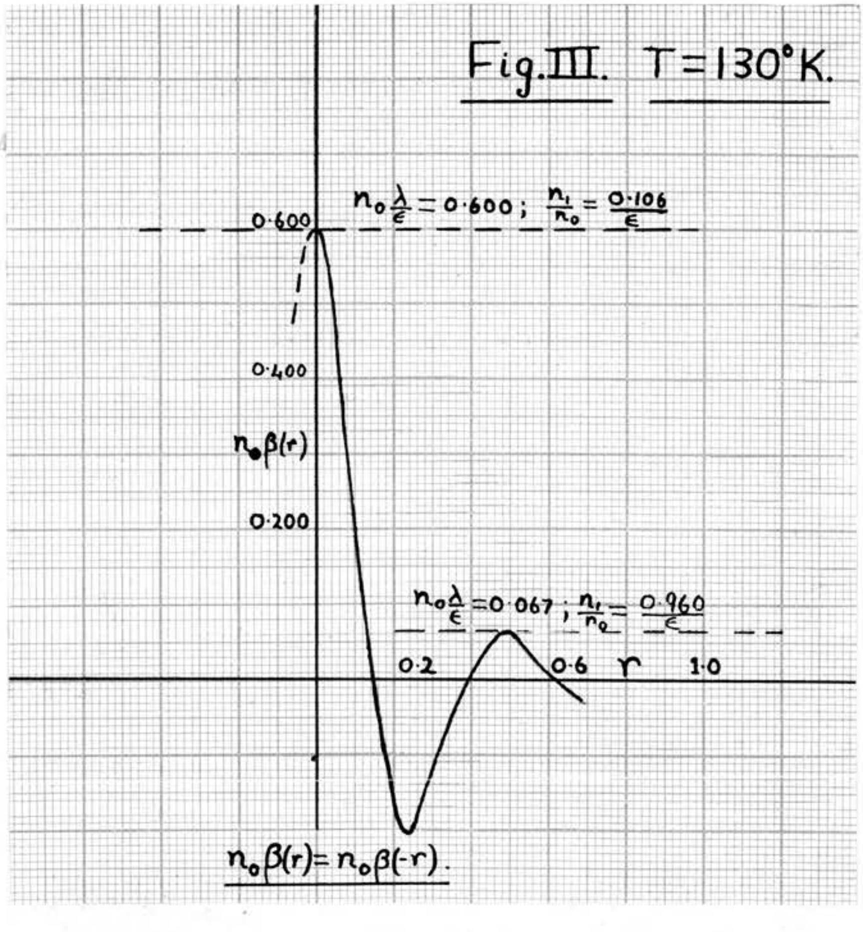

Fig. III. T = 130°K.

$n_0\beta(r) = n_0\beta(-r)$.

This result, it is seen from Fig. 1, is in the region where the liquid actually exists. The explanation is that more real roots would have to be taken into account to explain, the liquid phase.

The Fourier transform $\beta(s)$ of $\alpha(r)$ is an even function of s and has its greatest value when $s = 0$, and smaller subsidiary maxima symmetrical-ly placed about $s = 0$.

In Fig. 111 is reproduced $\beta(r)$ for Argon at T = 130°K. Here the units used are those described in Chapter 111, viz., unit of length is r_0, unit of energy is $|\phi_0|$, from the Lennard-Jones potential function

$$\phi(r) = |\phi_0| \left\{ -2\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12} \right\}$$

$\beta(r)$ has the dimensions of volume. From Fig. 111, it can be seen that the first two real roots occur at a density given by $\frac{n_1}{n_0} = \frac{0.106}{\epsilon}$, which is of the order of the density of the vapour at S.V.P. ($\frac{n_1}{n_0} = .069$, Exptl.). At a density given by $\frac{n_1}{n_0} = \frac{0.960}{\epsilon}$, another 4 real roots appear, where the horizontal line λ/ϵ touches the next two smaller maxima, one on each side of the largest maximum at $s = 0$. It is seen that this density is close to liquid densities, since ϵ has been assumed to be always nearly equal to 1.

Thus the original interpretation, is probably not comprehensive enough. The inclusion of more real roots will make the equation of state rise again so that $\frac{dp}{dV}$ is again negative, in exactly the same way as the behaviour of the equation of state when the first two real roots introduce themselves. Hence if this method is carried further it is probable that between the vapour phase and the liquid phase there will be two, at least, such "dips."

It is, of course, impossible to say how this would correspond to reality. The necessity of using a more accurate solution is obvious; at the very least a method is needed that takes into account all the terms linear in $f(r)$. This is what has been done and is described in the next chapter.

CHAPTER V.

ALTERNATIVE METHOD OF SOLVING THE INTEGRAL EQUATION FOR $n_2(r)$.

1. DISCUSSION

In a non-linear integral equation, like (1.27), an obvious method of solution is to assume $n_2(r)$ to be an arbitrary function with as many parameters as appears necessary. Since the correction function is known to be of an oscillatory nature, the most suitable choice would be cosine or sine functions, i.e. to take $f(r)$ to be a series of such functions with amplitudes and periods acting as the parameters. The difficulties of integration preclude this method from consideration.

The most simple function to take for $f(r)$ is a polynomial in r. The right-hand side of equation (1.27) can then be integrated. However a polynomial of a finite number of terms has the disadvantage of becoming infinite as r becomes infinite. This fact could upset the accuracy of the method. Hence the following device is used.

From the radial distribution function obtained by X-ray diffraction methods, it is found that, for values of $r > 1.5 r_0$, $n_2(r)/n_1^2$ is almost equal to 1. $f(r)$ in that region oscillates with a very small amplitude. Moreover, in equation (1.27) $n_2(s)$ occurs in combination with $\phi'(s)$ which rapidly tends to zero beyond $r = r_0$. Hence if $f(r)$ is defined in the region $0 \leq r \leq \beta$ and taken as zero outside this range, where β is a value of r beyond which $f(r)$ is very small; and if this restricted $f(r)$ is substituted in (1.27) a very small error is introduced . This determines $f(r)$ in the region of the first large maximum of $n_2(r)$ only, but this first approximation could be used in evaluating $n_2(r)/n_1^2$ for large r , and would show the smaller minima and maxima superposed on $e^{-\phi(r)/kT}$. It should be remarked that this is not a "first neighbour" approximation. The approximation consists in neglecting the difference between $n_2(r)/n_1^2$ at large r and the value 1 towards which it tends. As explained previously (Chapter II, p.15) the most important part of $f(r)$ is that in the region of the repulsive forces. Just as this determines the equation of state, it will determine the nature of $f(r)$ itself for large r . Simple calculations of magnitude verify this statement.

This statement can also be understood in the light of some considerations by J.D. Bernal(18) , who, taking a "molecularly homogeneous model" for a fluid, attempted to find the radial distribution function. He assumed that knowing the distribution close to each molecule, it was possible to find its complete radial distribution. This he did using some statistical and geometrical considerations, and obtained a radial distribution function in the form of a series of "co-ordination shells" for which he calculated the number of molecules in each shell and its position with respect to the central molecule. This assumption that the whole radial distribution function is principally determined by its values for small r seems therefore a reasonable one.

2. MATHEMATICAL TREATMENT.

The device, mentioned previously, of taking $f(r)$ finite over a certain range of r only and zero elsewhere, is best described with the help of a discontinuous function of r, $k^{r}_{\alpha,\beta}$. This function is defined by:-

$$(5.1)\quad \begin{cases} k^{r}_{\alpha,\beta} = 1 \text{ for } \alpha \leqslant r \leqslant \beta \\ k^{r}_{\alpha,\beta} = 0 \text{ for outside the range } (\alpha,\beta) \end{cases}$$

$k^{r}_{\alpha,\beta}$ is a function of r, but its argument r is written as a super-script for convenience. Such a function has obvious properties, for instance the product of two of these functions $k^{r}_{\alpha,\beta}\, k^{r}_{\gamma,\delta}$ will have different values depending on whether γ and δ lie in the range (α,β) or not, e.g., if γ lies in the range (α,β) and δ outside and greater than β then

$$k^{r}_{\alpha,\beta}\, k^{r}_{\gamma,\delta} = k^{r}_{\gamma,\beta}$$

also clearly

$$(5.2)\quad k^{r+\delta}_{\alpha,\beta} = k^{r}_{\alpha-\delta,\beta-\delta}$$

A result which is used frequently is

$$(5.3)\int_a^b k^{t}_{\gamma,\delta} f(t)\,dt = F(\delta)\left\{k^{a}_{-\infty,\delta} - k^{b}_{-\infty,\delta}\right\} - F(\gamma)\left\{k^{b}_{\gamma,\infty} - k^{a}_{\gamma,\infty}\right\} + F(b)\,k^{b}_{\gamma,\delta} - F(a)\,k^{a}_{\gamma,\delta}$$

$$(a \leqslant b\,;\ \gamma \leqslant \delta)$$

where $\int_0^t f(t)\,dt = F(t)$

The proof of this is straight forward and is best verified by considering all the values which γ and δ can take relative to the range (a, b). For instance if $\gamma < a$; $\delta > b$

(5.3) reduces to

$$\int_a^b f(t)\,dt = F(b) - F(a)$$

and so on.

We now take

(5.4) $$\frac{n_2(s)}{n_1^2} = e^{-\phi(s)/kT}\left\{1 + k_{0,\beta}^{s} \sum_{i=0}^{m} c_i s^i\right\}$$

i.e.,

(5.5) $$f(s) = k_{0,\beta}^{s} \sum_{i=0}^{m} c_i s^i$$

where β in this work is taken as 1·5(units $r_0 = 1$) (1.27) has become, on replacing $\frac{n_2(r)}{n_1^2}$ by $e^{-\phi(r)/kT}\{1+f(r)\}$

(5.6) $\log_e\left(1 + f(r)\right)$

$$= \frac{\pi n_1}{kTr}\int_0^\infty \int_{r-s}^{r+s} t(s^2 - t^2 - r^2 + 2tr)\left\{\frac{n_2(t)}{n_1^2} - 1\right\} dt\, e^{-\phi(s)/kT}\{1 + f(s)\}\,ds$$

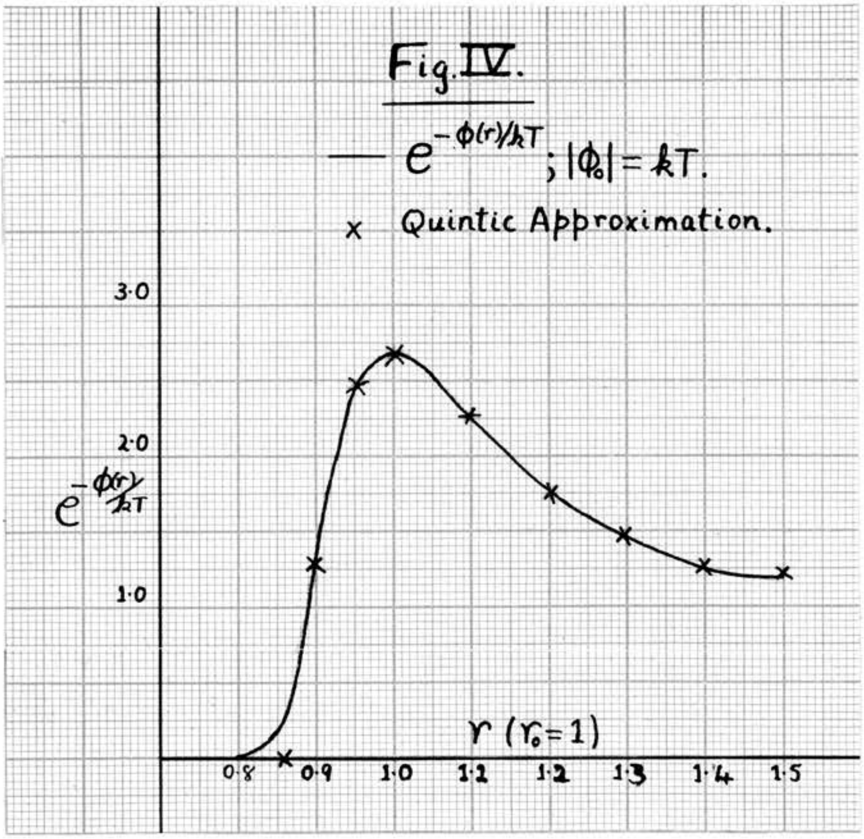

Fig. IV.

— $e^{-\phi(r)/kT}$; $|\phi_0| = kT$.
× Quintic Approximation.
3·0
2·0
1·0
$e^{-\phi(r)/kT}$
r (r_0=1)
0·8
0·9
1·0
1·1
1·2
1·3
1·4
1·5

where

$$(5.7) \quad \begin{cases} \phi(s) = -\frac{2}{s^6} + \frac{1}{s^{12}} \\ \phi'(s) = \frac{12}{s^7}\left(1 - \frac{1}{s^6}\right) \end{cases}$$

where r_0 , $|\phi_0|$, are the units of length and energy.

Nevertheless, with the functions chosen, it is practically impossible to calculate the internal integral of (5.6) in its present form explicitly, owing to the presence of the factor $e^{-\phi(t)/kT}$. This difficulty is overcome by fitting a polynomial expression to the values of $e^{-\phi(t)/kT}$ over the range (α, β), where α is a point taken where $e^{-\phi(\alpha)/kT}$ can be considered zero, and β is large enough so that $e^{-\phi(\beta)/kT}$ is very nearly one. e.g. for $kT = 1$, $\alpha = \cdot 860$, $\beta = 1{\cdot}500$.
For values of $t > \beta$, $e^{-\phi(t)/kT}$ is taken as 1. (Fig. IV shows $e^{-\phi(t)/kT}$ and its quintic polynomial approximation over this range (α, β) for $kT = 1$) i.e.

$$(5.8) \quad e^{-\phi(t)/kT} = k^t_{\alpha,\beta} \sum_{i=0}^{n} a_i t^i + k^t_{\beta,\infty}.$$

Hence for positive values of t , the form taken for use in the internal integral of (5.5) is

$$(5.9) \quad \frac{n_2(t)}{n_1^2} = k^t_{\alpha,\beta} \sum_{i=0}^{m+n} b_i t^i + k^t_{\beta,\infty}$$

where

$$(5.10) \quad b_i = a_i + \sum_{j+k=i} c_j a_k = \sum_{j+k=i} (\delta_{jo} + c_j) a_k .$$

δ_{jo} is the Kronecker delta, which is zero unless $j = o$, in which case $\delta_{oo} = 1$.

It is necessary to define $n_2(t)/n_1^2$ for negative t, by $n_2(t) = n_2(-t)$ the complete expression for positive and negative t being

(5.11)

$$\frac{n_2(t)}{n_1^2} = k^t_{\alpha,\beta} \sum_{i=0}^{m+n} b_i t^i + k^t_{-\beta,-\alpha} \sum_{i=0}^{m+n} (-1)^i b_i t^i + k^t_{\beta,\infty} + k^t_{-\infty,-\beta}$$

Hence

$$(5.12) \quad \frac{n_2(t)}{n_1^2} - 1 = k^t_{\alpha,\beta} \sum_{i=0}^{m+n} b_i t^i + k^t_{-\beta,-\alpha} \sum_{i=0}^{m+n} (-1)^i b_i t^i - k^t_{-\beta,\beta}$$

Denote the right-hand side of equation (5.6) by $\mathcal{R}(r)$, then on substituting the expression (5.12) into the internal integral, and the expression (5.4) into the outer integral we then obtain

$$(5.13) \quad \frac{r\, R(r)\, kT}{\pi n_1} = \mathcal{U}^{(1)} + \mathcal{U}^{(2)} + \mathcal{U}^{(3)} + V^{(1)} + V^{(2)} + V^{(3)}$$

the $\mathcal{U}$'s and V's all being functions of r.

Where

$$\mathcal{U}^{(1)} = \sum_{i=0}^{m+n} b_i \int_0^\infty \int_{r-s}^{r+s} k^t_{\alpha,\beta} \{ \overline{s^2-r^2}\, t^{i+1} + 2rt^{i+2} - t^{i+3} \} dt\, \phi'(s) e^{-\phi(s)/kT} ds,$$

$$\mathcal{U}^{(2)} = \sum_{i=0}^{m+n} (-1)^i b_i \int_0^\infty \int_{r-s}^{r+s} k^t_{-\beta,-\alpha} \{ \overline{s^2-r^2}\, t^{i+1} + 2rt^{i+2} - t^{i+3} \} dt\, \phi'(s) e^{-\phi(s)/kT} ds,$$

$$\text{(5.14)} \quad \mathcal{U}^{(3)} = \int_0^\infty \int_{r-s}^{r+s} k^t_{-\beta,\beta} \{ \overline{r^2-s^2}\, t - 2rt^2 + t^3 \} dt\, \phi'(s) e^{-\phi(s)/kT} ds,$$

$$V^{(1)} = \sum_{i=0}^{m+n} \sum_{j=0}^{m} b_i c_j \int_0^\beta \int_{r-s}^{r+s} k^t_{\alpha,\beta} \{ \overline{s^2-r^2}\, t^{i+1} + 2rt^{i+2} - t^{i+3} \} dt\, s^j \phi'(s) e^{-\phi(s)/kT} ds$$

$$V^{(2)} = \sum_{i=0}^{m+n} \sum_{j=0}^{m} (-1)^i b_i c_j \int_0^\beta \int_{r-s}^{r+s} k^t_{-\beta,-\alpha} \{ \overline{s^2-r^2}\, t^{i+1} + 2rt^{i+2} - t^{i+3} \} dt\, s^j \phi'(s) e^{-\phi(s)/kT} ds$$

$$V^{(3)} = \sum_{j=0}^{m} c_j \int_0^\beta \int_{r-s}^{r+s} k^t_{-\beta,\beta} \{ \overline{r^2-s^2}\, t - 2rt^2 + t^3 \} dt\, s^j \phi'(s) e^{-\phi(s)/kT} ds.$$

In the V's, the limits of integration of the variable s from 0 to ∞ have been changed to 0 to β, since $f(s)$ is non-zero only in the range $(0, \beta)$ and one can then omit the factor $k^s_{0,\beta}$ in the expression for $f(s)$ (5.5).

These expressions simplify if we restrict r, α and β to the conditions

$$\text{(5.15)} \quad \begin{cases} \alpha \leq r \leq \beta \\ \beta < 2\alpha \end{cases}$$

The second of these is easily satisfied, and by restricting r thus in this range, while one cannot then obtain $f(r)$ for large values of r, nevertheless one gets the most important part of $f(r)$.

Under these conditions (5.15)

$$V^{(2)} = 0$$

For since the upper limit $r+s$ of the inner integral is positive, this integral will be zero if the lower limit $r-s$ is greater than $-\alpha$ (the greatest value in the range ($-\beta, -\alpha$) occurring in $k^{t}_{-\beta,-\alpha}$).

i.e. if $s < r+\alpha$

i.e. if $\beta < 2\alpha$

since β is the greatest value of s, and α the least value of r.

Since the "k" functions in the expressions (5.14) serve merely to change the limits of integration in the manner shown by (5.3), all the integrals in (5.14) reduce to sums of integrals of the form

(5.16) $$J_n(\gamma,\delta) = \int_{\gamma}^{\delta} s^n e^{-\phi(s)/kT} \phi'(s)\, ds,$$

where $\gamma, \delta > 1$.

These integrals can be evaluated using Gamma integrals in the form of quickly convergent series. They are evaluated in Appendix I.

Because the evaluation of the integrals in (5.14) is mathematically simple but laborious, all the details will not be shown. As an example $U^{(1)}$ and $V^{(1)}$ will be worked out in detail, no additional considerations being required for the others.

$\mathcal{U}^{(1)}$ and $V^{(1)}$.

First evaluate

(5.17) $$\sum_{i=0}^{m+n} b_i \int_{r-s}^{r+s} k^{t}_{\alpha,\beta} \left\{ \overline{s^2-r^2}\, t^{i+1} + 2r t^{i+2} - t^{i+3} \right\} dt.$$

using (5.3).

This then equals

(5.18) $$F_1(\beta)\left\{ k^{s}_{r-\beta,\infty} - k^{s}_{-\infty,\beta-r} \right\} - F_1(\alpha)\left\{ k^{s}_{\alpha-r,\infty} - k^{s}_{-\infty,r-\alpha} \right\}$$
$$+ F_1(r+s)\, k^{s}_{\alpha-r,\beta-r} - F_1(r-s)\, k^{s}_{r-\beta,r-\alpha}$$

where

(5.19) $$F_1(t) = \sum_{i=0}^{m+n} b_i \left\{ (s^2-r^2)\frac{t^{i+2}}{i+2} + 2r\frac{t^{i+3}}{i+3} - \frac{t^{i+4}}{i+4} \right\}$$

s is positive and since in the outer integration, (5.18) is multiplied by the factor $e^{-\phi(s)/kT}$ which is effectively zero for $s < \alpha$, we can reject in (5.18) those k's whose ranges lie below α. Applying conditions (5.15), the only terms in (5.18) that do not become zero in the final integration are

(5.20) $$F_1(\beta)\, k^{s}_{\beta-r,\infty} - F_1(\alpha)\, k^{s}_{r-\alpha,\infty}$$

Then

(5.21) $$\begin{cases} \mathcal{U}^{(1)} = \displaystyle\int_{\beta-r}^{\infty} F_1(\beta)\,\phi'(s)\, e^{-\phi(s)/kT} ds - \int_{r-\alpha}^{\infty} F_1(\alpha)\,\phi'(s)\, e^{-\phi(s)/kT} ds \\ V^{(1)} = \displaystyle\sum_{j=0}^{m} c_j \left[\int_{\beta-r}^{\beta} F_1(\beta)\, s^j \phi'(s)\, e^{-\phi(s)/kT} ds - \int^{\beta} F_1(\alpha)\, s^j \phi'(s)\, e^{-\phi(s)/kT} ds \right] \end{cases}$$

Also both $\beta - r$ and $r - \alpha$ are less than α from (5.15), therefore one can change the lower limit of each integral in (5.21) to 0, because owing to the factor $e^{-\phi(s)/kT}$ no contribution is made as s moves from 0 to $\beta - r$ or $r - \alpha$. Then

$$(5.22)\quad \begin{cases} U^{(1)} = \displaystyle\int_0^\infty \{F_1(\beta) - F_1(\alpha)\}\,\phi'(s)\,e^{-\phi(s)/kT}\,ds\,, \\ V^{(1)} = \displaystyle\sum_{j=0}^{m} c_j \int_0^\beta \{F_1(\beta) - F_1(\alpha)\}\,s^j\,\phi'(s)\,e^{-\phi(s)/kT}\,ds \end{cases}$$

Substituting in the value of F_1 from (5.19) and using the integrals defined in (5.16) there results

$$(5.23)\quad \begin{cases} U^{(1)} = \displaystyle\sum_{i=0}^{m+n} b_i \left\{ \frac{\beta^{i+2} - \alpha^{i+2}}{i+2} J_2(0,\infty) - \left[r^2 \frac{\beta^{i+2} - \alpha^{i+2}}{i+2} - 2r\frac{\beta^{i+3} - \alpha^{i+3}}{i+3} + \frac{\beta^{i+4} - \alpha^{i+4}}{i+4} \right] J_0(0,\infty) \right\} \\ V^{(1)} = \displaystyle\sum_{i=0}^{m+n} \sum_{j=0}^{m} b_i c_j \left\{ \frac{\beta^{i+2} - \alpha^{i+2}}{i+2} J_{j+2}(0,\beta) - \left[r^2 \frac{\beta^{i+2} - \alpha^{i+2}}{i+2} - 2r\frac{\beta^{i+3} - \alpha^{i+3}}{i+3} + \frac{\beta^{i+4} - \alpha^{i+4}}{i+4} \right] J_j(0,\beta) \right\} \end{cases}$$

Let $U_i^{(1)}$ = coefficient of b_i in this expression for $U^{(1)}$

and $V_{ij}^{(1)}$ = coefficient of $b_i c_j$ in this expression for $V^{(1)}$.

Also from (5.10)

$$b_i = \sum_{j=0}^{m} (\delta_{j0} + c_j)\, a_{(i-j)}$$

Therefore

$$U^{(1)} = \sum_{i=0}^{m+n} U_i^{(1)} \sum_{j=0}^{m} (\delta_{j0} + c_j)\, a_{(i-j)}$$

$$= \sum_{j=0}^{m} (\delta_{j0} + c_j) \sum_{i=0}^{m+n} U_i^{(1)}\, a_{(i-j)}$$

$$= \sum_{j=0}^{m} (\delta_{j0} + c_j) \sum_{i=0}^{n} U_{i+j}^{(1)}\, a_i$$

Since a_i has values only for $0 \leq i \leq n$.

Therefore, finally, ~~if~~ we define the quantities

(5.24)
$$\alpha_j = \sum_{i=0}^{n} a_i \frac{\alpha^{i+j}}{i+j}$$
$$\beta_j = \sum_{i=0}^{n} a_i \frac{\beta^{i+j}}{i+j}$$
$$\alpha_j^{\pm} = r^2 \alpha_j \pm 2r\alpha_{j+1} + \alpha_{j+2}$$
$$\beta_j^{\pm} = r^2 \beta_j \pm 2r\beta_{j+1} + \beta_{j+2}$$

Then

(5.25)
$$\mathcal{U}^{(1)} = J_2(0,\infty) \sum_{j=0}^{m} (c_j + \delta_{j0})(\beta_{j+2} - \alpha_{j+2}) - J_0(0,\infty) \sum_{j=0}^{m} (c_j + \delta_{j0})(\beta^-_{j+2} - \alpha^-_{j+2})$$

Similarly

(5.26)
$$V^{(1)} = \sum_{j=0}^{m} c_j \left[(\beta_2 - \alpha_2) J_{j+2}(0,\beta) - (\beta_2^- - \alpha_2^-) J_j(0,\beta) \right] + \sum_{i=0}^{m} \sum_{j=0}^{m} c_i c_j \mathcal{B}_{ij}$$

where

(5.27)
$$2\mathcal{B}_{ij} = (\beta_{j+2} - \alpha_{j+2}) J_{i+2}(0,\beta) + (\beta_{i+2} - \alpha_{i+2}) J_{j+2}(0,\beta) - (\beta^-_{j+2} - \alpha^-_{j+2}) J_i(0,\beta) - (\beta^-_{i+2} - \alpha^-_{i+2}) J_j(0,\beta)$$

These quadratic terms in (5.26) are the only ones occurring.

Proceeding in a similar way, all the integrals in (5.14) are evaluated. The results are now summarised.

(5.5) $$f(s) = k^{s}_{0,\beta} \sum_{i=0}^{m} c_i s^i$$

(5.8) $$k^{s}_{\alpha,\beta}\, e^{-\phi(s)/kT} = k^{s}_{\alpha,\beta} \sum_{j=0}^{n} a_j s^j$$

(5.13) $$\frac{r R(r) kT}{\pi n_1} = U^{(1)} + U^{(2)} + U^{(3)} + V^{(1)} + V^{(2)} + V^{(3)} \quad \left(V^{(2)} = 0\right)$$

$$U^{(1)} = J_2(0,\infty) \sum_{j=0}^{m} (c_j + \delta_{j0})(\beta_{j+2} - \alpha_{j+2}) - J_0(0,\infty) \sum_{j=0}^{m} (c_j + \delta_{j0})(\beta^-_{j+2} - \alpha^-_{j+2})$$

$$U^{(2)} = \sum_{j=0}^{m} (c_j + \delta_{j0}) \left[J_2(r+\alpha,\infty)\alpha_{j+2} - J_2(r+\beta,\infty)\beta_{j+2} - J_0(r+\alpha,\infty)\alpha^+_{j+2} + J_0(r+\beta,\infty)\beta^+_{j+2} \right]$$

(5.28) $$- \sum_{j=0}^{m} (\delta_{j0} + c_j) \sum_{\ell=0}^{(m+n+4)} J_\ell(r+\alpha, r+\beta)\, T_{\ell j} \quad ,$$

where $$T_{\ell j} = \frac{2(-1)^\ell r^{4-\ell}(\ell-1)}{\ell!} \left\{ (-r)^j \sum_{i=0}^{n} (-r)^i a_i \frac{(i+j+1)!}{(i+j+4-\ell)!} \right\}$$

$$U^{(3)} = \tfrac{1}{12}\beta^2 \left[(3\beta^2 - 8\beta r + 6r^2) J_0(0,\infty) - (3\beta^2 + 8\beta r + 6r^2) J_0(\beta+r,\infty) - 6J_2(0,\beta+r) \right]$$
$$- \tfrac{1}{12} \left[r^4 J_0(0,\beta+r) - 6r^2 J_2(0,\beta+r) + 8r J_3(0,\beta+r) - 3J_4(0,\beta+r) \right]$$

$$V^{(1)} = \sum_{j=0}^{m} c_j \left[(\beta_2 - \alpha_2) J_{j+2}(0,\beta) - (\beta^-_2 - \alpha^-_2) J_j(0,\beta) \right]$$
$$+ \sum_{i=0}^{m} \sum_{j=0}^{m} c_i c_j B_{ij}$$

where $$2B_{ij} = (\beta_{j+2}-\alpha_{j+2})J_{i+2}(0,\beta) + (\beta_{i+2}-\alpha_{i+2})J_{j+2}(0,\beta) - (\bar{\beta}_{j+2}-\bar{\alpha}_{j+2})J_i(0,\beta) - (\bar{\beta}_{i+2}-\bar{\alpha}_{i+2})J_j(0,\beta)$$

$$V^{(3)} = \frac{1}{12}\sum_{j=0}^{m} c_j\Big[(3\beta+r)(\beta-r)^3 J_j(0,\beta) - 6(\beta^2-r^2)J_{j+2}(0,\beta) - 8r\,J_{j+3}(0,\beta) + 3\,J_{j+4}(0,\beta)\Big]$$

Finally on adding all the terms in (5.28) and dividing by $rkT/\sqrt{2}\pi$, we obtain (since $n_0 = \sqrt{2}$).

(5.29) $$\frac{n_0}{n_1}R(r) = \gamma(r) + \sum_{j=0}^{m} c_j\,A_j(r) + \sum_{i=0}^{m}\sum_{j=0}^{m} c_i c_j\,B'_{ij}(r).$$

The coefficients in the right-hand side being functions of r. If we substitute the assumed form for $f(r)$ in the left-hand side of equation (5.6) and equate this to the right-hand side obtained as in (5.29), then one must satisfy the equation

(5.30)
$$\frac{n_0}{n_1}\log_e\Big(1+\sum_{j=0}^{m} c_j r^j\Big) = \gamma(r) + \sum_{j=0}^{m} c_j A_j(r) + \sum_{i=0}^{m}\sum_{j=0}^{m} c_i c_j B'_{ij}(r)$$

for $\alpha \leq r \leq \beta$.

Here $B'_{ij}(r) = \frac{\sqrt{2}\pi}{kTr}B_{ij}(r)$ which is a simple function of r, viz.,

(5.31) $$B'_{ij}(r) = \frac{1}{r}C_{ij} + 2C'_{ij} + rC''_{ij}$$

where
$$2C_{ij} = \Big[(\beta_{j+2}-\alpha_{j+2})J_{i+2}(0,\beta) + (\beta_{i+2}-\alpha_{i+2})J_{j+2}(0,\beta) - (\beta_{j+4}-\alpha_{j+4})J_i(0,\beta) - (\beta_{i+4}-\alpha_{i+4})J_j(0,\beta)\Big]\frac{\sqrt{2}\pi}{kT}$$

$$2C'_{ij} = \left[(\beta_{j+3}-\alpha_{j+3})\, J_i(0,\beta) + (\beta_{i+3}-\alpha_{i+3})\, J_j(0,\beta)\right] \frac{\sqrt{2}\,\pi}{kT}$$

$$2C''_{ij} = -\left[(\beta_{j+2}-\alpha_{j+2})\, J_i(0,\beta) + (\beta_{i+2}-\alpha_{i+2})\, J_j(0,\beta)\right] \frac{\sqrt{2}\,\pi}{kT}$$

and are not functions of r .

CHAPTER VI.

1. THE LINEARISED SOLUTION.

A cubic form was taken for $f(r)$ and so (5.30) was satisfied for 4 points r_k $(k=1,\cdots 4)$.

Define

$$f_k = f(r_k) = \sum_{j=0}^{m} c_j r_k^j \quad (m=4).$$

$$L_k = \log_e(1+f_k)$$

(6.1)

$$\gamma_k = \gamma(r_k)$$

$$A_{jk} = A_j(r_k)$$

Further, using vector and matrix notation

$$\underline{L} = \begin{bmatrix} L_1 \\ L_2 \\ L_3 \\ L_4 \end{bmatrix} ; \quad \underline{f} = \begin{bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{bmatrix} ; \quad \underline{c} = \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix}$$

(6.2)

$$\underline{\gamma} = \begin{bmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ \gamma_4 \end{bmatrix} ; \qquad A = [A_{jk}] .$$

Then also

(6.3)

$$\underline{f} = \begin{bmatrix} 1 & r_1 & r_1^2 & r_1^3 \\ 1 & r_2 & r_2^2 & r_2^3 \\ 1 & r_3 & r_3^2 & r_3^3 \\ 1 & r_4 & r_4^2 & r_4^3 \end{bmatrix} \underline{c}$$

i.e. $\underline{f} = T\underline{c}$; $\underline{c} = T^{-1}\underline{f}$.

(5.30) becomes, if the quadratic terms are neglected.

(6.4) $\frac{n_0}{n_1} \underline{L} = \underline{\gamma} + A T^{-1} \underline{f}$

At low densities, we can expand $\underline{L} = \underline{f}$

Therefore

(6.5) $\frac{n_0}{n_1} \underline{f} = \underline{\gamma} + A T^{-1} \underline{f}$

So $\underline{f}$ is of the order $\frac{n_1}{n_0}$, and at gaseous densities a good approximation is

(6.6) $\underline{f} = \frac{n_1}{n_0} \underline{\gamma}$

However at vapour densities $\frac{n_1}{n_0} > 0.05$ roughly, the magnitude of the matrix $A T^{-1}$ makes (6.6) a poor approximation. (6.6) is, obviously, the first approximation obtained by substituting $\frac{n_2(r)}{n_1^2} = e^{-\phi(r)/kT}$ in the right-hand side of the original equation (1.27). This first approximation shows the development of a minimum in the radial distribution function at $r \sim 1.25\sigma$.

Solution of (6.5).

$A T^{-1}$ is a non-symmetrical matrix and has two complex eigen-values and two real, viz.,

$$\lambda_1 \,;\, \lambda_2 \pm i\lambda_3 \,;\, \lambda_4$$

Corresponding to these eigen values are the eigen-vectors $\underline{u}_1 \,;\, \underline{u}_2 \pm i\underline{u}_3 \,;\, \underline{u}_4$.

For the complex eigen-vectors, the following relations hold

$$A T^{-1} \underline{u}_2 = \lambda_2 \underline{u}_2 - \lambda_3 \underline{u}_3$$

(6.7) $$A T^{-1} \underline{u}_3 = \lambda_3 \underline{u}_2 + \lambda_2 \underline{u}_3$$

Although these four vectors are not orthogonal, they form an independent set, therefore they can be used as a representation, viz.,

(6.8)
$$\underline{f} = \sum_{t=1}^{4} s_t \underline{u}_t$$
$$\underline{\gamma} = \sum_{t=1}^{4} \chi_t \underline{u}_t$$

where $s_t \ (t = 1, \cdots 4.)$ are to be determined.

Substituting (6.8) in (6.5) and equating the coefficients of $\underline{u}_1$, $\underline{u}_2$, $\underline{u}_3$, $\underline{u}_4$.

(6.9)
$$\frac{n_0}{n_1} s_1 = \chi_1 + \lambda_1 s_1$$
$$\frac{n_0}{n_1} s_2 = \chi_2 + \lambda_2 s_2 + \lambda_3 s_3$$
$$\frac{n_0}{n_1} s_3 = \chi_3 - \lambda_3 s_2 + \lambda_2 s_3$$
$$\frac{n_0}{n_1} s_4 = \chi_4 + \lambda_4 s_4$$

Solving the two equations for s_2 and s_3

(6.10)
$$s_1 = \chi_1 \Big/ \left(\frac{n_0}{n_1} - \lambda_1\right)$$
$$s_2 = \frac{\lambda_3 \chi_3 + \left(\frac{n_0}{n_1} - \lambda_2\right) \chi_2}{\lambda_3^2 + \left(\frac{n_0}{n_1} - \lambda_2\right)^2}$$
$$s_3 = \frac{\left(\frac{n_0}{n_1} - \lambda_2\right) \chi_3 - \lambda_3 \chi_2}{\lambda_3^2 + \left(\frac{n_0}{n_1} - \lambda_2\right)^2}$$
$$s_4 = \chi_4 \Big/ \left(\frac{n_0}{n_1} - \lambda_4\right)$$

$$\underline{f} = \sum_{t=1}^{4} s_t \underline{u}_t$$

$$\underline{C} = \sum_{t=1}^{4} s_t T^{-1} \underline{u}_t = \sum_{t=1}^{4} s_t \underline{C}_t$$

Hence $f(r)$ has been found as a linear sum of 4 cubic polynomials whose parameters are given by the vectors

$\underline{C}_t \ (t=1,\cdots 4.)$

There are two points $1/\lambda_1$, $1/\lambda_4$, of divergence in the density range n_1/n_0. However, for $kT=1$, λ_4 is very large and negative (-2,800) and so this divergence does not affect results in the physical range of densities, and $\lambda_1 = 1{\cdot}455$ and so a divergence occurs for $\frac{n_1}{n_0} = {\cdot}687$, which is almost exactly the density of liquid Argon at this temperature and at S.V.P. ($\frac{n_1}{n_0} = {\cdot}690$). A complete solution of (5.30) does not, of course, contain this divergence.

2. COMPLETE SOLUTION OF (5.30).

From the linear solutions (6.10) since λ_4 is so large, the cubic function defined by $\underline{C}_4$, corresponding to the eigen-vector $\underline{u}_4$ of AT^{-1} can be considered negligible in $f(r)$. But from (6.10)

$$\lambda_4 s_4 = -\chi_4 \tag{6.11}$$

neglecting $\frac{n_0}{n_1}$ in comparison with λ_4. Therefore $\lambda_4 s_4$ cannot be neglected in the righthand side of (5.30), and has the function in this linear case, of applying the required correction to the first approximation terms γ_k.

In the quadratic terms of (5.30) one can consider the quadratic form as made up of the three vectors $\underline{C}_1$, $\underline{C}_2$, $\underline{C}_3$, only.

Let

$$\sum_{i=0}^{m} \sum_{j=0}^{m} c_i c_j B'_{ij}(r_k) = Q_k \tag{6.12}$$

Then, since $\underline{C} = s_1 \underline{C}_1 + s_2 \underline{C}_2 + s_3 \underline{C}_3$ where s_1, s_2, s_3 will be the solutions for the quadratic case,

$$Q_k = \sum_{i=1}^{3} \sum_{j=1}^{3} s_i s_j \left\{ \underline{C}'_i \left(\frac{1}{r_k} [C_{ij}] + 2 [C'_{ij}] + r_k [C''_{ij}] \right) \underline{C}_j \right\} \tag{6.13}$$

Where $\underline{C}'_i$ - Transpose vector of $\underline{C}_i$

Therefore (5.30) becomes

(6.14)

$$\frac{n_0}{n_1} \underline{L} = \underline{\gamma} + \lambda_1 s_1 \underline{u}_1 + (\lambda_2 s_2 + \lambda_3 s_3) \underline{u}_2 + (\lambda_2 s_3 - \lambda_3 s_2) \underline{u}_3$$
$$+ \lambda_4 s_4 \underline{u}_4 + \underline{Q}$$

where

$$\underline{Q} = \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \\ Q_4 \end{bmatrix},$$

and $\underline{L}$ has components

$$L_t = \log_e \left(1 + s_1 u_{1t} + s_2 u_{2t} + s_3 u_{3t} \right); (t = 1, \cdots 4)$$

where

$$\underline{u}_i = \begin{bmatrix} u_{i1} \\ u_{i2} \\ u_{i3} \\ u_{i4} \end{bmatrix}$$

(6.14) written out in full gives four simultaneous equations from which $\lambda_4 s_4$ can be eliminated, yielding three equations for s_1, s_2, s_3, which can be solved quite simply by successive approximations. For at relatively small densities, the linear result is nearly correct at (say) $\left(n_1/n_0\right)^0 = 0\cdot1$. If these solutions are s_1^0, s_2^0, s_3^0, then if $\left(\frac{n_1}{n_0}\right)^0$ is increased to $\left(\frac{n_1}{n_0}\right)^0 + \Delta\left(\frac{n_1}{n_0}\right)$, the solutions will be $s_1^0 + \Delta s_1$ etc. Then, using Taylor's theorem, the three equations from (6.14) are expanded to terms in first-order of the Δs_i, yielding 3 linear simultaneous equations for these quantities. By suitably choosing $\Delta\left(\frac{n_1}{n_0}\right)$, one such approximation for each change in density is very accurate. This process is repeated until $n_1/n_0 = 1\cdot0$, and remains convergent from one step to the next.

This method of solving the ~~equation for the~~ integral equation therefore presents no difficulties, and could be extended to obtain, as an approximation for $f(r)$, a six-order polynomial, which would give more accurate results than the present cubic polynomial.

Remarks on Computation.

This work must be done on a good calculating machine. Using polynomial approximations, one is continually confronted with the fact that some of the quantities required are a very small difference of large quantities. For instance, in calculating $\mathcal{U}^{(2)}$ a quantity occurs $\sum_{\ell=0}^{m+n+4} J_\ell(r+\alpha, r+\beta)\, T_{\ell j}$, where the $T_{\ell j}$ are alternating in sign with respect to ℓ and are of the order (300,000). For sufficient accuracy in the summation, then, the $J_\ell(r+\alpha, r+\beta)$ must be calculated to accuracy in the eighth decimal place. All the numerical details will be given in the appendix.

CHAPTER VII.

APPLICATION TO THE PROPERTIES OF FLUIDS.

In Chapter II, it was shown that many quantities determining the properties of fluids are determined by the integrals

$$(7.1)\quad \begin{aligned} J_n &= \int_0^\infty \frac{n_2(s)}{n_1^2}\,\phi'(s)\,s^n\,ds \\ I_n &= \int_0^\infty \frac{n_2(s)}{n_1^2}\,\phi(s)\,s^n\,ds\,. \end{aligned}$$

Here $n_2(s)/n_1^2 = e^{-\phi(s)/kT}\left\{1 + k^5_{0,\beta}\sum_{j=0}^{3} c_j s^j\right\}$

where the C_j are determined in terms of the compon:-ents of the 3 vectors $\underline{C}_1$, $\underline{C}_2$, $\underline{C}_3$.

$$(7.2)\quad C_j = s_1 C_{1j} + s_2 C_{2j} + s_3 C_{3j}$$

Hence

$$(7.3)\quad \begin{aligned} J_n &= J_n(0,\infty) + \sum_{j=0}^{3} C_j\,J_{n+j}(0,\beta) \\ I_n &= I_n(0,\infty) + \sum_{j=0}^{3} C_j\,I_{n+j}(0,\beta) \end{aligned}$$

where

$$(7.4)\quad I_n(0,\gamma) = \int_0^\gamma e^{-\phi(s)/kT}\phi(s)\,s^n\,ds$$

and is discussed in Appendix 1.

Hence using (7.2)

$$(7.5)\quad \begin{aligned} J_n &= J_n(0,\infty) + \sum_{i=1}^{3} s_i\,J_n^{(i)} \\ I_n &= I_n(0,\infty) + \sum_{i=1}^{3} s_i\,I_n^{(i)} \end{aligned}$$

where

$$(7.6)\quad \mathcal{J}_n^{(i)} = \sum_{j=0}^{3} c_{ij} J_{n+j}(0,\beta) \qquad (i=1,2,3)$$

$$\mathcal{I}_n^{(i)} = \sum_{j=0}^{3} c_{ij} I_{n+j}(0,\beta)$$

Knowing s_1 , s_2 , s_3 , from the linear or quadratic solutions and the components c_{ij} of the vectors $\underline{c}_i$, $\mathcal{J}_n$ and $\mathcal{I}_n$ can be evaluated.

Listed below are the quantities given in Chapter II.

Equation of State

$$(7.7)\quad \frac{p v_0}{kT} = \frac{v_0}{v}\left\{1 - \frac{2\sqrt{2}\pi}{kT}\,\frac{v_0}{v}\,\mathcal{J}_3\right\}$$

Surface Tension γ

$$(7.8)\quad \gamma = -\pi\left(\frac{n_1}{n_0}\right)^2 \mathcal{I}_3 \frac{|\phi_0|}{r_0^2}\ \text{erg}\,\text{cm}^{-2}.$$

Internal Energy E

$$(7.9)\quad E - \tfrac{3}{2}kT = 2\sqrt{2}\pi\left(\frac{n_1}{n_0}\right)\mathcal{I}_2\,|\phi_0|\ \text{ergs.}$$

Viscosity η

$$(7.10)\quad \eta = \frac{4\pi}{15}\left(\frac{m}{kT}\right)^{1/2}\left(\frac{n_1}{n_0}\right)^2 \mathcal{J}_4 \frac{|\phi_0|}{r_0^2}\ \text{dyne sec. cm}^{-2}.$$

where m = molecular mass.

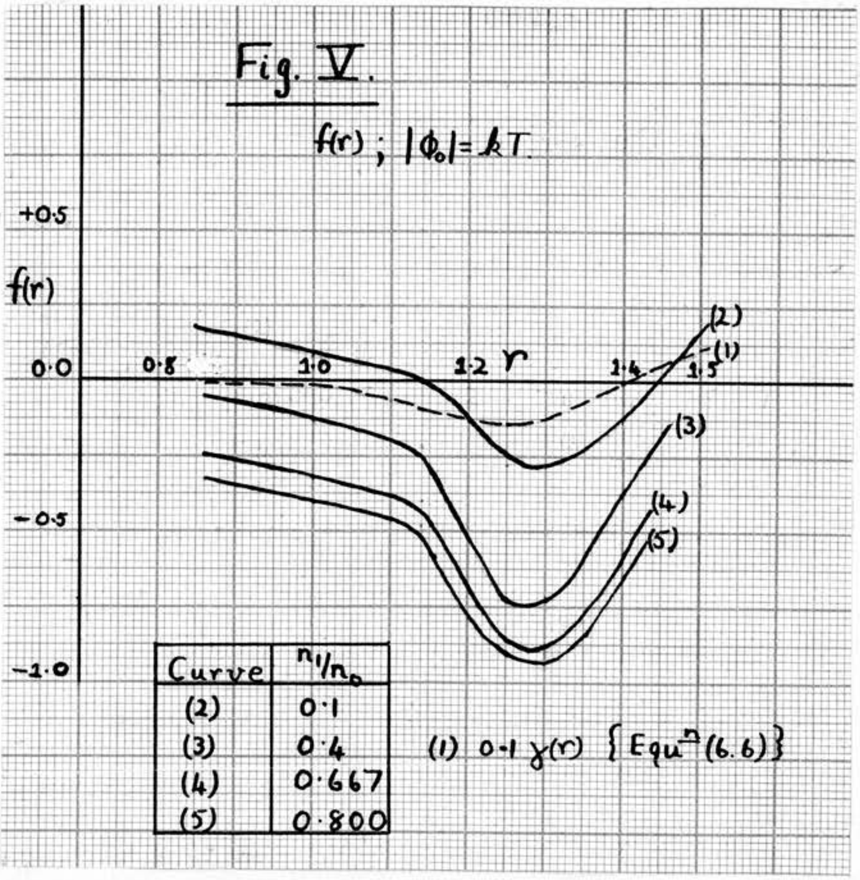

Fig. V.

$f(r)$; $|\Phi_0| = kT$.

Curve	n_1/n_0
(2)	0.1
(3)	0.4
(4)	0.667
(5)	0.800

Quantitative Results for $kT = |\phi_0|$.

The four points r_k ($k=1,\ldots 4$), $\alpha \leq r_k \leq \beta$, ($\alpha = \cdot 860$, $\beta = 1\cdot 500$) were chosen as r_1, r_2, r_3, r_4 $= \cdot 860$, $1\cdot 000$, $1\cdot 140$, $1\cdot 400$ respectively. These were chosen arbitrarily, but the first three were taken in the region where $\phi(r)$ and $\phi'(r)$ are of considerable magnitude. The last point $r_4 = 1\cdot 400$ was taken near the end of the range, in order to cover it adequately.

In addition, the right hand side of (5.6) was calculated for $r = 1\cdot 250$ using the $f(r)$ obtained from the other four points. As a first approximation this was taken equal to $\log_e(1+f(r))$ for $r = 1\cdot 250$. Had the cubic approximation been completely adequate, this value of $f(r)$ would have agreed exactly with the value got from the cubic approximation. This was not so, this new result showed that there is a minimum at $r \sim 1\cdot 250$. The cubic therefore, does not adequately describe $f(r)$ over the whole range (α, β). But values of $f(r)$ in the region of $r \sim 1\cdot 250$, are not very important in determining the properties of the fluid. Fig. V. shows $f(r)$ for various densities, the value of $f(r)$ obtained as described at $r = 1\cdot 250$ being used; also, shown dotted is the approximation for very low densities given in (6.6) (i.e. $f(r) = \frac{n_1}{n_0}\gamma(r)$) for a density $\frac{n_1}{n_0} = 0\cdot 1$. This approximation also shows a minimum at $r \sim 1\cdot 250$,

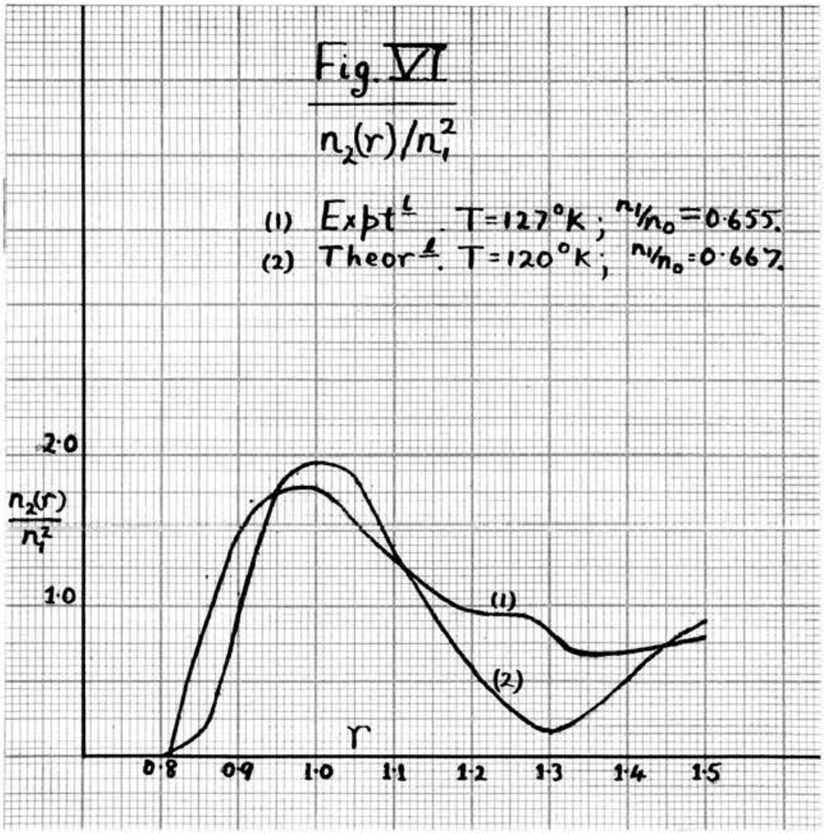

Fig. VI

$n_2(r)/n_1^2$

(1) Exptl. $T = 127°K$; $n_1/n_0 = 0{\cdot}655$.
(2) Theorl. $T = 120°K$; $n_1/n_0 = 0{\cdot}667$.

verifying the validity of taking the value of $f(1.250)$ from the cubic approximation.

The solutions for $f(r)$ are tabulated in Appendix II.

The Lennard-Jones potential function has been derived for some elements $^{(9)}$, so the results of this work can be converted for comparison with the fluid states of these elements. In Table III is given the relevant data for doing so, the last column, for instance giving the temperature for which $kT/|\phi_0| = 1$.

TABLE III.

Element	r_0 in Å	v_0 in Å^3	$\lvert\phi_0\rvert \times 10^{15}$ ergs.	$\lvert\phi_0\rvert/k$ °K.
Ne	3·08	20·66	4·89	35·7
A	3·83	39·73	16·50	120
H_2	3·28	24·96	4·25	31
N_2	4·17	51·28	13·25	97

1. $n_2(r)/n_1^2$

Fig. VI shows the derived $n_2(r)/n_1^2$ compared with that obtained by Eisenstein and Gingrich at a temperature 127°K and $\frac{n_1}{n_0} = \cdot 655$.

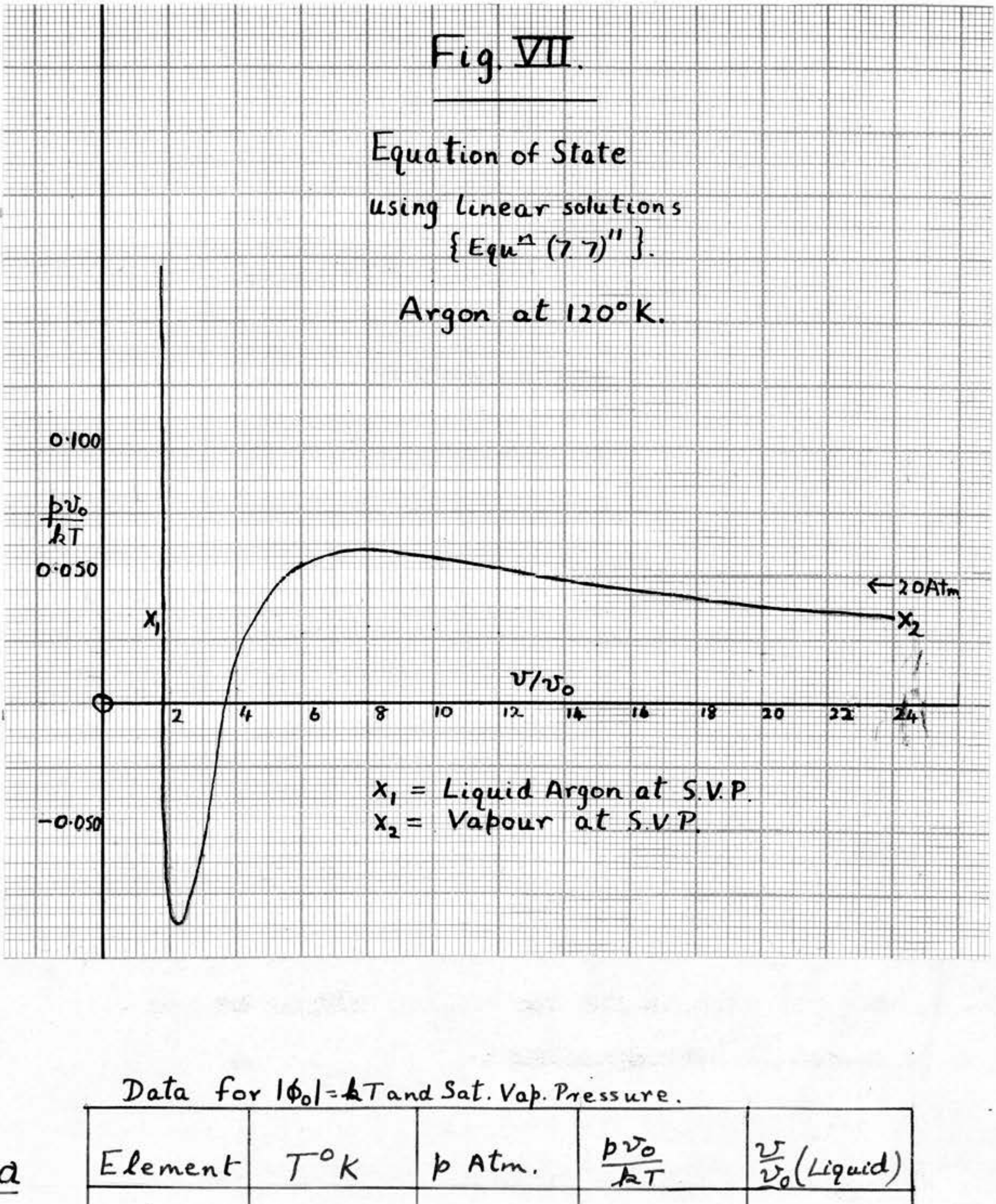

Fig. VII.

Equation of State using linear solutions $\{ \text{Equ}^{n} (7.7)'' \}$.

Argon at 120°K.

X_1 = Liquid Argon at S.V.P.
X_2 = Vapour at S.V.P.

Table III a (from Int. Crit. Tables 1, 103; 3, 203.)

Data for $|\phi_0| = kT$ and Sat. Vap. Pressure.

Element	T°K	p Atm.	$\frac{pv_0}{kT}$	$\frac{v}{v_0}$ (Liquid)
A	120	13·7	·033	1·46
Ne	35·7	7·4	·032	1·60
H_2	31	9·8	·059	1·63
N_2	97	6·4	·025	1·46

2. The Equation of State

$$(7.7)' \quad \frac{pv_0}{kT} = \frac{v_0}{v}\left\{1 - \frac{|\phi_0|}{kT}\frac{v_0}{v}\left[5.331 + 1.000S_1 - 8.991S_2 + 3.483S_3\right]\right\}$$

Using the linear solutions (6.10)

$$(7.7)'' \quad \frac{pv_0}{kT} = \frac{v_0}{v}\left\{1 - \frac{|\phi_0|}{kT}\frac{v_0}{v}\left[5.331 - \frac{.934}{\frac{v}{v_0} - 1.455} - \frac{11.312\frac{v}{v_0} + 4.26}{\left(\frac{v}{v_0} + 9.720\right)^2 + 207}\right]\right\}$$

Using the complete solutions of (5.6), the equation of state has not received sufficient correction to become positive at liquid densities, the accuracy required for this is described in the introduction of this thesis. Because of the divergent term (7.7)" gives an equation of state agreeing closer with experiment than any previously obtained theoretically. Fig. VII shows the curve (7.7)", compared with data on Argon.

3. Surface Tension γ

$$(7.8)' \quad \gamma\frac{r_0^2}{|\phi_0|} = \pi\left(\frac{n_1}{n_0}\right)^2\left\{1.176 + 1.436S_1 + 2.510S_2\right\}$$

S_3 is very small and can be neglected. Table IV. shows the results for the various fluids at the temperature corresponding to $kT/|\phi_0| = 1$.

TABLE IV.

$\frac{n_1}{n_0}$	$\gamma \frac{r_0^2}{\lvert\phi_0\rvert}$	γ dynes cm^{-1}			
		A. at 120°K	Ne at 35·7°K	N_2 at 97°K	H_2 at 31°K
0·667	1·144	12·87	5·90	8·72	4·52
0·800	1·467	16·50	7·56	11·18	5·80
1·000	1·885	21·20	9·72	14·36	7·45
Experimental[†]		12·5 at 87·3°K	4·45 at 28°K	6·16 at 90°K.	1·91 at 20·4°K.

[†] International Critical Tables. (1926) <u>4</u> 441.

These values can be compared with the value obtained experimentally for liquid Argon at 87·3°K, $\gamma = 12{\cdot}5$ dynes cm^{-1}. Very few data are available for Surface Tension and its variation with density for the liquids listed.

4. Internal Energy

$$(7.9)' \quad \frac{E - \frac{3}{2}kT}{|\phi_0|} = 2\sqrt{2}\,\pi\,\frac{n_1}{n_0}\left\{1{\cdot}044 + {\cdot}868\,S_1 - {\cdot}136\,S_2\right\}$$

Since no variation of E with temperature has been obtained, little can be said about this quantity. From the equipartition Theorem for monatomic molecules $E - \frac{3}{2}kT$ should tend to $\frac{3}{2}kT$, the contribution to E from the potential energy, when in the crystal state. From the solutions for $f(r)$ at $\frac{n_1}{n_0} = 1{\cdot}0$, $S_1 = -{\cdot}674$, $S_2 = +{\cdot}156$.

Therefore $E - \frac{3}{2} kT = 2{\cdot}0\, kT$

since $|\phi_0| = kT.$

This is in fair agreement with the equipartition principle.

Viscosity η

$$(7.10)' \quad \frac{\eta \, r_0^2}{\left(\frac{m}{kT}\right)^{\frac{1}{2}} |\phi_0|} = \frac{16\pi}{5} \left(\frac{n_1}{n_0}\right)^2 \left\{ \cdot 337 + \cdot 096\, S_1 - \cdot 208\, S_2 \right\}$$

No experimental data for viscosity have been discovered for the fluids to which this theory is applicable. Table V. displays some results of (7.10)' using the complete solutions of S_1 and S_2 (Appendix II).

TABLE V.

$\frac{n_1}{n_0}$	$\frac{\eta \, r_0^2}{\left(\frac{m}{kT}\right)^{\frac{1}{2}} \lvert\phi_0\rvert}$	η dyne Sec. cm^{-2}			
		A at 120°K	Ne at 35·7°K	N_2 at 97°K	H_2 at 31°K
0·667	1·07	770×10^{-6}	460×10^{-6}	490×10^{-6}	120×10^{-6}
1·000	2·41	$1{,}740 \times 10^{-6}$	$1{,}040 \times 10^{-6}$	$1{,}100 \times 10^{-6}$	280×10^{-6}
η (Exptl) for the Gas†		210×10^{-6} at 0°C.	312×10^{-6} at 15°C.	166×10^{-6} at 0°C.	86×10^{-6} at 0°C.

† Kaye and Laby (1932) Phys. and Chem. Constants, 31.

CONCLUSION.

A radial distribution function has been derived, which gives fair agreement with some of the experimentally determined properties of fluids. The equation of state has not been obtained very accurately for the liquid, although the linear solution obtained for $f(r)$ gives an equation of state, which has a divergence but gives better agreement with experiment than other theoretical derivations.

The presence of a minimum and second maximum of $n_2(r)$, has been shown. Of the other physical properties, little can be said as yet, because calculations have been limited to one temperature and also since there are not many experimental data available for the simple liquids to which the Lennard-Jones potential function can be applied.

The most important result, therefore, has been the demonstration of the divergence of the linear solution at the density of the liquid and not of the vapour at the saturation vapour pressure. For this reason, the method should be extended to obtain a quintic approximation which should give a better idea of the power of the method and of the Kirkwood "Superposition" approximation for n_3.

The author wishes to express his indebtedness to Professor Max Born for much advice and kindly supervision, also to Dr. H.S. Green for many discussions.

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APPENDIX I.

The evaluation of $J_n(0,\beta)$; $I_n(0,\beta)$.

$$J_n(0,\beta) = \int_0^\beta s^n \phi'(s) e^{-\phi(s)/kT} ds,$$

(1)
$$I_n(0,\beta) = \int_0^\beta s^n \phi(s) e^{-\phi(s)/kT} ds.$$

$$(\beta > 1)$$

Another integral on which these depend is

(2) $$K_n(0,\beta) = \int_0^\beta s^n e^{-\phi(s)/kT} ds.$$

For if $J_n(0,\beta)$ is integrated by parts, one obtains

(3) $$J_n(0,\beta) = -kT\left\{\beta^n e^{-\phi(\beta)/kT} - n\int_0^\beta s^{n-1} e^{-\phi(s)/kT} ds\right\}$$

i.e.

(4) $$\epsilon^2 J_n(0,\beta) = -\beta^n e^{-\phi(\beta)/kT} + n\, K_{n-1}(0,\beta)$$

where

(5) $$\epsilon^2 = 1/kT$$

$I_n(0,\beta)$ can also be expressed in terms of $K_n(0,\beta)$.

For since

(6) $$\phi(s) = \frac{1}{s^6}\left(-2 + \frac{1}{s^6}\right) = -\frac{1}{12} s \phi'(s) - \frac{1}{s^6}$$

then

(7) $$I_n(0,\beta) = -\int_0^\beta s^n\left\{\tfrac{1}{12}s\phi'(s)+s^{-6}\right\}e^{-\epsilon^2\phi(s)}\,ds.$$

Therefore

(8) $$I_n(0,\beta) = -\tfrac{1}{12}J_{n+1}(0,\beta) - K_{n-6}(0,\beta)$$

Using (4)

(9) $$I_n(0,\beta) = \frac{1}{12\epsilon^2}\beta^{n+1}e^{-\epsilon^2\phi(\beta)} - \frac{n+1}{12\epsilon^2}K_n(0,\beta) - K_{n-6}(0,\beta).$$

The evaluation of $K_n(0,\beta)$.

On substituting (6) into (2), one obtains

$$K_n(0,\beta) = \int_0^\beta s^n e^{(2\epsilon^2 s^{-6}-\epsilon^2 s^{-12})}\,ds.$$

Changing the variable to $y = \epsilon^2 s^{-12}$, and let $\mu = \epsilon\beta^{-6} \ll 1$,

(10) $$K_n(0,\beta) = \tfrac{1}{12}\epsilon^{\frac{n+1}{6}}\int_{\mu^2}^\infty y^{-\frac{n+13}{12}}e^{(2\epsilon y^{\frac{1}{2}}-y)}\,dy$$

Expand $e^{2\epsilon y^{\frac{1}{2}}}$ and thus obtain

(11) $$K_n(0,\beta) = \tfrac{1}{12}\epsilon^{\frac{n+1}{6}}\sum_{r=0}^{\infty}\frac{2^r\epsilon^r}{r!}\int_{\mu^2}^\infty y^{\frac{r}{2}-\frac{n+13}{12}}e^{-y}\,dy$$

These are Gamma integrals provided $\frac{r}{2}-\frac{n+13}{12} > -1$ i.e., since $r \geqslant 0$, provided $n < -1$.

In the work done here $K_n(0,\beta)$ was required for $-3 \leqslant n \leqslant 11$. When $n = 1$, the index of y in the first term of (11) is -2, in the second $-\frac{3}{2}$, in the third -1.

Thus, depending on the value of n, the first two or three terms of the series in (11) are not incomplete Gamma integrals or exponential integrals. But since $\mu^2 \neq 0$, they can be transformed into these by integrating by parts.

The exponential integral is defined by

$$(12) \quad -Ei(-x) = \int_x^\infty \frac{e^{-t}}{t}\,dt$$

and when x is small, $Ei(-x)$ can be expressed as a convergent series (Glaisher J.W.L.(19)):-

$$(13) \quad Ei(-x) = \gamma + \tfrac{1}{4}\log_e x^4 + \sum_{r=1}^{\infty} \frac{(-1)^r x^r}{r!\,r}$$

$\gamma = \cdot 5772,1567.$ (Euler's constant).

After integrating by parts the exponential integral occurs in the first, and third terms for $n = 11$; the second for $n = 5$, the first for $n = -1$.

To repeat in detail all the separate cases would be merely very tedious, and no real difficulty occurs. Hence here we summarise the various cases for $-3 \leq n \leq 11$ by expressing

$$(14), \quad K_n(0,\beta) = k(\mu^2) + \tfrac{1}{12}\,\epsilon^{\frac{n+1}{6}} \sum_{r=j}^{\infty} \frac{2^r \epsilon^r}{r!} \int_{\mu^2}^{\infty} y^{\frac{r}{2}-\frac{n+13}{12}} e^{-y}\,dy$$

where $k(\mu^2)$ can be obtained as a series in μ^2 and j is a small integer (1, 2 or 3) depending on the value of n.

Therefore

$$(15)\quad K_n(0,\beta) = k(\mu^2) + \frac{1}{12}\epsilon^{\frac{n+1}{6}}\sum_{r=j}^{\infty}\frac{2^r\epsilon^r}{r!}\Gamma\left(\frac{r}{2}-\frac{n+1}{12}\right) - \frac{1}{12}\epsilon^{\frac{n+1}{6}}\sum_{r=j}^{\infty}\sum_{s=0}^{\infty}\frac{2^r\epsilon^r}{r!}\frac{(-1)^s}{s!}\int_0^{\mu^2} y^{\left(\frac{r}{2}+s-\frac{n+13}{12}\right)}dy$$

on expanding e^{-y}.

Thus

$$(16)\quad K_n(0,\beta) = k(\mu^2) + \frac{1}{12}\epsilon^{\frac{n+1}{6}}\sum_{r=j}^{\infty}\frac{2^r\epsilon^r}{r!}\Gamma\left(\frac{r}{2}-\frac{n+1}{12}\right) - \frac{1}{6}\epsilon^{\frac{n+1}{6}}\sum_{r=j}^{\infty}\sum_{s=0}^{\infty}\frac{2^r\epsilon^r}{r!}\frac{(-1)^s}{s!}\frac{\mu^{\left(r+2s-\frac{n+1}{6}\right)}}{r+2s-\frac{n+1}{6}}$$

Hence $K_n(0,\beta)$ has been obtained as a series in μ. The results are given in the form

$J_n(0,\beta)$, $0 \leqslant n \leqslant 12$; $K_n(0,\beta)$, $-12 \leqslant n \leqslant -1$;

since this is a convenient form for the calculations done. Conversion from $J_n(0,\beta)$ to $K_n(0,\beta)$ and vice versa is quite simple. $I_n(0,\beta)$ can be obtained using (9).

$J_n(0,\beta)\ ;\ 0 \leq n \leq 12.$

Let $\epsilon^2 = 1/kT\ ;\ \mu = \epsilon\beta^{-6}\ ;\ p = n/12\ ;\ \gamma = $ Euler's Const.

$n = 0$

(17)
$$\epsilon^2 J_0(0,\beta) = -e^{-\phi(\beta)\epsilon^2}$$

$0 < n < 6$

(18a)
$$\epsilon J_n(\beta,\infty) = \beta^{n-6}\left\{\frac{2\epsilon}{1-2p} + \mu\frac{2\epsilon^2-1}{1-p} + \mu^2\frac{2\epsilon(2\epsilon^2-3)}{3-2p} + \mu^3\frac{1-4\epsilon^2+\frac{4}{3}\epsilon^4}{2-p} + \mu^4\frac{5\epsilon\left(1-\frac{4}{3}\epsilon^2+\frac{4}{15}\epsilon^4\right)}{5-2p} - \mu^5\frac{1-6\epsilon^2+4\epsilon^4-\frac{8}{15}\epsilon^6}{6-2p} + \cdots\cdots\right\}$$

(18b)
$$\epsilon^{2(1-p)}J_n(0,\infty) = \Gamma(1-p)\left\{-1 + p\sum_{s=1}^{\infty}\frac{2^{2s}\epsilon^{2s}}{(2s)!}F(s-1-p)\right\} + p\,\Gamma\!\left(\tfrac{1}{2}-p\right)\sum_{s=0}^{\infty}\frac{2^{2s+1}\epsilon^{2s+1}}{(2s+1)!}F\left(s-\tfrac{1}{2}-p\right)$$

where $F(s-1-p) = (s-1-p)(s-2-p)\cdots\cdots(1-p)\ ;\ F(-p) = 1.$
$F\left(s-\frac{1}{2}-p\right) = \left(s-\frac{1}{2}-p\right)\left(s-\frac{3}{2}-p\right)\cdots\cdots\left(\frac{1}{2}-p\right)\ ;\ F\left(-\frac{1}{2}-p\right) = 1.$

$n = 6$

(19)
$$\epsilon J_6(0,\beta) = -\sqrt{\pi} - \epsilon(\gamma+2) + \tfrac{1}{2}\sqrt{\pi}\sum_{s=1}^{\infty}\frac{2^{2s}\epsilon^{2s}}{(2s)!}F\left(s-\tfrac{3}{2}\right) + \sum_{s=1}^{\infty}\frac{2^{2s+1}\epsilon^{2s+1}(s-1)!}{(2s+1)!} - \left\{2\epsilon\log_e\mu + 2\mu(2\epsilon^2-1) + \mu^2\epsilon(2\epsilon^2-3) + \tfrac{1}{3}\mu^3\left(2-8\epsilon^2+\tfrac{8}{3}\epsilon^4\right) + 5\mu^4\epsilon\left(\tfrac{1}{4}-\tfrac{1}{3}\epsilon^2+\tfrac{1}{15}\epsilon^4\right) - \tfrac{1}{5}\mu^5\left(1-6\epsilon^2+4\epsilon^4-\tfrac{8}{15}\epsilon^6\right)\cdots\cdots\right\}$$

where $F\left(s-\frac{3}{2}\right) = \left(s-\frac{3}{2}\right)\left(s-\frac{5}{2}\right)\cdots\cdots\left(\frac{1}{2}\right)\ ;\ F\left(-\frac{1}{2}\right) = 1.$

$7 \leqslant n \leqslant 11$.

$$(20)\quad \epsilon^{2(1-p)} J_n(0,\beta) = \Gamma(1-p)\left\{-1 + p\sum_{s=1}^{\infty}\frac{2^{2s}\epsilon^{2s}}{(2s)!}F(s-1-p)\right\}$$

$$+\,\Gamma(\tfrac{3}{2}-p)\left\{\frac{-4p\epsilon}{2p-1} + p\sum_{s=1}^{\infty}\frac{2^{2s+1}\epsilon^{2s+1}}{(2s+1)!}F'(s-\tfrac{1}{2}-p)\right\}$$

$$+\,\mu^{1-2p}\left\{\frac{2\epsilon}{2p-1} + \mu\,\frac{1-2\epsilon^2}{1-p} + \mu^2\,\frac{2\epsilon(3-2\epsilon^2)}{3-2p}\right.$$

$$-\,\mu^3\,\frac{1-4\epsilon^2+\frac{4}{3}\epsilon^4}{2-p} - \mu^4\,\frac{\epsilon(5-\frac{20}{3}\epsilon^2+\frac{4}{3}\epsilon^4)}{(5-2p)}$$

$$+\,\mu^5\,\frac{\frac{1}{2}-3\epsilon^2+2\epsilon^4-\frac{4}{15}\epsilon^6}{3-p}$$

$$\left.+\,\frac{7\mu^6}{7-2p}\left(\frac{\epsilon}{3}-\frac{2\epsilon^3}{3}+\frac{4\epsilon^5}{15}-\frac{8\epsilon^7}{315}\right)\cdots\right\}$$

Here $F'(s-\frac{1}{2}-p) = (s-\frac{1}{2}-p)(s-\frac{3}{2}-p)\cdots(\frac{3}{2}-p)$; $F'(\frac{1}{2}-p) = 1$.

— — — — — — —

$n = 12$

$$(21)\quad J_{12}(0,\beta) = (1-2\epsilon^2)\gamma - 4\epsilon\sqrt{\pi} - 2\epsilon^2 + \sum_{s=2}^{\infty}\frac{2^{2s}\epsilon^{2s}(s-2)!}{(2s)!}$$

$$+\sqrt{\pi}\sum_{s=1}^{\infty}\frac{2^{2s+1}\epsilon^{2s+1}}{(2s+1)!}F(s-\tfrac{3}{2}) + 2(1-2\epsilon^2)\log_e\mu$$

$$+\,2\epsilon\mu^{-1} + 2\mu\epsilon(3-2\epsilon^2) + \mu^2(-1+4\epsilon^2-\tfrac{4}{3}\epsilon^4)$$

$$+\,\epsilon\mu^3(-\tfrac{5}{3}+\tfrac{20}{9}\epsilon^2-\tfrac{4}{9}\epsilon^4) + \mu^4(\tfrac{1}{4}-\tfrac{3}{2}\epsilon^2+\epsilon^4-\tfrac{2}{15}\epsilon^6)$$

$$+\,\epsilon\mu^5\left(\frac{7}{15}-\frac{14}{15}\epsilon^2+\frac{28}{75}\epsilon^4-\frac{8\epsilon^6}{225}\right) + \cdots .$$

— — — — — — —

$K_n(0,\beta)$

$-12 \leqslant n < -1$

$$(22a)\quad 12\,\epsilon^{-\left(\frac{n+1}{6}\right)} K_n(0,\infty) = \Gamma\left(-\frac{n+1}{12}\right)\sum_{s=0}^{\infty}\frac{2^{2s}\epsilon^{2s}}{(2s)!}F\left(s-\frac{n+13}{12}\right)$$

$$+\Gamma\left(-\frac{n-5}{12}\right)\sum_{s=0}^{\infty}\frac{2^{2s+1}\epsilon^{2s+1}}{(2s+1)!}F\left(s-\frac{n+7}{12}\right).$$

$$(22b)\quad \epsilon^{-\left(\frac{n+1}{6}\right)} K_n(\beta,\infty) = \mu^{-\left(\frac{n+1}{6}\right)}\Big\{\frac{-1}{n+1} + \mu\frac{2\epsilon}{5-n} + \mu^2\frac{2\epsilon^2-1}{11-n}$$

$$+\mu^3\,\frac{2\epsilon\left(\frac{2}{3}\epsilon^2-1\right)}{17-n}$$

$$+\mu^4\,\frac{\frac{2}{3}\epsilon^4-2\epsilon^2+\frac{1}{2}}{23-n}$$

$$+\mu^5\,\frac{\epsilon\left(\frac{4}{15}\epsilon^4-\frac{4}{3}\epsilon^2+1\right)}{29-n}+\cdots\Big\}$$

where $F\left(s-\frac{n+13}{12}\right) = \left(s-\frac{n+13}{12}\right)\left(s-\frac{n+13}{12}-1\right)\cdots\left(-\frac{n+1}{12}\right);\ F\left(-\frac{n+13}{12}\right)=1.$

$F\left(s-\frac{n+7}{12}\right) = \left(s-\frac{n+7}{12}\right)\left(s-\frac{n+7}{12}-1\right)\cdots\left(-\frac{n-5}{12}\right);\ F\left(-\frac{n+7}{12}\right)=1.$

— — — — — — — —

$n = -1$

$$(23)\quad 12\,K_{-1}(0,\beta) = -\gamma + \sum_{s=1}^{\infty}\frac{2^{2s}\epsilon^{2s}(s-1)!}{(2s)!} + \sqrt{\pi}\sum_{s=0}^{\infty}\frac{2^{2s+1}\epsilon^{2s+1}}{(2s+1)!}F\left(s-\tfrac{1}{2}\right)$$

$$-2\log_e\mu - \mu\Big\{4\epsilon + \mu(2\epsilon^2-1) + \mu^2\frac{4}{3}\epsilon\left(\frac{2}{3}\epsilon^2-1\right)$$

$$+\mu^3\left(\frac{1}{3}\epsilon^4-\epsilon^2+\frac{1}{4}\right)$$

$$+\mu^4\frac{2\epsilon}{5}\left(\frac{4}{15}\epsilon^4-\frac{4}{3}\epsilon^2+1\right)+\cdots\Big\}$$

where $F\left(s-\frac{1}{2}\right) = \left(s-\frac{1}{2}\right)\left(s-\frac{3}{2}\right)\cdots\left(\frac{1}{2}\right);\ F\left(-\frac{1}{2}\right) = 1.$

— — — — — — —

Appendix II

Table VI. Complete Solutions of (5.30)

(a) $f(r) = k^{r}_{0,1\cdot5} \sum_{i=0}^{3} \left\{ \sum_{t=1}^{3} s_t c_{ti} \right\} r^{i}$

$f(1{\cdot}250)$ is obtained from (5.30), in which the solutions for the $C_i = \sum_{t=1}^{3} s_t c_{ti}$ have been substituted, viz.

(b)

$$\mathcal{L}og_e(1+f(1{\cdot}250)) = \gamma(1{\cdot}250) + \sum_{i=0}^{3} A_i(1{\cdot}250)\left\{\sum_{t=1}^{3} s_t c_{ti}\right\} + \sum_{i=1}^{3}\sum_{j=1}^{3} s_i s_j \left\{ \underline{c}'_i \left[B'_{ij}(1{\cdot}250) \right] \underline{c}_j \right\}$$

				$f(r)$				
$\frac{n_1}{n_0}$	S_1	S_2	S_3	r = ·860	r = 1·000	r = 1·140	r = 1·250	r = 1·400
0·1	−0·106	+0·115	+0·013	0·164	0·084	0·005	−0·284	−0·137
0·125	−0·122	+0·110	+0·009	0·132	0·057	−0·018	−0·337	−0·155
0·167	−0·165	+0·125	+0·002	0·120	0·037	−0·047	−0·435	−0·210
0·200	−0·190	+0·128	−0·002	0·096	0·016	−0·070	−0·497	−0·241
0·250	−0·231	+0·132	−0·005	0·058	−0·025	−0·111	−0·574	−0·286
0·333	−0·295	+0·135	−0·010	−0·014	−0·094	−0·179	−0·667	−0·356
0·400	−0·334	+0·138	−0·013	−0·054	−0·133	−0·219	−0·731	−0·399
0·500	−0·414	+0·139	−0·013	−0·154	−0·229	−0·310	−0·787	−0·480
0·667	−0·505	+0·146	−0·018	−0·249	−0·323	−0·404	−0·864	−0·578
0·800	−0·573	+0·150	−0·019	−0·325	−0·397	−0·477	−0·902	−0·649
1·000	−0·674	+0·156	−0·019	−0·437	−0·509	−0·586	−0·930	−0·752

Table VII. The Vectors $\underline{c}_i \ (i = 1,2,3)$

t	c_{1t}	c_{2t}	c_{3t}
0	+1·522	+6·475	+5·359
1	−0·182	−3·804	−8·968
2	−0·084	−0·689	+0·025
3	−0·036	−0·065	+2·971

Table VIII. Linear Solutions of (6.10).

$S_1 =$	$\dfrac{-.939}{\frac{n_o}{n_1} - 1.455}$
$S_2 =$	$\dfrac{1.917\frac{n_o}{n_1} + 53.1}{(\frac{n_o}{n_1} + 9.72)^2 + 207}$
$S_3 =$	$\dfrac{1.701\frac{n_o}{n_1} - 11.1}{(\frac{n_o}{n_1} + 9.72)^2 + 207}$
$S_4 =$	$\dfrac{-3.360}{\frac{n_o}{n_1} + 2{,}854}$

i	χ_i
1	$-.939$
2	$+1.917$
3	$+1.701$
4	-3.360

Table IX Equation (6.3) and (6.4).

$T^{-1} =$

+ 75·397	− 175·071	+ 118·132	− 17·457
− 195·389	+ 482·194	− 339·874	+ 53·070
+ 167·234	− 433·673	+ 319·859	− 53·419
− 47·241	+ 127·551	− 98·116	+ 17·806

$AT^{-1} =$

− 4,738·748	+ 12,297·215	− 9,101·153	+ 1,545·881
− 2,188·597	+ 5,702·445	− 4,238·202	+ 726·939
− 1,999·223	+ 5,198·080	− 3,852·475	+ 655·583
− 105·044	+ 222·718	− 132·931	+ 17·321

Eigen-values of AT^{-1}	
λ_1	1·455
λ_2	−9·724
$\pm i\lambda_3$	±i 14·381
λ_4	−2,853·524

Eigen-Vectors of AT^{-1}

$\underline{u}_1$	($\underline{u}_2$	$\underline{u}_3$)	$\underline{u}_4$
+ 1·276,108	+ 2·653,976	− 0·449,478	+ 1·000,000
+ 1·215,786	+ 1·918,211	− 0·617,606	+ 0·463,184
+ 1·147,948	+ 1·147,750	− 0·435,122	+ 0·422,131
+ 1·000,000	− 0·378,823	+ 1·000,000	+ 0·020,202

Table X. Linear Terms; Equation (5.30).

r	$\gamma(r)$.
0·860	−0·236
1·000	−0·073
1·140	−1·035
1·250	−1·434
1·400.	−0·019

$A_j(r)$

r \ j	0	1	2	3
0·860	+3·196	+10·812	−5·493	+41·247
1·000	+2·585	+6·416	+0·592	+26·013
1·140	+1·965	+4·743	−2·279	+17·771
1·250	+0·682	+4·014	+8·902	+12·702
1·400	+2·064	+5·088	+6·219	+6·489

Table XI. Quadratic Terms of (5.30).

$$B'_{ij}(r) = \frac{1}{r}[C_{ij}] + 2[C'_{ij}] + r[C''_{ij}]$$

(The C's are Sym. Matrices)

$$[C_{ij}] = \begin{array}{|c|c|c|c|}\hline +0{\cdot}174{,}718 & +0{\cdot}187{,}863 & +0{\cdot}210{,}274 & +0{\cdot}246{,}529 \\ \hline & +0{\cdot}194{,}638 & +0{\cdot}210{,}265 & +0{\cdot}237{,}419 \\ \hline & & +0{\cdot}219{,}014 & +0{\cdot}237{,}168 \\ \hline & & & +0{\cdot}244{,}118 \\ \hline \end{array} \; 12\sqrt{2}\pi\frac{|\phi_0|}{kT}$$

$$[C'_{ij}] = \begin{array}{|c|c|c|c|}\hline -0{\cdot}150{,}496 & -0{\cdot}132{,}138 & -0{\cdot}114{,}862 & -0{\cdot}101{,}147 \\ \hline & -0{\cdot}099{,}587 & -0{\cdot}065{,}646 & -0{\cdot}031{,}136 \\ \hline & & -0{\cdot}012{,}238 & +0{\cdot}046{,}371 \\ \hline & & & +0{\cdot}134{,}456 \\ \hline \end{array} \; 12\sqrt{2}\pi\frac{|\phi_0|}{kT}$$

$$[C''_{ij}] = \begin{array}{|c|c|c|c|}\hline +0{\cdot}129{,}279 & +0{\cdot}110{,}645 & +0{\cdot}094{,}505 & +0{\cdot}079{,}178 \\ \hline & +0{\cdot}082{,}411 & +0{\cdot}053{,}953 & +0{\cdot}023{,}922 \\ \hline & & +0{\cdot}010{,}052 & -0{\cdot}038{,}229 \\ \hline & & & -0{\cdot}107{,}980 \\ \hline \end{array} \; 12\sqrt{2}\pi\frac{|\phi_0|}{kT}$$

Table XII.

Co-efficients of the Right hand side of (6.14)

Linear

r	1	S_1	S_2	S_3	$\lambda_4 S_4$
0·860	−0·236	+1·857	−19·334	+42·544	+1·000
1·000	−0·073	+1·769	−9·769	+35·592	+0·463
1·140	−1·035	+1·670	−4·904	+20·721	+0·422
1·250	−1·434	−0·898	−17·812	+5·617	−0·032
1·400	−0·019	+1·455	−10·697	−15·143	+0·020

Quadratic

r	S_1^2	S_2^2	S_3^2	$S_3 S_2$	$S_3 S_1$	$S_1 S_2$
0·860	−1·250	−17·669	−2·647	+17·908	+14·502	−23·767
1·000	−1·759	−14·875	−2·347	+15·888	+13·542	−22·498
1·140	−1·759	−11·761	−2·128	+14·188	+12·565	−20·035
1·250	−1·508	−9·157	−1·995	+13·009	+11·788	−17·513
1·400	−0·925	−5·455	−1·853	+11·554	+10·721	−13·507

Table XIII

Numerical Details

$\frac{\lvert\phi_0\rvert}{kT} = 1$	$k^{t}_{\alpha,\beta}\, e^{-\phi(t)/kT} = k^{t}_{\alpha,\beta} \sum_{i=0}^{5} a_i t^{i}$	
	i	a_i
$\alpha = 0{\cdot}860$	0	$-1,639{\cdot}468$
$\beta = 1{\cdot}500$	1	$+6,558{\cdot}257$
$r_1 = 0{\cdot}860$	2	$-10,391{\cdot}984$
r_2 1·000	3	$+8,175{\cdot}650$
r_3 1·140	4	$-3,197{\cdot}446$
r_4 1·400	5	$+497{\cdot}709$

Table XIV.

n	$\frac{1}{12}J_n(0,\infty)$	$\frac{1}{12}J_n(0,\beta)\ \{\beta=1\cdot5\}$
0	−0·083,333	−0·098,566
1	−0;026,652	−0·053,974
2	+0·045,563	−0·005,448
3	+0·149,558	+0·048,071
4	+0·337,271	+0·110,442
5	+0·859,560	+0·184,969
6	—	+0·276,545
7	—	+0·391,739

n	$K_n(0,\infty)$	$K_n(0,\beta)\ \{\beta=1\cdot5\}$
0		+1·134
−1		+1·000
−2		+0·908
−3	+1·071	+0·839
−4	+0·894	+0·790

Table XV.

$$\frac{1}{12}\, J_n(r+\alpha, r+\beta)$$

n \ r	0·860	1·000	1·140	1·250	1·400
0	0.0055,90	0·0033,89	0·0021,34	0·0015,15	0·0009,76
1	—	—	—	—	—
2	0.0209,1681	0·0146,7576	0·0105,6897	0·0082,9169	0·0060,7470
3	0·0409,2237	0·0308,4961	0·0237,4761	0·0195,7662	0·0152,7399
4	0·0807,0197	0·0653,0385	0·0536,9083	0·0464,6876	0·0385,9822
5	0·1604,5537	0·1392,3094	0·1221,5907	0·1109,3980	0·0980,4001
6	0·3216,8284	0·2990,0819	0·2797,2357	0·2664,0579	0·2503,1216
7	0·6503,3696	0·6468,4646	0·6446,5091	0·6434,8879	0·6424,0720
8	1·3256,6480	1·4094,9125	1·4951,8526	1·5633,8773	1·6572,2184
9	2·7245,9079	3·0934,5136	3·4899,2931	3·8203,1409	4·2970,8597
10	5·6447,44	6·8371,29	8·1966,46	9·3884,86	11·1984,17
11	11·7856,14	15·2148,78	19·3679,62	23·2004,46	29·3279,28
12	24·7926,61	34·0824,16	46·0346,73	57·6407,34	77·1784,47

$$\frac{1}{12}\, J_n(0, \beta+r)$$

n \ r	0·860	1·000	1·140	1·250	1·400
0	−0·084,302	−0·084,018	−0·083,827	−0·083,719	−0·083,614
1	—	—	—	—	—
2	+0·037,485	+0·039,153	+0·040,410	+0·041,188	+0·042,026
3	+0·124,198	+0·128,196	+0·131,424	+0·133,518	+0·135,883
4	+0·247,369	+0·257,189	+0·265,478	+0·271,117.	+0·277,793