ASPECTS OF THE STATISTICAL MECHANICS OF GASES

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by

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Preface

With the exception of chapter 1, which is a re-statement of the basic equations of the subject, this thesis describes original work carried out by the candidate at The Australian National University. Where it has been appropriate to relate the candidate's work to that of others, proper acknowledgment has been made in the form of specific references.

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Acknowledgments

I wish to thank my supervisor, Professor K.J. Le Couteur, for his advice and interest concerning the problems considered in this thesis and continual encouragement during the period of my Research Scholarship.

I also wish to express my appreciation of the interest and goodwill of the departmental secretaries, Miss Hope Dodds and Mrs. Louise Nicholson, and in particular to thank the latter for typing this thesis.

The Australian National University's I.B.M. 1620 computer was indispensable for calculations, and I gratefully acknowledge the assistance of the operator, Miss Margaret Campbell.

I am indebted to The Australian National University for the award of a Research Scholarship and for providing excellent facilities to enable me to carry out this work.

Summary

The 'raison d'être' of this thesis may fairly be described as the paucity of useful exact calculations of the statistical mechanical properties of a gas of particles with known interaction between pairs. Formally this problem was solved by J.W. Gibbs in 1902 in terms of the canonical and grand-canonical partition functions, but it was not till 1936 that L. Tonks obtained explicitly the exact equation of state of a one-dimensional gas of non-interacting hard rods. Since then a number of calculations of the thermodynamic properties and distribution functions of classical one-dimensional continuum gases with simple interaction potential have been performed, using either combinatorial analysis or the techniques of statistical theory (Lenard, 1961; Edwards and Lenard, 1962; Prager, 1962; Kac, 1959).

Following a re-statement in chapter 1 of the relevant results of Gibbs, it is shown in chapter 2 of this thesis that the statistical mechanical properties of any classical one-dimensional gas may be expressed in terms of the eigenvalues of a functional operator and the corresponding matrix elements of a related operator. This result is derived by the simple device of differentiating the canonical partition function of the gas with respect to the 'volume' (i.e. the length of the line on which the particles are confined).

Although purely formal, this result has three significant corollaries : firstly, the 'ring approximation', normally derived by the rather ad hoc procedure of summing those terms in the virial expansion which correspond to potential bond diagrams of ring type (Mayer, 1950), can be obtained by a variational approximation; secondly, the distribution functions and their derivatives with respect to the mean particle density satisfy a simple relation; and finally, when the interaction potential satisfies a homogeneous linear differential equation of order p (say), explicit, exact results may be obtained in terms of an eigenvalue equation involving at most p variables.

The last corollary ensures that the method may be used to obtain the properties of the one-dimensional plasma. This gas is considered in chapter 3 and explicit exact results obtained for both a system of equal and opposite charges and one of negative charges moving in a uniform neutralizing background of positive charge.

In chapter 4 it is shown that the method of differentiating the canonical partition function is also capable of yielding useful exact results when the interaction potential consists of a repulsive hard core together with an interaction satisfying a homogeneous linear differential equation of finite order. It follows that all the exact results previously obtained for one-dimensional continuum gases with particular interactions may be derived by this technique.

It is also shown in this chapter that the formal results of chapter 2 are applicable to the simple Tonk's gas of hard rods, even though the potential function appears to violate the differentiability condition originally imposed in the general derivation. It is therefore reasonable to suppose that the results are valid for any 'physical' potential.

In chapter 5 an attempt is made to consider gases of higher dimensionality by replacing the continuum by a lattice and transforming the grand-canonical partition function by a method used by S.F. Edwards (1959). It is found that this technique is particularly appropriate when the interaction potential satisfies a decaying wave equation (the Coulomb potential is thereby included as a special case), for then the problem becomes mathematically equivalent to that of calculating the canonical partition function of a system with nearest-neighbour interaction. In one dimension such a problem may be solved exactly, but in two dimensions it reduces to one identical with that of calculating the lowest energy level of a one-dimensional quantum mechanical system of particles with Hook's law attraction between first and second, second and third, third and fourth, etc., and with an applied external potential. Although this problem remains unsolved, it appears to be the obvious starting point for any possible further progress towards the exact calculation of the thermodynamic properties of two- or higher-dimensional gases, in particular plasmas.

The form of the relation derived in chapter 2 between the distribution functions of a one-dimensional gas and their derivatives with respect to density suggests that it is applicable in any number of dimensions. In chapter 6 it is shown that this is in fact the case and new functions are defined which satisfy an even simpler relation. As the two-particle function of this set is the Ornstein-Zernike direct correlation function, it seems natural to term them the direct correlation functions.

In view of the attractiveness of being able to predict statistical mechanical properties at one density in terms of those at an adjacent density, a closure of the relations by means of a superposition approximation is considered. The resulting equation for the two-particle direct correlation function is particularly straightforward to handle numerically.

Publications

Some of the material of this thesis is contained in four published papers written by the candidate. These are:

'Statistical Mechanics of a one-dimensional Coulomb system with a uniform charge background',
Proc. Camb. Phil. Soc. 59, 779 (1963)

'Many-Body Functions of a One-Dimensional Gas',
Phys. Fluids, 7, 38 (1964)

'On the equilibrium properties of a two-dimensional system with a repulsive radial interaction',
Physics Letters, 8, 255 (1964)

'Direct Correlation Functions and their Derivatives with Respect to Particle Density',
(to be published in volume 41 of the Journal of Chemical Physics).

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Chapter 1

THE BASIC EQUATIONS OF STATISTICAL MECHANICS

1. The thermodynamic properties in terms of the canonical partition function

The name 'statistical mechanics' was coined by Willard Gibbs in 1901 to describe that branch of physics which is concerned with the average or most probable behaviour of a mechanical system (c.f. page 1 of ter Haar, 1955). In the cases where statistical mechanics is appropriate it is usually not only impossible to determine exactly the detailed behaviour of the system, but, more significantly, such knowledge would be quite redundant. Consider for instance the gas molecules in a room. For a reasonably sized room there would be of the order of 10^{27} such molecules. Clearly a specification of the exact location and velocity of each molecule would be an embarrassment to any experimental investigator, who desires only to know a few average properties of the gas as a whole, such as its temperature, density and pressure. What is required is not a detailed investigation of the equations of motion, but some method of averaging over all possible states of the system.

The first steps in this direction were taken by Clausius, Maxwell, Boltzmann and others (c.f. page viii of Gibbs, 1902), who considered the most likely state of a system consisting of a large number of elements, each of which could be assigned its own individual energy (the microcanonical ensemble). While their results were extremely useful, the method of obtaining them is open to two very serious criticisms. Firstly, it is sometimes desirable to apply statistical mechanics to a system of only a few elements, and secondly most physical systems cannot be divided into elements which have independent energies; rather they interact one with another and it is only meaningful to consider the energy of the complete system.

These difficulties were overcome by Gibbs (1902), who suggested considering not an individual physical system, but a large collection or 'ensemble' of replicas of the system, all identical in so far as their physical composition and external constraints are the same, but differing from one another in the particular configurations or states that they assume. For the purposes of the present discussion it is convenient to suppose these states to be discrete, a concept which is easily understood in terms of the quantum mechanics, but appears inapplicable to a classical formulation. However, this difficulty may be overcome by regarding the phase space of the system as divided into infinitesimal sections of equal extension, each such section being regarded as a state.

Gibbs obtained his results by assuming the probable number of systems of the ensemble occupying a certain state to be inversely proportional to the exponential of the energy of that state, multiplied by a constant factor, called the modulus. This distribution of systems Gibbs called 'canonical', and justified his use of it by the physically meaningful results obtained. A slightly more fundamental procedure which leads to the same equations is to suppose an individual system is equally likely to assume any of the states available to it and apply an elementary probability argument to the total ensemble.

Adopting this latter procedure, the probability of an ensemble of s systems being arranged so that s_j are in the j th state is

$$Y = \frac{s!}{\prod_j s_j!} \quad . \tag{1.1}$$

Clearly the numbers s_j must satisfy the condition

$$\sum_j s_j = s \quad , \tag{1.2}$$

and in addition, if the total energy E_{total} of the ensemble is known,

$$\sum_j s_j E_j = E_{total} \quad , \tag{1.3}$$

where E_j is the energy of the system when it is in the j th state.

It is now necessary to invoke a theorem which will not be proved here, namely that the total number of arrangements (the sum of all Y) is very nearly exhausted by those values of s_j which lie close to the values which maximise Y (c.f. page 6 of Schrodinger, 1957). In the limit of s infinitely large this is rigorously true, so as this is precisely the limit implicit in the present discussion the theorem may be adopted without the reservations necessary in the parallel argument for the microcanonical ensemble.

The values of s_j which maximise Y, or more conveniently $\log Y$, subject to the restrictions (1.2) and (1.3), are readily determined by the method of Langrange's undetermined multipliers. Using this technique it is required to find the unconditional maximum of

$$\log Y - \alpha \sum_j s_j - \beta \sum_j s_j E_j \quad . \tag{1.4}$$

In the limit of s large it may be supposed that all the s_j are large, so that the factorials occurring in the definition (1.1) of Y may be approximated by Stirling's formula:

$$\log n! \sim n (\log n - 1) \quad . \tag{1.5}$$

Accordingly, if (1.4) is maximized with respect to each s_j, it is found that

$$\log s_j + \alpha + \beta E_j = 0 , \tag{1.6}$$

or

$$s_j = \exp(-\alpha - \beta E_j) . \tag{1.7}$$

α may be eliminated by using (1.2), giving

$$s_j = s Z^{-1} \exp(-\beta E_j) , \tag{1.8}$$

where

$$Z = \sum_j \exp(-\beta E_j) . \tag{1.9}$$

The mean system energy U may be determined in terms of β and the energy levels E_j from (1.3) and (1.8), giving

$$U = Z^{-1} \sum_j E_j \exp(-\beta E_j) . \tag{1.10}$$

In the light of the above procedure the constant β should be regarded as defined in terms of U by (1.10). However, β turns out to be a fundamental quantity in its own right, being proportional to the inverse temperature, and it is more convenient to regard (1.10) as defining U in terms of β.

The quantity Z defined by (1.9) is therefore to be viewed as a function of β and the system energy levels E_j. This is the canonical partition function introduced by Gibbs, from which the thermodynamic properties of the system may be derived. In particular, (1.10) may be written:

$$U = -\frac{\partial}{\partial\beta}\log Z \quad . \tag{1.11}$$

To identify β with the inverse temperature and derive the other thermodynamic quantities, it is necessary to consider the effect of external work. Suppose the energy levels of every system of the ensemble to be changed by some external agency from E_j to $E_j + dE_j$. Then the average work done on a system is

$$W = s^{-1} \sum_j s_j \, dE_j \quad . \tag{1.12}$$

If the quantity F is defined by

$$F = \log \sum_j \exp(-\beta E_j) \quad , \tag{1.13}$$

then the resulting increase in F is

$$dF = \frac{\partial F}{\partial\beta} d\beta + \sum_j \frac{\partial F}{\partial E_j} dE_j \quad , \tag{1.14}$$

which from (1.8) and (1.11) is

$$dF = -U\, d\beta - \beta\, s^{-1} \sum_j s_j \, dE_j \tag{1.15}$$

($d\beta$ being the corresponding increase in β).

In view of (1.12), (1.15) may with a slight re-arrangement be written:

$$d(F + \beta U) = \beta\,(dU - W) \quad , \tag{1.16}$$

but as dU is the mean increase in energy of a system, the quantity (dU - W) occurring on the right-hand side of this relation must be the amount dQ of heat added, so that

$$d(F + \beta U) = \beta\,dQ \quad . \tag{1.17}$$

It is now apparent that β is an integrating factor of dQ, which from the second law of thermodynamics can only mean that

$$\beta = 1/\varkappa T \quad , \tag{1.18}$$

where T is the absolute temperature and $\varkappa$ is a constant, namely Boltzmann's constant (c.f. page 80 of ter Haar, 1955, and Pippard, 1957).

(1.16) may now be written:

$$dU = T\,dS + W \quad , \tag{1.19}$$

where

$$S = \varkappa F + U/T \quad , \tag{1.20}$$

and this is precisely the second law of thermodynamics, with U the internal energy and S the entropy (to within additive constants) of the system.

In the case of a gas the most usual form of work done on the system is that of increasing its volume. If increasing it by an amount dV requires the amount W of work, the pressure P of the gas is defined by

$$W = - P\, dV \quad . \tag{1.21}$$

Comparing this expression with (1.12) and using (1.8), it is readily deduced that

$$\begin{aligned} P &= - Z^{-1} \sum_j \exp(-\beta E_j) \frac{\partial}{\partial V} E_j \quad , \\ &= \beta^{-1} \frac{\partial}{\partial V} \log Z \quad . \end{aligned} \tag{1.22}$$

Summarising, if Z is defined by

$$Z = \sum_j \exp(-E_j/\varkappa T) \quad , \tag{1.23}$$

or in classical mechanics by

$$Z = \int \cdots \int d\underline{p}\, d\underline{x} \quad \exp\left\{ -E(\underline{p},\underline{x})/ \varkappa T \right\} \quad , \tag{1.24}$$

the integrations in (1.24) being over all available coordinate $(\underline{x})$ and momentum $(\underline{p})$ space of the system, then the internal energy U and the pressure P are determined in terms of the volume V and the temperature T by

$$U = \varkappa T^2 \frac{\partial}{\partial T} \log Z \tag{1.25}$$

and

$$P = \varkappa T \frac{\partial}{\partial V} \log Z \quad . \tag{1.26}$$

2. Application to an imperfect gas

2.1 The thermodynamic variables

With the exception of the introduction of the concept of pressure, the above discussion is perfectly general and applies to any isolated system, the detailed internal structure not having been considered at all. It is now convenient to specialize the results to the case when the system consists of a large number N of identical particles of mass m, confined within a volume V and with an interaction potential $\upsilon(x,y)$ acting between any pair of particles at points x and y (in dimensions higher than one x and y are to be interpreted as vectors). The discussion will be confined to particles which have no internal degrees of freedom, in which case for any physical gas $\upsilon(x,y)$ must be a function only of the radial distance between x and y, so that it is possible to write

$$\begin{aligned}\upsilon(x,y) &= \upsilon(x-y) \\ &= \upsilon(y-x) \quad .\end{aligned} \tag{1.27}$$

Clearly the functions υ on either side of (1.27) are mathematically different, but there is no possibility of confusion and the two forms will be used interchangeably.

Writing x_j for the position coordinate or vector of the j th particle and p_j for its momentum (also a vector in a two- or three-dimensional system), the total energy $E(\underline{p},\underline{x})$ of the system may be divided into two parts, the kinetic and the potential, i.e.

$$E(\underline{p},\underline{x}) = E_{kin} + E_{pot} \quad , \tag{1.28}$$

where

$$E_{kin} = \sum_{j=1}^{N} p_j^2 / 2m \tag{1.29}$$

and

$$E_{pot} = \sum_{1 \leqslant j<k \leqslant N} \upsilon(x_j - x_k) \quad . \tag{1.30}$$

Throughout this thesis classical mechanics will be employed. The reasons for this are two-fold, firstly in the case of most gases quantum mechanical effects could only be observed at very great extremes of temperature and pressure, phase transitions and other interesting phenomena lying well inside the domain of validity of the classical theory, and secondly the mathematical treatment of the classical theory is quite complicated enough without introducing the even more difficult equations of the quantum theory.

There is one very significant exception to the first statement, namely that of a plasma, or gas of positively and negatively charged particles interacting via the Coulomb potential. In two or three dimensions this potential diverges at short distances, causing the classical partition function to diverge (though whether the same is true of the thermodynamic variables is not quite clear). This divergence does not occur in the quantum theory.

Adopting the classical formulation (1.24), the canonical partition function of the system is

$$Z_N = \int\!\cdot\!\int dp_1\ldots dp_N \, dx_1\ldots dx_N \exp\left\{-(E_{kin} + E_{pot}) / \varkappa T\right\} , \qquad (1.31)$$

where the momentum integrations range over all values and the coordinate integrations over the volume V. The suffix N has been attached to Z to indicate the number of particles.

Substituting the explicit expression (1.29) for E_{kin}, the momentum integrations may be performed to give:

$$Z_N = (2\pi m \varkappa T)^{ND/2} \, Q_N , \qquad (1.32)$$

where Q_N is the configuration integral defined by

$$Q_N = \int\!\cdot\!\int_V dx_1\ldots dx_N \exp(-E_{pot}/\varkappa T) \qquad (1.33)$$

and D is the dimensionality of the system.

As it is well-known that the properties of a gas of given density are independent of its volume, so long as this is large enough that surface effects may be ignored, for a 'physical' potential function υ, Q_N must satisfy certain limit theorems. In particular it must be true that

$$\eta(\rho) = \lim N^{-1} \log(V^{-N} Q_N) \tag{1.34}$$

exists when N and V both tend to infinity, the particle density

$$\rho = N / V \tag{1.35}$$

being kept fixed.

In addition to its explicit dependence on ρ, $\eta(\rho)$ is also a function of the temperature T. Whenever the derivative of $\eta(\rho)$ with respect to either of these occurs it is to be assumed that the other variable is kept constant while performing the differentiation. Unless otherwise indicated the same is true of the derivatives with respect to ρ and T of any other quantity.

In order that the limit (1.34) should exist some care is necessary in choosing the potential function υ. For instance, adding a constant to υ, while it does not change the equations of motion, introduces a multiplicative factor of type $\exp(-N^2)$ in Q_N, which would in general lead to a violation of the limit condition. For potentials which tend to zero sufficiently fast with increasing particle distance (1.34) is certainly satisfied, but long-range potentials, in particular the Coulomb potential, must be handled with some care if physically meaningful results are to be obtained.

The dependence of $\eta(\rho)$ on ρ and T completely determines the thermodynamic properties of the system. The pressure P and internal energy U may be shown from (1.25), (1.26), (1.32) and (1.34) to be given by:

$$P / \varkappa T = \rho - \rho^2 \frac{\partial}{\partial \rho} \eta(\rho) \tag{1.36}$$

and

$$U / N\varkappa T = D/2 + T \frac{\partial}{\partial T} \eta(\rho) \quad . \tag{1.37}$$

Two other thermodynamic variables will be used later and are conveniently defined here, namely the concentration activity coefficient (Salpeter, 1958)

$$\gamma = V \, Q_{N-1} / Q_N \tag{1.38}$$

(where Q_{N-1} and Q_N both refer to the same volume V and it is to be supposed that N and V are large, but ρ, given by (1.35), is finite) and the quantity μ which is related to the isothermal compressibility and is defined by

$$\mu^{-1} = \frac{\partial}{\partial \rho} P/\varkappa T \quad . \tag{1.39}$$

Using (1.34) and (1.36), γ and μ may be determined in terms of $\eta(\rho)$. It is found that

$$\log \gamma = - \eta(\rho) - \rho \, \eta'(\rho) \tag{1.40}$$

and

$$\mu^{-1} = 1 - 2\rho \, \eta'(\rho) - \rho^2 \, \eta''(\rho) \tag{1.41}$$

(the primes on $\eta(\rho)$ denoting differentiation with respect to ρ, T being kept constant).

2.2 The distribution functions

In addition to the thermodynamic variables, it is frequently convenient to consider the functions which determine the probability that a particle is contained in each of the j volume elements $dx_1,\ldots,dx_j$ situated at the points $x_1,\ldots,x_j$. If this probability is

$$n(x_1,\ldots,x_j)\, dx_1\ldots dx_j \quad ,$$

then the j-particle distribution function $n(x_1,\ldots,x_j)$ is readily seen to be

$$n(x_1,\ldots,x_j) = \frac{N!}{(N-j)!\,Q_N} \int\ldots\int_V dx_{j+1}\ldots dx_N \exp(-E_{pot}/\kappa T) \quad , \qquad (1.42)$$

where the right-hand side is evaluated in the limit of N and V large, but ρ, given by (1.35), fixed.

These functions may be shown to have certain properties. In particular they are symmetric, invariant with respect to equal translation of all variables, and satisfy the relation

$$n(x_1,\ldots,x_j) \longrightarrow \rho\, n(x_1,\ldots,x_{j-1}) \qquad (1.43)$$

when x_j becomes far removed from $x_1,\ldots,x_{j-1}$. In addition, if (1.42) is differentiated with respect to x_1, a recurrence relation between the distribution functions may be derived (c.f. page 70 of H.S. Green, 1952), namely

$$\varkappa T \frac{\partial}{\partial x_1} n(x_1,..,x_j) = -\sum_{k=2}^{j} \upsilon'(x_1-x_k)\, n(x_1,..,x_j) - \int_{-\infty}^{\infty} dx_{j+1}\, \upsilon'(x_1-x_{j+1})\, n(x_1,..,x_{j+1}) \quad , \tag{1.44}$$

the primes on the function υ denoting its derivative. In dimensions higher than one (1.44) is a vector equation and the derivatives should be replaced by gradient operators.

The thermodynamic variables are of course completely specified by a knowledge of the two-particle distribution function. As this is a function only of the distance between the two particles, it is possible to define a function $g(x)$ by

$$g(x_1-x_2) = \rho^{-2}\, n(x_1,x_2) \quad . \tag{1.45}$$

This function has the advantage that it exhibits the translational invariance explicitly and is normalized so as to tend to unity at large particle separations (in the absence of interaction between the particles $g(x)$ is equal to unity everywhere).

To obtain the internal energy U and pressure P of the gas in terms of the function $g(x)$ it is necessary to consider the effects of small variations in the temperature and volume on the configuration integral Q_N defined by (1.30) and (1.33) and then to use the equations (1.36) and (1.37), together with the definitions (1.42) and

(1.45) of $g(x)$. Applying this procedure it is readily found that

$$U / N\varkappa T = D/2 + \frac{\rho}{2\varkappa T} \int_{-\infty}^{\infty} dx \ \upsilon(x) \ g(x) \tag{1.46}$$

and

$$P / \rho\varkappa T = 1 - \frac{\rho}{2\varkappa TD} \int_{-\infty}^{\infty} dx \ \{x \cdot \nabla \ \upsilon(x)\} g(x) \tag{1.47}$$

(c.f. page 53 of H.S. Green, 1952).

2.3 The grand-canonical partition function

Instead of considering the limiting behaviour of the canonical partition function Z it is sometimes convenient to define a grand-canonical partition function Z^* (otherwise called the grand-partition function) by

$$Z^* = \sum_{N=0}^{\infty} \frac{w^N}{N!} Q_N \quad , \tag{1.48}$$

where Q_N is the N-particle configuration integral defined by (1.33) and Q_o is taken to be unity, and to consider the asymptotic behaviour of Z^* in the limit of V infinitely large. It should be noted that the definition (1.48) differs slightly from the normal one (c.f. page 274 of Rushbrooke, 1949) in that Q_N rather than Z_N occurs as the coefficient of $w^N/N!$. The effect of this is merely to include a factor

$$(2\pi m\varkappa T)^{D/2}$$

in the variable w.

As N is now a dummy suffix it is no longer reasonable to regard ρ as an independent variable. The appropriate variables for this formulation are the temperature T and the quantity w.

The grand-canonical partition function was originally obtained by Gibbs (1902) when he considered an ensemble of systems, each containing an unspecified number of particles. However, the thermodynamic properties may be derived from Z^* by using the known limiting behaviour (1.34) of Q_N. In some ways this is a retrograde step, but the technique falls naturally into the order of this exposition.

Retaining only the most significant terms when N and V are large, it follows from (1.34) that

$$Q_N = V^N \exp N\,\eta(N/V) \quad . \tag{1.49}$$

It is now possible to prove that in the limit of V infinitely large the summation (1.48) is dominated by its maximum term, i.e.

$$Z^* \sim \frac{w^{N_o}}{N_o!} Q_{N_o} \quad , \tag{1.50}$$

where N_o is the value of N which maximizes

$$\frac{w^N}{N!} Q_N \quad .$$

Using Stirling's formula (1.5) for the factorial and differentiating logarithmically with respect to N, it follows that N_o is given by

$$\log w - \log(N_o/V) + \eta(N_o/V) + \frac{N_o}{V}\,\eta'(N_o/V) = 0 \tag{1.51}$$

(for the moment the temperature T is to be regarded as constant).

(1.51) is exact in the limit of V infinitely large, when it determines the limiting value of N_o/V. This value may very naturally be identified with the density, i.e.

$$\rho = N_o/V \quad . \tag{1.52}$$

Taking the logarithm of both sides of (1.50) and using (1.49) and (1.51), the asymptotic behaviour of Z^* is given by

$$\log Z^* \sim V\rho\left[1 - \rho\frac{\partial}{\partial\rho}\eta(\rho)\right] \quad . \tag{1.53}$$

Accordingly,

$$\lambda = \lim_{V\to\infty} V^{-1}\log Z^* \tag{1.54}$$

exists and satisfies

$$\lambda = \rho - \rho^2\frac{\partial}{\partial\rho}\eta(\rho) \quad , \tag{1.55}$$

so that from (1.36) λ has a very direct thermodynamic significance, namely

$$\lambda = P/\varkappa T \quad . \tag{1.56}$$

Also, eliminating the derivative of $\eta(\rho)$ between (1.51) and (1.55) and differentiating the resulting equation with respect to w, it is found that

$$\rho = w \frac{\partial}{\partial w} \lambda \quad . \tag{1.57}$$

If the dependence of λ on w and T is known, the equations (1.56) and (1.57) together give the equation of state of the gas. In addition the internal energy U may be obtained by considering the effect of varying T, keeping ρ fixed, and using the relation (1.37). This procedure yields:

$$U / N\varkappa T = D/2 + T \rho^{-1} \frac{\partial}{\partial T} \lambda \quad , \tag{1.58}$$

where the differentiation of λ with respect to T is to be performed at a constant value of w.

The quantity w has not as yet been given any thermodynamic significance, but from (1.51) it may be written

$$w = \rho \exp\left\{- \eta(\rho) - \rho \frac{\partial}{\partial \rho} \eta(\rho)\right\} \quad , \tag{1.59}$$

so that from the definition (1.40) of the concentration activity coefficient γ,

$$w = \rho \gamma \quad . \tag{1.60}$$

w may now be identified with the fugacity of the gas (Salpeter, 1958).

A useful relation between w and μ may be established at this stage, for differentiating (1.59) logarithmically with respect to ρ, keeping T constant, it is found that

$$\rho \frac{\partial}{\partial \rho} \log w = 1 - 2 \rho \eta'(\rho) - \rho^2 \eta''(\rho) \quad , \tag{1.61}$$

which from (1.41) is precisely the reciprocal of μ, so that

$$\mu \rho \frac{\partial}{\partial \rho} \log w = 1 \quad . \tag{1.62}$$

Just as it is possible to define distribution functions in the canonical formalism, it is possible to do so in the grand-canonical. If the grand-canonical distribution functions are defined to be

$$n^*(x_1, \ldots, x_j) = \frac{1}{Z^*} \sum_{N=j}^{\infty} \frac{w^N}{(N-j)!} \int_V \!\!\cdot\!\cdot \!\int dx_{j+1} \cdot\cdot dx_N \exp(-E_{pot}/\varkappa T) \quad , \tag{1.63}$$

where the right-hand side is to be evaluated in the limit of V infinitely large, it follows in analogy with the above considerations that the summation is dominated by the maximum term. This term is given by (1.51), so that it is readily seen that the grand-canonical and canonical distribution functions are identical, provided w and ρ correspond to the same thermodynamic state of the gas.

3. Discussion of results

The object of this chapter has been to state as systemically as possible the basic equations of statistical mechanics and to present a notation that can be used in the following chapters without continual re-definition. Naturally many interesting concepts and theorems such as irreversibility, Boltzmann's H-theorem, and a detailed discussion of the micro-canonical ensemble have had to be omitted as not being directly relevant to the subject matter of this thesis.

One possible criticism that may be made of the present approach is that it appears to consider a gas of one species only. However, all the general results obtained may be readily extended to the case of a gas containing more than one species of particle (the obvious example in the present context is the plasma, which must contain both ions and electrons), while to do so explicitly in every equation would result in a considerable complication of notation.

Chapter 2

A MATRIX FORMULATION OF THE STATISTICAL MECHANICS OF A ONE-DIMENSIONAL GAS

1. Introduction

Although the mathematical foundations for the study of the equilibrium properties of a statistical mechanical system were laid in 1901 (Gibbs, 1902), it was not till 1936 that Tonks (1936) obtained the exact solution of the equations for a gas of one-dimensional hard rods. Since then a number of exact solutions of one-dimensional systems with particular interaction have been obtained (Lenard, 1961; Edwards and Lenard, 1962; Prager, 1962; Kac, 1959; Baker, 1961; Baur and Nosanow, 1962). The methods used to obtain these solutions vary with the particular interaction under consideration, but in every case the thermodynamic properties are found to be given by the behaviour of the greatest eigenvalue of an operator and the distribution functions to be the corresponding matrix elements of related operators. In this chapter a formalism is set up which exhibits these properties explicitly when the system under consideration is a one-dimensional gas of particles with arbitrary two-particle interaction. This formalism is particularly appropriate when the interaction potential function satisfies a homogeneous linear differential equation of order p (say) with constant coefficients over the domain $(0, \infty)$, as the operator equations then reduce to difference-differential equations involving at most p variables. It is therefore possible to derive exact solutions for a decaying exponential potential or, so long as care is taken to avoid the introduction of redundant variables, the one-dimensional Coulomb potential.

The underlying principle used to derive the results is to note a simple fact which appears to be much neglected, namely that the partition function is a differentiable function of the volume of the system. In one dimension differentiation with respect to the 'volume', i.e. the length of the line on which the particles are confined, may be interpreted as fixing a particle at one boundary; so that if an arbitrary external potential is introduced, acting on the particles and centred on this boundary, a recurrence relation may be obtained between the partition functions. Such a relation leads immediately to an equation for the grand-partition function.

For simplicity a system containing only one species of particle is considered in the derivation, but the extension to a system of two or more species is quite straightforward and the appropriate generalisation of the results is stated in section 8.

2. Derivation of a recurrence relation between configuration integrals in terms of functional operators J and K.

Consider a gas of N identical particles on the line segment between $x=0$ and $x=A$, interacting one with another by a force of potential $\upsilon(x)$. Then the total potential energy is

$$E = \sum_{j<k} \upsilon(x_j - x_k) \quad , \tag{2.1}$$

where $x_1, \ldots, x_N$ are the position coordinates of the particles and the summations over j and k range from 1 to N.

E is of course identical with the total potential energy E_{pot} introduced in chapter 1. The suffix is dropped as the contribution to the partition function from the kinetic energy terms is known from section 2.1 of chapter 1 to be trivial, so that the interest in this and subsequent chapters is focussed on the configuration integral, which is the contribution from the potential energy terms.

Putting

$$u(x) = \upsilon(x) / \varkappa T \quad , \tag{2.2}$$

$u(x)$ must be an even function and the discussion will be confined to potentials such that $u(x)$ has continuous derivatives of all orders in the interval $(0, \infty)$. However, it seems that the results derived can be applied when this condition is violated, for in chapter 4 it will be shown that they are true when the system under consideration is the one-dimensional gas of hard rods.

Derivatives at the origin are to be regarded as right-derivatives, so that potentials which are regular functions of mod(x) are permissible.

To obtain the distribution functions it is necessary to suppose that some of the particles, say those at $x_1, \ldots, x_r$, are fixed, while the remainder are free to occupy any position between 0 and A. As A is here regarded as a variable with range $[0, \infty)$ it is therefore necessary to consider the possibility of it being less than some or all of the fixed particle coordinates, even though the r-particle distribution function will of course still be evaluated when A is much greater than any of them.

If

$$x_1 \geqslant x_2 \geqslant \cdots \geqslant x_r \geqslant 0 \tag{2.3}$$

and A lies in the interval

$$x_q \geqslant A \geqslant x_{q+1} \quad , \tag{2.4}$$

it is convenient to define a modified potential energy

$$E' = \sum_{j<k} u(x_j - x_k) + \sum_j G(A - x_j) \quad , \tag{2.5}$$

where the summations <u>are no longer over all particles</u>, but only over those lying between 0 and A. Thus j and k range from q+1 to N. This restriction is extremely important, for it ensures that the arbitrary function G(x) that has been introduced need only be defined over the domain $[0,\infty)$.

It is now possible to define the modified configuration integral

$$Q_{N,r} = \frac{1}{(N-r)!} \int_0^A \!\!\cdot\!\! \int dx_{r+1} \cdot\cdot dx_N \exp(-E') \quad . \qquad (2.6)$$

When G(x) is identically zero $Q_{N,o}$ is equal to the configuration integral Q_N defined by (1.33), divided by N!. It turns out that it is frequently convenient to consider $Q_N/N!$, rather than Q_N itself, and the name 'configuration integral' will be applied to either of these quantities, it being clear from the equations which is meant.

Also, when G(x) is identically zero and A is greater than all of the fixed particle coordinates, the r-particle distribution function defined by (1.42) can be seen to be

$$n(x_1,\ldots,x_r) = Q_{N,r} / Q_{N,o} \quad . \qquad (2.7)$$

$Q_{N,r}$ is to be regarded as a function of A and a functional of G(x), so that its functional derivative with respect to G(x) may be formed. If f is any functional of G(x) and h(x) is an arbitrary function, the notation

$$\frac{\delta}{\delta h}$$

will be used to represent the linear operator which acting on f gives the functional derivative

$$\lim_{\epsilon \to 0} \epsilon^{-1} \left[f\{G(x) + \epsilon h(x)\} - f\{G(x)\}\right] \quad . \tag{2.8}$$

On inspecting (2.5) and (2.6) it is apparent that differentiation of $Q_{N,r}$ gives rise to two terms, one corresponding to differentiating the limits of integration and the other to differentiating the integrand. The first of these is equivalent to multiplying by N-r and setting x_N equal to A. From (2.5), E' is then equal to

$$\sum_{j<k} u(x_j - x_k) + \sum_j \{G(A-x_j) + u(A-x_j)\} + G(0) \quad ,$$

with the summations ranging from q+1 to N-1. Apart from the additive term G(0) this is precisely the modified potential energy of the N-1 particle system with G(x) replaced by G(x)+u(x), so that the first contribution to the derivative of $Q_{N,r}$ is

$$e^{-G(0)} \quad Q_{N-1,r}\{G(x) + u(x)\}$$

(exhibiting the functional dependence explicitly).

As

$$\frac{\partial}{\partial A} e^{-G(A-x)} = - G'(A-x) \; e^{-G(A-x)}$$

$$= \frac{\delta}{\delta G'} e^{-G(A-x)} \quad ,$$

where $G'(x)$ is the derivative of $G(x)$, the second contribution to the derivative is

$$\frac{\delta}{\delta G'} \quad Q_{N,r} \quad .$$

Accordingly, if $f\{G(x)\}$ is an arbitrary functional and the linear operators K and J are defined by

$$K\, f\{G(x)\} = e^{-G(0)} \quad f\{G(x) + u(x)\} \tag{2.9}$$

and

$$J = \frac{\delta}{\delta G'} \quad , \tag{2.10}$$

the derivative of $Q_{N,r}$ with respect to A is given by the equation

$$\frac{\partial}{\partial A} \quad Q_{N,r} = K\, Q_{N-1,r} + J\, Q_{N,r} \quad , \tag{2.11}$$

which may be regarded as a recurrence relation between the configuration integrals.

As the definition of E' depends on the number of fixed particles with coordinates greater than A, $Q_{N,r}$, considered as a function of A, has a step discontinuity at each fixed particle coordinate. Inspection of (2.5) and (2.6) reveals that

$$Q^{+}_{N,r} = K\, Q^{-}_{N,r} \quad , \tag{2.12}$$

where the plus and minus signs denote the value just above and below any fixed particle coordinate.

Also, when $A = 0$,

$$Q_{N,r} = \delta_{N,r} \tag{2.13}$$

from its definition.

The recurrence relation (2.11), together with the boundary conditions (2.12) and (2.13), determines each $Q_{N,r}$ uniquely, and so determines all the statistical mechanical properties of the system. The remainder of this chapter is devoted to exploiting these equations.

3. The thermodynamic properties and distribution functions

It is advantageous to introduce the generalised r-particle grand-partition function f_r defined by

$$f_r = \sum_{N=r}^{\infty} w^N \, Q_{N,r} \tag{2.14}$$

(c.f. section 2.3 of chapter 1).

Like $Q_{N,r}$, f_r is a function of A and a functional of $G(x)$. When $G(x)$ is identically zero f_o is the normal grand-partition function and when it is also true that A is much greater than all the fixed particle coordinates it follows from (2.7) that the r-particle distribution function satisfies the equation

$$n(x_1,..,x_r) = f_r \,/\, f_o \quad . \tag{2.15}$$

(2.11), (2.12) and (2.13) give the following three equations to define each f_r :

between fixed particle positions

$$\frac{\partial}{\partial A} f_r = H f_r \quad , \qquad (2.16)$$

across a fixed particle position

$$f_r^+ = K f_r^- \qquad (2.17)$$

and at $A = 0$

$$f_r = w^r \quad , \qquad (2.18)$$

where the operator H that has been introduced is defined by

$$H = w K + J \quad . \qquad (2.19)$$

Formally these equations may be solved immediately to yield

$$f_o = e^{AH} . 1 \quad , \qquad (2.20a)$$

$$f_1 = w\, e^{(A-x_1)H} . K . e^{x_1 H} . 1 \quad , \qquad (2.20b)$$

$$f_2 = w^2\, e^{(A-x_1)H} . K . e^{(x_1-x_2)H} . K . e^{x_2 H} . 1 \quad , \qquad (2.20c)$$

etc.,

when A is greater than all the fixed particle coordinates and

$$x_1 \geqslant x_2 \geqslant .. \geqslant x_r \quad .$$

It is apparent from these equations that it is unnecessary to consider H and K operating on any functional of $G(x)$ which does not lie in the functional space $\{f\}$ spanned by all functionals of the form

$$H^{m_1} \cdot K^{n_1} \cdot H^{m_2} \cdot K^{n_2} \cdot \ldots \cdot H^{m_k} \cdot K^{n_k} \cdot 1 \quad ,$$

where k and the m_j , n_j are arbitrary non-negative integers. All such functionals can be seen to be Taylor expandable about $G(x) \equiv 0$, so that $\{f\}$ is a sub-space of the space of all Taylor expandable functionals.

Suppose the eigenfunctionals $y_m\{G(x)\}$ of H which lie in $\{f\}$ form a basis of $\{f\}$. Then there exist constants c_m such that

$$1 = \sum_m c_m y_m \qquad (2.21)$$

and matrix elements $K_{m,n}$ such that

$$K y_m = \sum_n K_{m,n} y_n \quad . \qquad (2.22)$$

If λ_m is the eigenvalue of H associated with the eigenfunctional $y_m\{G(x)\}$, the equations (2.20) may be written in the more explicit form

$$f_o = \sum_{\ell} c_\ell \, e^{\lambda_\ell A} \, y_\ell \quad , \tag{2.23a}$$

$$f_1 = \sum_{\ell,m} c_\ell \, e^{\lambda_\ell x_1} \, K_{\ell,m} \, e^{\lambda_m (A-x_1)} \, y_m \quad , \tag{2.23b}$$

$$f_2 = \sum_{\ell,m,n} c_\ell \, e^{\lambda_\ell x_2} \, K_{\ell,m} \, e^{\lambda_m (x_1-x_2)} \, K_{m,n} \, e^{\lambda_n (A-x_1)} \, y_n \, , \tag{2.23c}$$

etc.

As f_o is the grand-partition function when $G(x)$ is identically zero, it is to be expected on thermodynamic grounds that

$$\lim_{A \to \infty} A^{-1} \log f_o$$

exists and is real. It then follows from (2.23a) that there exists an eigenvalue λ_o which is real and greater than the real part of any other, so that when A is large

$$f_o \sim c_o \, e^{\lambda_o A} \, y_o \quad . \tag{2.24}$$

As H depends on the fugacity w and the temperature T, λ_o may be regarded as a function of these two variables and then from section 2.3 of chapter 1, the equation of state and internal energy U of the N-particle gas are given by

$$P \,/\, \varkappa T = \lambda_o \quad , \tag{2.25}$$

$$\rho = w \frac{\partial}{\partial w} \lambda_o \tag{2.26}$$

and

$$U \,/\, N \varkappa T = \tfrac{1}{2} + \rho^{-1} \, T \frac{\partial}{\partial T} \lambda_o \tag{2.27}$$

(ρ being the mean particle density N/A of the gas).

In principle these equations are quite capable of describing a phase transition as it is possible to imagine a situation in which the two greatest eigenvalues cross over at some critical value of the fugacity w, so that λ_o undergoes a discontinuous change in its derivative. Unfortunately it has been shown by Landau and Lifshitz (1958) and van Hove (1950) that under normal circumstances a one-dimensional system cannot exhibit a phase transition, but Kac, Uhlenbeck and Hemmer (1963), Baker (1961) and Baur and Nosanow (1962) have constructed systems for which these proofs are invalid, and for which a phase transition does occur. The model of Kac et al. is studied in some detail in chapter 4 and it is shown that the transition is in fact due to the crossing of two eigenvalues.

To obtain the r-particle distribution function it is desirable to suppose that both $A-x_1$ and x_r are large, so that $x_1,\ldots,x_r$ are all far removed from the boundaries of the gas and surface effects can be ignored. Then from (2.23):

$$f_1 \sim w\, c_o\, e^{\lambda_o A}\, K_{o,o}\, y_o \quad , \tag{2.28a}$$

$$f_2 \sim w^2\, c_o\, e^{\lambda_o A} \sum_m K_{o,m}\, K_{m,o}\, e^{(x_1-x_2)(\lambda_m-\lambda_o)}\, y_o \quad , \tag{2.28b}$$

etc.

The distribution functions may now be obtained from (2.15) and (2.24). It is found that

$$n(x_1,\ldots,x_r) = w^r \sum_{m_1,\ldots,m_{r-1}} K_{o,m_1} K_{m_1,m_2} \cdots K_{m_{r-1},o}$$

$$\exp\left\{ \sum_{j=1}^{r-1} (x_j - x_{j+1})(\lambda_{m_j} - \lambda_o) \right\} , \qquad (2.29)$$

when

$$x_1 \geqslant x_2 \geqslant \cdots \geqslant x_r \quad .$$

As the distribution functions are by definition symmetric with respect to interchange of any two x's, they are completely defined by (2.29).

4. Reduction of the functional operators to difference-differential operators involving a finite number of variables

As yet it has been supposed that $G(x)$ is a completely arbitrary function, so that the above operators K, J and H act on quite general functionals. However, examination of (2.9) and (2.10) shows that if $u(x)$ and its right-derivatives over the domain $x \geqslant 0$ form a function space of finite dimensionality p (say), then the recurrence relation (2.11) may be derived using a function $G(x)$ which is restricted to this space and so may be defined in terms of p arbitrary variables.

H and K are then difference-differential operators involving only these variables, so if p is small the equations for λ_o and the distribution functions may be handled by numerical methods.

The two most obvious choices of u(x) such that the function space formed by it and its derivatives is of finite dimensionality are the decaying exponential and Coulomb potentials.

5. Application to a potential which is a sum of decaying exponentials

5.1 A symmetric representation of the operators

In view of the above remarks, the equations can be written more explicitly when the potential function is a sum of decaying exponentials, i.e.

$$\upsilon(x) = \tfrac{1}{2} \sum_{\alpha} \frac{c_\alpha}{a_\alpha} \exp(-a_\alpha |x|) \quad , \tag{2.30}$$

for then G(x) may be restricted to the form

$$\sum_{\alpha} v_\alpha \exp(-a_\alpha x) \quad . \tag{2.31}$$

The functionals of G(x) are then just functions of the variables v_α, and the operators K and J are given by:

$$K = \exp\left(-\sum_{\alpha} v_{\alpha}\right) \cdot \exp\left(\sum_{\alpha} \frac{c_{\alpha}}{2a_{\alpha}\varkappa T} \frac{\partial}{\partial v_{\alpha}}\right) \tag{2.32}$$

and

$$J = -\sum_{\alpha} a_{\alpha} v_{\alpha} \frac{\partial}{\partial v_{\alpha}} \quad . \tag{2.33}$$

Provided the a_{α} are all distinct, the functional space $\{f\}$ discussed in section 3 is now the set of functions of the v_{α} which are Taylor expandable about the origin.

It is convenient to apply a similarity transformation to the operators by replacing the basis functions $y(v_1, v_2, \ldots)$ by the functions $z(t_1, t_2, \ldots)$ defined by

$$z(t_1, t_2, \ldots) = \exp\left(-\tfrac{1}{2}\sum_{\alpha} a_{\alpha} t_{\alpha}^2\right) \int\!\!\int_{-\infty}^{\infty} dv_1 \, dv_2 \ldots y(v_1, v_2, \ldots)$$

$$\exp\left\{-\sum_{\alpha} a_{\alpha}\left(it_{\alpha} + v_{\alpha}/2b_{\alpha}\right)^2\right\} \quad , \tag{2.34}$$

where

$$b_{\alpha} = (c_{\alpha}/\varkappa T)^{\frac{1}{2}} \quad . \tag{2.35}$$

With respect to this new basis the operators K and J are given by:

$$K = \exp\left(\sum_{\alpha} b_{\alpha}^2/4a_{\alpha}\right) \cdot \exp\left(i\sum_{\alpha} b_{\alpha} t_{\alpha}\right) \tag{2.36}$$

and

$$J = \tfrac{1}{2}\sum_{\alpha}\left(\frac{\partial^2}{\partial t_{\alpha}^2} - a_{\alpha}^2 t_{\alpha}^2 + a_{\alpha}\right) \quad . \tag{2.37}$$

The basic space $\{f\}$ spanned by all functions $y(v_1, v_2, ..)$ which are products of powers of the v_α is from (2.34) readily seen to be in this new representation spanned by all functions $z(t_1, t_2, ..)$ which are of the form of a product of powers of the t_α multiplied by

$$\exp(-\tfrac{1}{2}\sum_\alpha a_\alpha t_\alpha^2) \qquad .$$

Clearly the integral over all t_α-space of the product of any two such functions converges.

The advantage of the present form of the operators is that H, which from (2.19) is defined by

$$H = w K + J \qquad , \tag{2.38}$$

is symmetric. Its eigenfunctions therefore are orthogonal and form a basis of the space $\{f\}$, which provides some justification for the assumption that this is the case in section 3. As K is complex it does not follow that the eigenvalues are real, but using the fact that negating every t_α has the same effect on H as complex conjugation, it can be shown that they are either real or occur in pairs of complex conjugates.

It is convenient to adopt a vector notation for the eigenfunctions $z_m(t_1, t_2, ..)$ of H which lie in $\{f\}$ and to represent them as $\underline{z}_m$. Then the scalar product of any two such vectors may be defined as

$$\underline{z}_m' \, \underline{z}_n = \int_{-\infty}^{\infty}\!\!..\!\!\int dt_1 \, dt_2 \, ... \, z_m(t_1, t_2, ..) \, z_n(t_1, t_2, ..) \qquad . \tag{2.39}$$

5.2 A variational approximation

Unfortunately, unless the number of decaying exponential components of (2.30) is very small, the equations are still too complicated to handle numerically. It is therefore natural to seek an approximate solution, and as the operator H is now expressed in an explicitly symmetric form the most obvious procedure to obtain its maximum eigenvalue λ_o is to find the turning value of

$$I = \underline{z}'H\,\underline{z} \,/\, \underline{z}'\underline{z} \qquad , \qquad (2.40)$$

where $\underline{z}$ represents some trial function $z(t_1,t_2,..)$.

Considering the eigenfunctions when the exponential term in K is Taylor expanded to second order about some set of values of the t_α, it seems that a very reasonable choice of the trial function is

$$z(t_1,t_2,..) = \exp\left\{-\tfrac{1}{2}\sum_{\alpha,\beta} R_{\alpha,\beta}\,(t_\alpha - ir_\alpha)(t_\beta - ir_\beta)\right\} \qquad , \qquad (2.41)$$

where the $R_{\alpha,\beta}$ may be regarded as elements of an arbitrary symmetric matrix $\underline{R}$ and the r_α as components of an arbitrary vector $\underline{r}$. It must be clearly understood that these and similar matrices and vectors which are introduced in this section are purely a convenient way of describing the properties of the trial function and are quite different from the vector representation of the eigenfunctions of H.

Using this trial function, I may be computed from (2.40) and is found to be

$$I = h + \frac{1}{2} \sum_{\alpha} a_\alpha - \frac{1}{4} \mathrm{Tr}(\underline{D}\, \underline{R}^{-1}) - \frac{1}{4} \mathrm{Tr}\, \underline{R} + \sum_{\alpha} a_\alpha^2 r_\alpha^2 , \qquad (2.42)$$

where the matrix $\underline{D}$ is defined by

$$D_{\alpha,\beta} = a_\alpha^2 \delta_{\alpha,\beta} \qquad (2.43)$$

and

$$h = w \exp\left\{ - \sum_{\alpha} b_\alpha r_\alpha + \frac{1}{4} \sum_{\alpha} b_\alpha^2 / a_\alpha - \frac{1}{4} \underline{b}' \underline{R}^{-1} \underline{b} \right\} . \qquad (2.44)$$

As H is complex it is not quite true to say that λ_o is, to this approximation, equal to the maximum value of I, rather it is given by I when I is maximized with respect to $\underline{R}$ and minimized with respect to $\underline{r}$.

Minimizing (2.42) with respect to each r_α gives the set of equations

$$r_\alpha = b_\alpha h / a_\alpha^2 , \qquad (2.45)$$

while maximizing with respect to $\underline{R}$ gives the matrix equation

$$\underline{R}^2 = \underline{D} + h\, \underline{b}\, \underline{b}' . \qquad (2.46)$$

Strictly, equations (2.44), (2.45) and (2.46) should be regarded as defining h, $\underline{r}$ and $\underline{R}$. However, it turns out to be more convenient to regard h as an independent variable and to interpret (2.44) as a definition of w.

From the form (2.41) of the trial function $\underline{R}$ must be a positive definite matrix, so that (2.46) defines it uniquely. Fortunately it is not necessary to determine $\underline{R}$ explicitly, rather it is sufficient to evaluate the quantities

$$\mathrm{Tr}\,(\underline{D}\,\underline{R}^{-1}) \quad , \quad \mathrm{Tr}\,\underline{R} \quad \text{and} \quad \underline{b}'\underline{R}^{-1}\underline{b} \quad ,$$

as $\underline{R}$ contributes to the maximum value of I only through these three expressions. Further, a relation can be obtained between them by multiplying (2.46) on the right by $\underline{R}^{-1}$ and taking the trace of each side, giving

$$\mathrm{Tr}\,\underline{R} = \mathrm{Tr}\,(\underline{D}\,\underline{R}^{-1}) + h\,\underline{b}'\underline{R}^{-1}\underline{b} \quad , \tag{2.47}$$

so that it is only necessary to determine $\mathrm{Tr}\,\underline{R}$ and $\underline{b}'\underline{R}^{-1}\underline{b}$.

To do this it is desirable to consider the eigenvalues μ_β and associated eigenvectors $\underline{x}_\beta$ of $\underline{R}$. From (2.46) these must satisfy the equation

$$(\underline{D} + h\,\underline{b}\,\underline{b}')\,\underline{x} = \mu^2\,\underline{x} \tag{2.48}$$

(dropping the suffix β).

If x_α is the α th component of the vector $\underline{x}$, (2.48) may be written

$$a_\alpha^2 \, x_\alpha + h \, (\underline{b}'\underline{x}) \, b_\alpha = \mu^2 \, x_\alpha \quad , \tag{2.49}$$

so that

$$x_\alpha = - h \, (\underline{b}'\underline{x}) \, b_\alpha \, / \, (a_\alpha^2 - \mu^2) \quad . \tag{2.50}$$

Multiplying (2.50) by b_α and summing over α, the term $\underline{b}'\underline{x}$ cancels out, leaving

$$1 + h \sum_\alpha b_\alpha^2 \, / \, (a_\alpha^2 - \mu^2) = 0 \quad . \tag{2.51}$$

Together with the positive-definiteness condition that μ be greater than zero, (2.51) defines the eigenvalues of $\underline{R}$ and (2.50) the associated eigenvectors. One property of each eigenvector that will be required is the ratio of the square of $\underline{b}'\underline{x}$ to $\underline{x}'\underline{x}$; this may be determined by squaring each side of (2.50) and summing over α, giving:

$$\underline{x}'\underline{x} = h^2 \, (\underline{b}'\underline{x})^2 \sum_\alpha b_\alpha^2 \, / \, (a_\alpha^2 - \mu^2)^2 \quad . \tag{2.52}$$

To evaluate $\underline{b}'\underline{R}^{-1}\underline{b}$ note that the eigenvectors $\underline{x}_\beta$ must be orthogonal, so that

$$\underline{b} = \sum_\beta \underline{x}_\beta \, (\underline{b}'\underline{x}_\beta) \, / \, (\underline{x}_\beta' \, \underline{x}_\beta) \quad , \tag{2.53}$$

and as

$$\underline{R}^{-1}\,\underline{x}_\beta = \mu_\beta^{-1}\,\underline{x}_\beta \quad , \tag{2.54}$$

it follows immediately that

$$\underline{b}'\underline{R}^{-1}\underline{b} = \sum_\beta \mu_\beta^{-1}\,(\underline{b}'\underline{x}_\beta)^2/\,(\underline{x}_\beta'\,\underline{x}_\beta) \quad . \tag{2.55}$$

$\underline{x}_\beta$ may now be eliminated from this equation by using the result (2.52), giving:

$$\underline{b}'\underline{R}^{-1}\underline{b} = h^{-2}\sum_\beta\left\{\mu_\beta \sum_\alpha b_\alpha^2\,/\,(a_\alpha^2 - \mu_\beta^2)^2\right\}^{-1} \quad . \tag{2.56}$$

The trace of $\underline{R}$ is trivial to determine, for it is given by

$$\mathrm{Tr}\,\underline{R} = \sum_\beta \mu_\beta \quad . \tag{2.57}$$

These expressions may be greatly simplified if a function $\phi(h)$ is introduced and defined by

$$\phi(h) = \sum_\beta \mu_\beta \quad , \tag{2.58}$$

for clearly

$$\mathrm{Tr}\,\underline{R} = \phi(h) \quad , \tag{2.59}$$

and as it can be shown by differentiating (2.51) with respect to h that

$$\frac{d}{dh}\mu_\beta = \tfrac{1}{2}\,h^{-2}\left\{\mu_\beta \sum_\alpha b_\alpha^2\,/\,(a_\alpha^2 - \mu_\beta^2)^2\right\}^{-1} \quad , \tag{2.60}$$

(2.56) may be written

$$\underline{b}'\underline{R}^{-1}\underline{b} = 2 \sum_{\beta} \frac{d}{dh} \mu_{\beta} ,$$

$$= 2 \phi'(h) . \qquad (2.61)$$

Also, inspection of (2.51) reveals that when h is small,

$$\mu_{\beta} = a_{\beta} + h\, b_{\beta}^{2} / 2a_{\beta} + 0(h^{2}) \qquad (2.62)$$

(with appropriate ordering of the μ_{β}), so that

$$\phi(0) = \sum_{\beta} a_{\beta} \qquad (2.63)$$

and

$$\phi'(0) = \sum_{\beta} b_{\beta}^{2} / 2a_{\beta} . \qquad (2.64)$$

From (2.47), (2.59) and (2.61),

$$\mathrm{Tr}\,(\underline{D}\,\underline{R}^{-1}) = \phi(h) - 2\,h\,\phi'(h) . \qquad (2.65)$$

The expressions $\mathrm{Tr}(\underline{D}\,\underline{R}^{-1})$, Tr $\underline{R}$ and $\underline{b}'\underline{R}^{-1}\underline{b}$ are thus completely determined by the function $\phi(h)$. Substituting their values in (2.42) and eliminating the r_{α} by (2.45) gives the turning value of I, which in this approximation is λ_{o}.

Using also the relation (2.63), it follows that

$$\lambda_o = h + h^2 \sum_{\alpha} b_\alpha^2 / 2\, a_\alpha^2 + \tfrac{1}{2}\{\phi(0) - \phi(h) + h\, \phi'(h)\} \quad , \qquad (2.66)$$

and from (2.44), (2.61) and (2.64), w is given by:

$$w = h \exp\left\{ h \sum_{\alpha} b_\alpha^2 / a_\alpha^2 + \tfrac{1}{2}\left[\phi'(h) - \phi'(0)\right] \right\} \quad . \qquad (2.67)$$

The equation of state may now be derived directly from these equations, for from (2.67),

$$h \frac{d}{dh} \log w = 1 + h \sum_{\alpha} b_\alpha^2 / a_\alpha^2 + \tfrac{1}{2} h\, \phi''(h) \quad ; \qquad (2.68)$$

but from (2.66) this is precisely the same as the derivative with respect to h of λ_o, i.e.

$$\frac{d}{dh} \lambda_o = h \frac{d}{dh} \log w \quad . \qquad (2.69)$$

If the temperature is regarded as constant, so that λ_o is viewed as a function of the single variable w, it is known from (2.26) that the mean particle density is

$$\rho = w \frac{d}{dw} \lambda_o \quad , \qquad (2.70)$$

or, as λ_o and w are each functions of h,

$$\rho = \frac{d}{dh} \lambda_o \Big/ \frac{d}{dh} \log w \quad . \qquad (2.71)$$

Comparing (2.69) and (2.71) it is apparent that

$$h = \rho \quad . \qquad (2.72)$$

h may therefore be assigned a direct physical significance, namely the density of particles in the gas. This result is not surprising when it is noted that in view of the form (2.38) of the operator H, the effect of an infinitesimal change of w on the eigenvalue λ_o is, by first order perturbation theory, given by

$$w \frac{d}{dw} \lambda_o = w \, \underline{z}_o' \, K \, \underline{z}_o \, / \, \underline{z}_o' \, \underline{z}_o \quad , \qquad (2.73)$$

for when $\underline{z}_o$ is the trial function (2.41) the right-hand side of this equation is precisely the definition (2.44) of h.

As, from (2.25), the pressure P is given by

$$P / \varkappa T = \lambda_o \quad , \qquad (2.74)$$

the equation of state may now be written in terms of the function ϕ, for using (2.72) and (2.74), (2.66) becomes

$$P/\varkappa T = \rho + \rho^2 \sum_\alpha b_\alpha^2/2a_\alpha^2 + \tfrac{1}{2}\left\{ \phi(0) - \phi(\rho) + \rho\, \phi'(\rho) \right\} . \qquad (2.75)$$

The results of this section are more conveniently expressed in terms of the differentiated equation of state expressing the derivative of the pressure with respect to the density as a function of the density and the temperature. Differentiating (2.75) with respect to ρ, this is

$$\frac{\partial}{\partial \rho} P/\varkappa T = 1 + \rho \sum_{\alpha} b_{\alpha}^{2} / a_{\alpha}^{2} + \tfrac{1}{2} \rho \, \phi''(\rho) \quad . \qquad (2.76)$$

At this stage it is obviously desirable to obtain a more explicit interpretation of the function $\phi(\rho)$ in terms of the potential function $\upsilon(x)$, for its definition as the sum of the positive roots of (2.51) seems somewhat obscure. To do this it is convenient to introduce the Fourier transform $\overline{\upsilon}(s)$ of $\upsilon(x)$ defined by

$$\overline{\upsilon}(s) = \int_{-\infty}^{\infty} dx \; \upsilon(x) \; e^{-isx} \quad . \qquad (2.77)$$

Substituting the explicit form (2.30) of $\upsilon(x)$, the integration in (2.77) may be performed, giving

$$\overline{\upsilon}(s) = \sum_{\alpha} c_{\alpha} / (a_{\alpha}^{2} + s^{2}) \quad , \qquad (2.78)$$

or, using the definition (2.35) of b_{α},

$$\overline{\upsilon}(s) = \varkappa T \sum_{\alpha} b_{\alpha}^{2} / (a_{\alpha}^{2} + s^{2}) \quad . \qquad (2.79)$$

Comparing (2.79) and (2.51) it is now apparent that the μ_{β} are related to the poles of the function

$$\omega(s) = 1 / (1 + \rho \, \overline{\upsilon}(s)/\varkappa T) \quad . \qquad (2.80)$$

In fact the poles of $\omega(s)$ lie on the imaginary axis of the complex s-plane at the points

$$s = \pm i \mu_\beta \quad . \tag{2.81}$$

This suggests investigating the integral

$$F(\rho) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds \left[\omega(s) - 1\right] \quad , \tag{2.82}$$

where the term -1 has been introduced to ensure convergence.

As $\omega(s) - 1$ tends to zero as s^{-2} when s becomes large, the integration may be extended to include the semicircle at infinity in the upper half-plane and then by Cauchy's theorem,

$$F(\rho) = i \sum \text{residues of } \omega(s) - 1 \text{ at poles on the upper imaginary axis.} \tag{2.83}$$

These residues may be determined in terms of the μ_β and it is found that

$$F(\rho) = -\frac{1}{2\rho} \sum_\beta \left\{ \mu_\beta \sum_\alpha b_\alpha^2 / (a_\alpha^2 - \mu_\beta^2)^2 \right\}^{-1} \quad . \tag{2.84}$$

Comparing this result with the equation (2.60), it follows that

$$F(\rho) = -\rho \sum_\beta \frac{d}{dh} \mu_\beta \quad , \tag{2.85}$$

which in view of the definition (2.58) of $\phi(h)$ and the equality of ρ and h implies that

$$F(\rho) = - \rho \, \phi'(\rho) \qquad . \tag{2.86}$$

(2.80), (2.82) and (2.86) therefore define the function $\phi(\rho)$ (or rather its derivative) directly in terms of $\bar{\upsilon}(s)$. Noting also that, from (2.79),

$$\bar{\upsilon}(0) = \varkappa T \sum_{\alpha} b_{\alpha}^{2} / a_{\alpha}^{2} \qquad , \tag{2.87}$$

the differentiated equation of state (2.76) may be written:

$$\frac{\partial}{\partial \rho} P/\varkappa T = 1 + \frac{\rho \, \bar{\upsilon}(0)}{\varkappa T} - \frac{\rho}{4\pi(\varkappa T)^{2}} \int_{-\infty}^{\infty} ds \, \frac{\bar{\upsilon}^{2}(s)}{[1+\rho\bar{\upsilon}(s)/\varkappa T]^{2}} \quad . \tag{2.88}$$

This equation contains no explicit reference to the particular form (2.30) of the potential function and it seems reasonable to suppose that it is a good approximation when $\upsilon(x)$ is any Fourier analysable function. Further, its extension to systems of dimensionality greater than one is obvious.

In view of the fact that it has been derived by a variational technique, the result may be regarded as a justification of the rather ad hoc procedure frequently used to obtain the Debye-Huckel theory, namely summing over υ-bond diagrams of ring type (Mayer, 1950; Abe, 1959), for it is precisely the 'ring approximation' derived by this method.

6. The derivatives of the eigenvalues of H and the matrix elements of K with respect to fugacity

In section 5 it has been shown that a basis of the functional space $\{f\}$ may be chosen with respect to which both K and J are symmetric operators, provided the potential function is a sum of decaying exponentials. This form for the potential is sufficiently general to suggest that such a basis exists for at least a wide class of potentials.

Suppose that such a basis has been chosen and that with respect to this the eigenfunctionals of H are represented by the vectors $\underline{z}_m$, the associated eigenvalues being λ_m. Then from the definition (2.19) of H,

$$(w\,K + J)\,\underline{z}_m = \lambda_m\,\underline{z}_m \quad . \tag{2.89}$$

As K and J are symmetric operators, the eigenvectors $\underline{z}_m$ are orthogonal, and if they are normalized so that

$$\underline{z}_m'\,\underline{z}_m = 1 \quad , \tag{2.90}$$

then the matrix elements of K occurring in the equation (2.29) for the distribution functions may be defined by

$$K_{m,n} = \underline{z}_m'\,K\,\underline{z}_n \quad . \tag{2.91}$$

It is now desired to consider the effect of small variations of w on λ_m and $K_{m,n}$, i.e. to evaluate their derivatives with respect to the fugacity w.

To do this it is first necessary to consider the change induced in the eigenvectors. If $\delta \underline{z}_m$ is the increment in $\underline{z}_m$ induced by incrementing w by the infinitesimal amount δw, a matrix $\underline{L}$ may be defined by

$$\delta \underline{z}_m = \delta w \sum_n L_{m,n} \, \underline{z}_n \quad . \qquad (2.92)$$

To determine $\underline{L}$ consider the effect of such an increment on the equation (2.89). If $\delta\lambda_m$ is the increment induced in λ_m it is readily seen that

$$(w K + J - \lambda_m) \, \delta \underline{z}_m = (\delta\lambda_m - \delta w \, K) \, \underline{z}_m \quad . \qquad (2.93)$$

Substituting the expression (2.92) for $\delta \underline{z}_m$ and noting that

$$K \, \underline{z}_m = \sum_n K_{m,n} \, \underline{z}_n \quad , \qquad (2.94)$$

it follows that

$$\delta w \sum_n L_{m,n} (\lambda_n - \lambda_m) \, \underline{z}_n = \delta\lambda_m \, \underline{z}_m - \delta w \sum_n K_{m,n} \, \underline{z}_n \, . \quad (2.95)$$

which, as the $\underline{z}_m$ are orthogonal, implies that

$$\delta\lambda_m = \delta w \, K_{m,m} \qquad (2.96)$$

and

$$L_{m,n} = K_{m,n} / (\lambda_m - \lambda_n) \quad , \qquad (2.97)$$

provided $m \neq n$.

The values of $L_{m,m}$ may be determined by considering the effect of incrementing w on the normalization condition (2.90). This shows that

$$\underline{z}_m^{\prime} \, \delta \underline{z}_m = 0 \quad , \qquad (2.98)$$

so that from (2.92),

$$L_{m,m} = 0 \quad . \qquad (2.99)$$

As, from the symmetry property of the operator K,

$$K_{m,n} = K_{n,m} \quad , \qquad (2.100)$$

it follows from (2.97) and (2.99) that $\underline{L}$ is an antisymmetric matrix.

Consider now the effect of incrementing w on the definition (2.91) of $K_{m,n}$; clearly

$$\delta K_{m,n} = \delta \underline{z}_m^{\prime} \, K \, \underline{z}_n + \underline{z}_m^{\prime} \, K \, \delta \underline{z}_n \quad . \qquad (2.101)$$

Applying (2.92), this gives

$$\delta K_{m,n} = \delta w \sum_{\ell} (L_{m,\ell} \, K_{\ell,n} + L_{n,\ell} \, K_{\ell,m}) \quad . \qquad (2.102)$$

Substituting the expressions (2.97) for the elements of $\underline{L}$ and recalling the definition of a derivative, (2.102) implies that

$$\frac{d}{dw} K_{m,n} = \sum_{\ell \neq m} \frac{K_{m,\ell} K_{\ell,n}}{\lambda_m - \lambda_\ell} + \sum_{\ell \neq n} \frac{K_{m,\ell} K_{\ell,n}}{\lambda_n - \lambda_\ell} \tag{2.103}$$

(using the symmetry property (2.100)). Also it follows from (2.96) that

$$\frac{d}{dw} \lambda_m = K_{m,m} \quad . \tag{2.104}$$

In principle the equations (2.103) and (2.104) completely define the statistical mechanical properties of the system if the values of the λ_m and $K_{m,n}$ can be determined at zero fugacity, but unfortunately there appears to be no simple way of evaluating or classifying these values for an arbitrary potential. However, the equations do enable simple relations between the distribution functions and their derivatives with respect to fugacity (or density) to be established, as will be shown in the following section.

7. The derivatives of the distribution functions with respect to fugacity and density

Having established the relations (2.103) and (2.104) for the derivatives of the matrix elements $K_{m,n}$ and the eigenvalues λ_m with respect to fugacity (the temperature being regarded as a constant), it is a trivial, though cumbersome, matter to obtain from (2.29) an expression for the derivative of the r-particle distribution function.

Defining the matrices $\underline{Y}^{(1)}$ and $\underline{Y}^{(2)}$ by

$$Y^{(1)}_{m,n} = \sum_{\ell \neq m} K_{m,\ell}\, K_{\ell,n} \,/\, (\lambda_m - \lambda_\ell) \tag{2.105}$$

and

$$Y^{(2)}_{m,n} = \sum_{\ell \neq n} K_{m,\ell}\, K_{\ell,n} \,/\, (\lambda_n - \lambda_\ell) \quad , \tag{2.106}$$

the relation (2.103) may be written

$$\frac{d}{dw} K_{m,n} = Y^{(1)}_{m,n} + Y^{(2)}_{m,n} \quad , \tag{2.107}$$

so that dividing each side of (2.29) by w^r and differentiating with respect to w, it is found that when $x_1 \geqslant x_2 \geqslant \cdots \geqslant x_r$,

$$\frac{d}{dw} w^{-r} n(x_1,\ldots,x_r) = w^{-r} \sum_{j=1}^{r-1} A_j + w^{-r} \sum_{j=0}^{r-1} \left\{ B^{(1)}_j + B^{(2)}_j \right\}, \tag{2.108}$$

where

$$A_j = w^r \sum_{m_1 \cdot\cdot m_{r-1}} K_{o,m_1} K_{m_1,m_2} \cdots K_{m_{r-1},o} \; (K_{m_j,m_j} - K_{o,o})$$

$$(x_j - x_{j+1}) \exp\left\{ \sum_{k=1}^{r-1} (x_k - x_{k+1})(\lambda_{m_k} - \lambda_o) \right\} \qquad (2.109)$$

and

$$B_j^{(\alpha)} = w^r \sum_{m_1,\ldots,m_{r-1}} K_{o,m_1} K_{m_1,m_2} \cdots K_{m_{j-1},m_j} Y^{(\alpha)}_{m_j,m_{j+1}}$$

$$K_{m_{j+1},m_{j+2}} \cdots K_{m_{r-1},o} \exp\left\{ \sum_{k=1}^{r-1} (x_k - x_{k+1})(\lambda_{m_k} - \lambda_o) \right\} \qquad (2.110)$$

(interpreting m_o and m_r as 0).

These equations are obviously far too complicated to be either useful or interesting in their present form. However, it will now be shown that the right-hand side of (2.108) can be quite simply expressed as

$$w^{-r-1} \int_{-\infty}^{\infty} dx' \quad \tau(x') \qquad ,$$

where

$$\tau(x') = n(x_1,\ldots,x_r,x') - \rho\, n(x_1,\ldots,x_r) \quad . \qquad (2.111)$$

As $x_1 \geqslant x_2 \geqslant \cdots \geqslant x_r$, it is convenient to divide this integral into the $r+1$ components:

$$S_o = \int_{x_1}^{\infty} dx' \quad \tau(x') \quad , \tag{2.112a}$$

$$S_j = \int_{x_{j+1}}^{x_j} dx' \quad \tau(x') \quad (1 \leqslant j \leqslant r-1) \tag{2.112b}$$

and

$$S_r = \int_{-\infty}^{x_r} dx' \quad \tau(x') \quad . \tag{2.112c}$$

The ordering of the variables $x_1,..,x_r,x'$ is completely specified in each of the integrals S_j, so that from (2.29) the function $\tau(x')$ is a simple exponential less a constant. The integrations are therefore trivial to perform, though rather unwieldy, and after some re-labelling of dummy suffixes and noting that, from (2.26) and (2.104),

$$\rho = w\, K_{o,o} \quad , \tag{2.113}$$

they yield:

$$S_o = w\, B_o^{(1)} \quad , \tag{2.114a}$$

$$S_j = w\, (A_j + B_j^{(1)} + B_{j-1}^{(2)}) \qquad (1 \leqslant j \leqslant r-1) \tag{2.114b}$$

and

$$S_r = w\, B_{r-1}^{(2)} \quad . \tag{2.114c}$$

Summing all the components S_j it is apparent that

$$\int_{-\infty}^{\infty} dx'\ \tau(x') = w \sum_{j=1}^{r-1} A_j + w \sum_{j=0}^{r-1} \left\{ B_j^{(1)} + B_j^{(2)} \right\} , \tag{2.115}$$

which is precisely w^{1+r} times the right-hand side of (2.108). Accordingly it follows that

$$w^{r+1} \frac{d}{dw} w^{-r}\ n(x_1,..,x_r) = \int_{-\infty}^{\infty} dx' \left[n(x_1,..,x_r,x') - \rho\ n(x_1,..,x_r) \right] \tag{2.116}$$

(using the definition (2.111) of $\tau(x')$).

This is clearly a relation between the distribution functions and their derivatives with respect to fugacity. In view of the equation (1.62), namely

$$\mu\ \rho \frac{d}{d\rho} \log w = 1 , \tag{2.117}$$

where μ is the quantity related to the isothermal compressibility defined by (1.39) and the temperature is to be regarded as a constant, the fugacity derivative may be replaced by a density derivative to give:

$$(\mu\ \rho \frac{d}{d\rho} - r)\ n(x_1,..,x_r) = \int_{-\infty}^{\infty} dx' \left[n(x_1,..,x_r,x') - \rho\ n(x_1,..,x_r) \right] . \tag{2.118}$$

Although this result has been proved only when

$$x_1 \geqslant x_2 \geqslant \cdots \geqslant x_r \qquad ,$$

it follows from the known symmetry of the distribution functions that it is true for any ordering of the variables.

As the relation (2.118) contains no explicit reference to the potential and is meaningful in any number of dimensions, it may be expected to be applicable to a gas of arbitrary interaction and dimensionality. This point is discussed in chapter 6, where the relation is shown to be of general validity and is used to derive similar results for the Ursell-Mayer cluster functions (Mayer and Montroll, 1941; page 203 of M. Green, 1961; page 78 of Uhlenbeck, 1963) and a new set of functions, termed the direct correlation functions.

8. Extension of the results to a many-species system

In statistical mechanics it is frequently necessary to consider the behaviour of a gas which is a mixture of various types, or species, of particles. One obvious example is air, which contains nitrogen, oxygen and other gases in known proportions. Another is a plasma, or gas of charged particles, where it is essential to suppose the existence of both electrons and positive ions to ensure that the system as a whole be electrically neutral. The above formulation is therefore deficient in so far as it considers a system containing only one type of particle.

However, the derivation of similar results for a many-species system, while involving a considerable complication of the equations, follows exactly the same logical steps as those used above. For this reason it seems sufficient merely to state the generalization of the more significant results of this chapter, namely those of section 3.

If the gas contains p species of particles, with the interaction potential

$$\upsilon_{\alpha,\beta}(x - x')$$

between a particle of the α th species at the point x and a particle of the β th species at the point x', then by the physical requirements of symmetry the functions $\upsilon_{\alpha,\beta}(x)$ must satisfy the equations:

$$\upsilon_{\alpha,\beta}(-x) = \upsilon_{\alpha,\beta}(x) \tag{2.119}$$

and

$$\upsilon_{\alpha,\beta}(x) = \upsilon_{\beta,\alpha}(x) \quad . \tag{2.120}$$

As in section 2, it is convenient to incorporate the Boltzmann factor into the potential by defining

$$u_{\alpha,\beta}(x) = \upsilon_{\alpha,\beta}(x) / \varkappa T \quad . \tag{2.121}$$

In general it is now necessary to consider functionals not of one function $G(x)$, but of p functions $G_1(x),\ldots,G_p(x)$, and to define the $p+1$ functional operators $K_1,\ldots,K_p$ and J by

$$K_\alpha \, f\{G_1(x),\ldots,G_p(x)\} = e^{-G_\alpha(0)} f\{G_1(x)+u_{1\alpha}(x),\ldots,G_p(x)+u_{p\alpha}(x)\} \tag{2.122}$$

and

$$J = \sum_{\alpha=1}^{p} \frac{\delta}{\delta G'_\alpha} \quad . \tag{2.123}$$

Further, there must be p fugacities w_α relating to each type of particle and the operator H of (2.19) is now defined by

$$H = J + \sum_{\alpha=1}^{p} w_\alpha K_\alpha \quad . \tag{2.124}$$

If λ_o is the greatest eigenvalue of H, then the thermodynamic properties of the system are determined by its dependence on the w_α and the temperature T, for the pressure P is given by

$$P / \varkappa T = \lambda_o \quad , \tag{2.125}$$

the density ρ_α of particles of the α th species by

$$\rho_\alpha = w_\alpha \frac{\partial}{\partial w_\alpha} \lambda_o \quad , \tag{2.126}$$

and if N and ρ are the total number and density respectively of all particles, the internal energy U of the system is determined by

$$U / N\varkappa T = \tfrac{1}{2} + \rho^{-1} T \frac{\partial}{\partial T} \lambda_o \quad . \tag{2.127}$$

Also, the distribution function specifying the probability that particles of type $\alpha_1, \ldots, \alpha_r$ are situated in the neighbourhoods of the points $x_1, \ldots, x_r$ respectively is (when $x_1 \geqslant x_2 \geqslant \ldots \geqslant x_r$)

$$n_{\alpha_1, \ldots, \alpha_r}(x_1, \ldots, x_r) = w_{\alpha_1} \ldots w_{\alpha_r} \sum_{m_1, \ldots, m_{r-1}} K^{(\alpha_1)}_{o, m_1} K^{(\alpha_2)}_{m_1, m_2} \ldots$$

$$\ldots K^{(\alpha_r)}_{m_{r-1}, o} \exp\left\{ \sum_{k=1}^{r-1} (x_k - x_{k+1}) (\lambda_{m_k} - \lambda_o) \right\} \quad , \tag{2.128}$$

where the $K^{(\alpha)}_{m,n}$ are the matrix elements of the operator K_α.

9. Discussion of results

It has been shown that all the statistical mechanical properties of a one-dimensional gas are completely determined by a knowledge of the eigenvalues of an operator H and the matrix elements of a related operator K. A basis may be chosen with respect to which both H and K are symmetric, so that it is possible to apply a variational approximation. The most obvious choice of a trial function leads to results which are identical with the 'ring approximation' of cluster theory.

The symmetry of the operators is also of consequence in that it enables exact expressions to be derived for the derivatives of the eigenvalues of H and the matrix elements of K with respect to fugacity, from which expressions follow relations between the distribution functions and their derivatives with respect to either fugacity or density.

If the system contains only one species of particles and the interaction potential satisfies a homogeneous linear differential equation of order p with constant coefficients over the domain $(0,\infty)$, H and K may be reduced to difference-differential operators involving at most p variables. If p is small the resulting eigenvalue equation may be solved numerically, so that potentials such as

$$\exp(-a\,|x|)\quad ,$$

$$|x|\ \exp(-a\,|x|)$$

and the Coulomb potential

$$|x|$$

are amenable to investigation by this method (the last case is slightly more complicated as a two-species system containing both positively and negatively charged particles must be considered to obtain meaningful results).

However, it should be emphasized that when considering any particular interaction potential it is not always desirable to follow the above working blindly. From the point of view of obtaining solutions it may be preferable to revert to the basic procedure of section 2, namely to consider the canonical partition functions of a gas of particles constrained to lie on the line segment $[0,A]$ and interacting via the known potential, and to introduce as specialized as possible a form of the variable external potential $G(A-x)$ such that relations may be established between the partition functions (or configuration integrals) and their derivatives with respect to A. These relations lead to an equation for the grand-partition function, and if this can be shown to have solutions of the form

$$y_m \exp(\lambda_m A) \qquad ,$$

where y_m is independent of A, then the thermodynamic properties of the system may immediately be investigated.

Thus in chapter 3 it is shown that direct application of the results of section 8 to a one-dimensional plasma gives an eigenvalue equation involving four variables, whereas a relation may be established between the canonical partition functions without explicitly introducing a variable external potential at all. Also, in chapter 4 it is shown that the basic procedure is capable of handling potentials which contain a hard core, and that eigenvalues λ_m and matrix elements $K_{m,n}$ may be defined such that the statistical mechanical properties of a gas of hard rods are given by (2.25), (2.26), (2.27) and (2.29), even though this potential appears to violate the differentiability condition of section 2.

Chapter 3

THE ONE-DIMENSIONAL PLASMA

1. Introduction

It has been shown in chapter 2 that the statistical mechanical properties of a one-dimensional gas with a two-particle interaction may be calculated exactly if the function space spanned by the potential function and its derivatives over the domain $(0,\infty)$ is of finite dimensionality. It is fortunate therefore that the one-dimensional Coulomb potential, which is proportional to mod(x), falls into this class, as the properties of a plasma, or gas of charged particles, are of obvious physical interest, notably in the field of thermonuclear fusion. While the properties of a one-dimensional system are obviously not those of a real three-dimensional gas, they may be expected to be of some value as a qualitative guide.

One problem to which such a guide would seem to be relevant is that which arises from the common device of representing a three-dimensional plasma as a gas of electrons moving, not amongst discrete ions, but in a uniform background of positive charge (Salpeter 1958, Abe 1959). Although such a device is a convenient means of avoiding the divergences which arise in the classical theory from the infinite negative energy of an ion pair in contact, it is clearly not an exact description of reality, so that it is of interest to determine its accuracy in the one-dimensional case, where no divergences occur and the thermodynamic properties can be calculated both with this approximation and without it.

Accordingly, the aim of this chapter is threefold: firstly to obtain the statistical mechanical properties of a one-dimensional gas of discrete electrons and ions, paying particular attention to the case when their respective charges are of equal magnitude but opposite sign; secondly to obtain the properties of a one-dimensional gas of electrons moving in a uniform neutralising charge background; and finally to compare the behaviour of the two systems.

2. The gas of discrete electrons and ions

2.1 Definition of the problem

Consider a system of positively charged ions of charge $\eta\sigma$ and electrons of charge $-\sigma$ constrained to lie on the line segment $[0,A]$. Then as the Coulomb interaction potential $\upsilon(x)$ between two charges σ_1, σ_2 may be defined as the solution, subject to certain boundary conditions, of the equation

$$\nabla^2 \upsilon(x) = - \sigma_1 \sigma_2 \delta(x) \qquad (3.1)$$

($\delta(x)$ being the Dirac delta function), in one dimension it follows that

$$\upsilon(x) = -\tfrac{1}{2}\,\sigma_1\,\sigma_2\,|x| \quad , \tag{3.2}$$

so that the interaction potential between two positive ions at x,y is $\upsilon_{ii}(x-y)$, between an electron at x and an ion at y is $\upsilon_{ei}(x-y)$, and between two electrons at x,y is $\upsilon_{ee}(x-y)$, where

$$\upsilon_{ii}(x) = -\tfrac{1}{2}\,\eta^2\,\sigma^2|x| \quad , \tag{3.3a}$$

$$\upsilon_{ei}(x) = \tfrac{1}{2}\,\eta\,\sigma^2|x| \tag{3.3b}$$

and

$$\upsilon_{ee}(x) = -\tfrac{1}{2}\,\sigma^2\,|x| \quad . \tag{3.3c}$$

This is clearly a two-species system of the general type discussed in section 8 of chapter 2. As the function space spanned by the potential functions and their derivatives over the domain $(0,\infty)$ consists of all linear functions, it would appear to be necessary to define two functions $G_i(x)$ and $G_e(x)$, each dependent on two variable parameters:

$$G_i(x) = v_i x + t_i$$

and

$$G_e(x) = v_e x + t_e \quad .$$

The statistical mechanical properties can then be determined in terms of the eigenvalues and matrix elements of the differential operators H, K_i and K_e, which involve all the four variables v_i, v_e, t_i and t_e.

However, this procedure is quite unnecessarily complicated and obscures certain simplifications that arise from the linearity of the potential function. Also it is open to objection on more fundamental grounds as it appears to determine the intensive thermodynamic properties of a mixture of ions and electrons in arbitrary proportions when the volume of the system is infinitely large, whereas physically such properties may be expected to exist only when the proportions are such that the gas is electrically neutral.

It is therefore desirable to revert to the basic procedure of chapter 2 and to incorporate the neutrality of the gas into the original equations, rather than attempt to add it as an afterthought.

2.2 Derivation of a recurrence relation between configuration integrals

As the method of chapter 2 is based on differentiation of the limits of integration of the configuration integral, which is equivalent to setting a particle at the point A, it is convenient to consider a system of M ions and N electrons, together with a charge at A. To ensure the neutrality of the system, this charge must be $(N-M\eta)\sigma$.

If the ions are located at the points $x_1,\ldots,x_M$ and the electrons at $y_1,\ldots,y_N$, the total potential energy of the system is E, where

$$E = \tfrac{1}{2}\sigma^2\Big\{-\eta^2\sum_{j<j'}|x_j-x_{j'}| + \eta\sum_{j,k}|x_j-y_k| - \sum_{k<k'}|y_k-y_{k'}|$$

$$- \eta(N-M\eta)\sum_{j}(A-x_j) + (N-M\eta)\sum_{k}(A-y_k)\Big\} \quad , \qquad (3.4)$$

the summations over j and j' being from 1 to M, and those over k and k' from 1 to N.

It is now possible to see the simplifications referred to earlier. Setting x_M (or y_N) equal to A in (3.4) is equivalent to reducing the value of M (or N) by 1, and as (3.4) may be written

$$E = \tfrac{1}{2}\sigma^2(N-M\eta)^2 A + \text{terms independent of } A,$$

differentiation of the integrand $\exp(-E/\varkappa T)$ of the configuration integral with respect to A is equivalent to multiplying it by

$$-\sigma^2(N-M\eta)^2/2\varkappa T \quad .$$

Accordingly, if the configuration integral $Q_{M,N}$ is defined by

$$Q_{M,N} = \frac{1}{M!\ N!} \int_0^A \!\!\cdots\!\! \int dx_1 \cdots dx_M\ dy_1 \cdots dy_N\ \exp(-E/\varkappa T) \quad , \tag{3.5}$$

its derivative with respect to A is given by

$$\frac{\partial}{\partial A} Q_{M,N} = Q_{M-1,N} + Q_{M,N-1} - \frac{\sigma^2}{2\varkappa T} (N-M\eta)^2 Q_{M,N} \quad . \tag{3.6}$$

Together with the boundary condition that

$$Q_{M,N} = \delta_{M,0}\ \delta_{N,0} \tag{3.7}$$

when $A = 0$, the recurrence relation (3.6) completely determines the $Q_{M,N}$ and hence the thermodynamic properties of the system.

2.3 The thermodynamic properties

To investigate the behaviour of the $Q_{M,N}$ when A is large it is convenient to define a generalised grand partition function by

$$f = \sum_{M=0}^{\infty} \sum_{N=0}^{\infty} w^{M+N}\ \eta^{-M}\ e^{-it(N-M\eta)}\ Q_{M,N} \quad , \tag{3.8}$$

for then (3.6) is equivalent to the relation

$$\frac{\partial f}{\partial A} = Hf \quad , \tag{3.9}$$

where the operator H is given by

$$H = \frac{\sigma^2}{2\varkappa T} \frac{\partial^2}{\partial t^2} + w\left(e^{it} + \frac{1}{\eta} e^{-i\eta t}\right) \quad . \tag{3.10}$$

The boundary condition (3.7) becomes that

$$f = 1 \tag{3.11}$$

when $A = 0$, and if η is rational and of the form η_n/η_d, where η_n and η_d are integers, it is apparent from (3.8) that f is a periodic function of t of period $2\pi\eta_d$.

Assuming that it is possible to choose a set of constants b_m such that

$$1 = \sum_m b_m z_m(t) \quad , \tag{3.12}$$

where the $z_m(t)$ are the eigenfunctions of the operator H subject to the periodicity condition, it is apparent from (3.9) and (3.11) that for any value of A,

$$f = \sum_m \exp(\lambda_m A)\, b_m\, z_m(t) \tag{3.13}$$

(λ_m being the eigenvalue of H associated with the eigenfunction $z_m(t)$).

As negating t in (3.10) is equivalent to complex conjugation, the eigenvalues λ_m of H are either real or occur in pairs of complex conjugates. On thermodynamic grounds it is to be expected that there exists an eigenvalue which is real and greater than the real part of any other (when w vanishes this is easily seen to be true), so choosing this to be λ_o, the asymptotic behaviour of f in the limit of A large is given by

$$f \sim \exp(\lambda_o A)\, b_o\, z_o(t) \quad . \tag{3.14}$$

To determine the thermodynamic properties of the real system, i.e. when there is no fixed charge at A, it is desirable to evaluate the grand partition function Z^* obtained by summing the right-hand side of (3.8) only over those values of M and N for which $N = M\eta$. The dependence of f upon t is such that this is readily seen to imply that

$$Z^* = \int_0^{2\pi\eta_d} dt \quad f/2\pi\eta_d \quad , \tag{3.15}$$

so that as

$$\int_0^{2\pi\eta_d} dt\ z_o(t)$$

can be shown to be non-zero, the asymptotic behaviour of Z^* when A is large is such that

$$\lim_{A \to \infty} A^{-1} \log Z^* = \lambda_o \quad . \tag{3.16}$$

The dependence of λ_o on w and T therefore completely determines the thermodynamic properties of the plasma. In particular, the pressure P is given by

$$P/\varkappa T = \lambda_o \quad , \tag{3.17}$$

the total density ρ of all the particles by

$$\rho = w \frac{\partial}{\partial w} \lambda_o \quad , \tag{3.18}$$

and the total internal energy of the system when it contains M ions and N electrons by

$$U/(M+N)\varkappa T = \tfrac{1}{2} + \frac{T}{\rho} \frac{\partial}{\partial T} \lambda_o \quad . \tag{3.19}$$

It is convenient in the following sections to consider not only the total particle density ρ, but also the individual ion and electron densities ρ_i and ρ_e. Clearly these are given by

$$\rho_i = \rho/(1+\eta) \tag{3.20a}$$

and

$$\rho_e = \eta\rho/(1+\eta) \quad . \tag{3.20b}$$

2.4 The distribution functions

The working of sections 2.2 and 2.3 has been concerned only with the configuration integrals over all particle coordinates, rather than with those which are required for the determination of the distribution functions, namely the integrals over all but a finite number of coordinates. The generalization of the working that is necessary in order to include these follows precisely similar lines to that of section 3 of chapter 2. Rather than explicitly perform this generalization with its inevitably complicated notation, it can be stated that if a fugacity w_i is defined for the ion species and a fugacity w_e for the electron species by

$$w_i = w/\eta \tag{3.21a}$$

and

$$w_e = w \quad , \tag{3.21b}$$

and if H is defined not by (3.10), but by the equivalent expression

$$H = \frac{\sigma^2}{2\varkappa T} \frac{\partial^2}{\partial t^2} + w_i K_i + w_e K_e \quad , \tag{3.22}$$

where

$$K_i = e^{-i\eta t} \tag{3.23a}$$

and

$$K_e = e^{it} \quad , \tag{3.23b}$$

so that formally λ_o may be regarded as a function of both w_i and w_e, then the results of section 8 of chapter 2 may be applied immediately to the present case, including the equation (2.128) for the distribution functions.

For numerical work it is convenient to consider not the two-particle ion-ion, electron-ion and electron-electron distribution functions given by (2.128), but the related functions $g_{ii}(x)$, $g_{ei}(x)$ and $g_{ee}(x)$ defined by

$$g_{ii}(x-y) = n_{ii}(x,y) / \rho_i^2 \quad , \tag{3.24a}$$

$$g_{ei}(x-y) = n_{ei}(x,y) / \rho_e \; \rho_i \tag{3.24b}$$

and

$$g_{ee}(x-y) = n_{ee}(x,y) / \rho_e^2 \quad , \tag{3.24c}$$

as these have the advantage of exhibiting the translational invariance explicitly and are normalised so as to tend to unity at large particle separations.

Applying (2.128) and the definitions of the fugacities w_i and w_e, it follows that

$$g_{\alpha\beta}(x) = (w_\alpha w_\beta / \rho_\alpha \rho_\beta) \int_0^{2\pi\eta_d} dt \; z_o(t) \; K_\alpha \; \exp\left\{ (H-\lambda_o)|x| \right\} K_\beta \; z_o(t) \quad , \tag{3.25}$$

where α, β are to be regarded as variable indices, each assuming either of the two 'values' i or e, and $z_o(t)$ is normalised so that

$$\int_0^{2\pi\eta_d} dt \; z_o^2(t) = 1 \quad . \tag{3.26}$$

2.5 The system of equal and opposite charges

When $\eta = 1$ the system is composed of equal numbers of ions of charge σ and electrons of charge $-\sigma$. An interesting study of this system has been made by Eldridge and Feix (1962), using a high-speed computer to follow the motion of the particles; and exact results have been derived by Lenard (1961, 1963), Edwards and Lenard (1962), and Prager (1961) by means of combinatorial analysis and functional integration, so that the results here obtained are identical with these, though the method involves more elementary mathematical techniques.

This case has the advantage that the operator H becomes

$$H = \frac{\sigma^2}{2\varkappa T} \frac{d^2}{dt^2} + 2w \cos(t) \quad , \tag{3.27}$$

which is real and symmetric, so that the eigenvalues and eigenfunctions are all real. Further, the eigenvalue equation is none other than the Mathieu equation, so that the eigenvalues and eigenfunctions may be obtained from tables (N.B.S., 1951).

Accordingly it is quite a simple matter to calculate the thermodynamic properties and two-particle functions. It is readily seen from first principles that these depend in a non-trivial way only on the dimensionless parameter

$$\tau = (\sigma^2 / 4\rho\varkappa T)^{\frac{1}{2}} \quad , \tag{3.28}$$

so the equation of state is plotted in figure 3.1 in the form of the dependence of $P/\rho\varkappa T$ on the parameter τ, and the two-particle functions are plotted in figures 3.2 and 3.3 for $\tau = 0.4$ and 2.0 respectively.

The maximum eigenvalue λ_o of H may be expanded in inverse powers of $w^{\frac{1}{2}}$ when w is large, giving

$$\lambda_o = 2w - (w\sigma^2/2\varkappa T)^{\frac{1}{2}} + \sigma^2/32\varkappa T + \ldots , \qquad (3.29a)$$

and when w is small it may be expanded in powers of w^2, giving

$$\lambda_o = 4w^2\varkappa T / \sigma^2 - 28\, w^4 (\varkappa T / \sigma^2)^3 + \ldots . \qquad (3.29b)$$

(c.f. N.B.S., 1951, pp. xvii and xviii).

These two cases correspond to the high- and low-temperature expansions of the thermodynamic properties. Determining the equation of state from (3.17) and (3.18), it is found that

$$P / \rho\varkappa T = 1 - \tfrac{1}{2}\tau + O(\tau^3) \qquad (3.30a)$$

when $\tau \ll 1$, and

$$P / \rho\varkappa T = \tfrac{1}{2} + 7/(64\,\tau^2) + O(\tau^{-4}) \qquad (3.30b)$$

when $\tau \gg 1$.

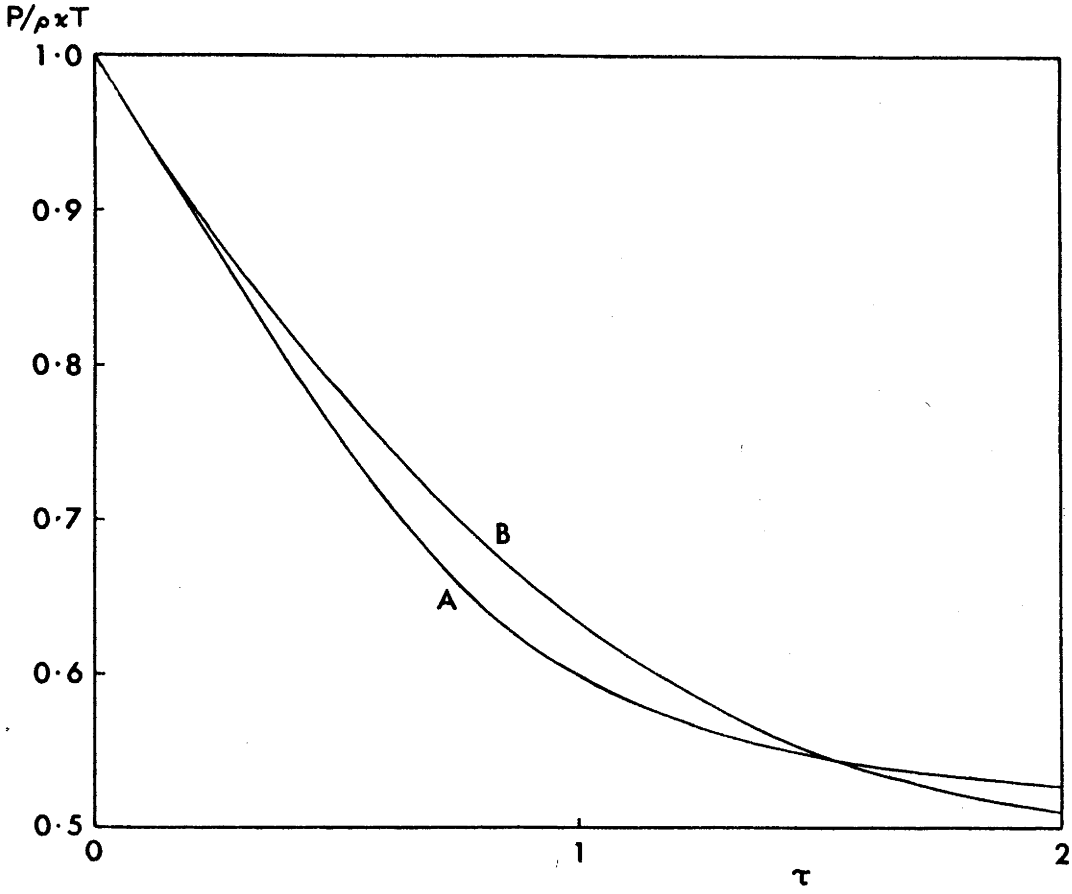

Figure 3.1: The equation of state of a one-dimensional plasma; curve A corresponds to that of a gas of equal and opposite charges, curve B to that of a gas of electrons in a uniform neutralizing charge background. The dimensionless parameter τ is given by $\tau = (\sigma^2/4\rho\kappa T)^{\frac{1}{2}}$.

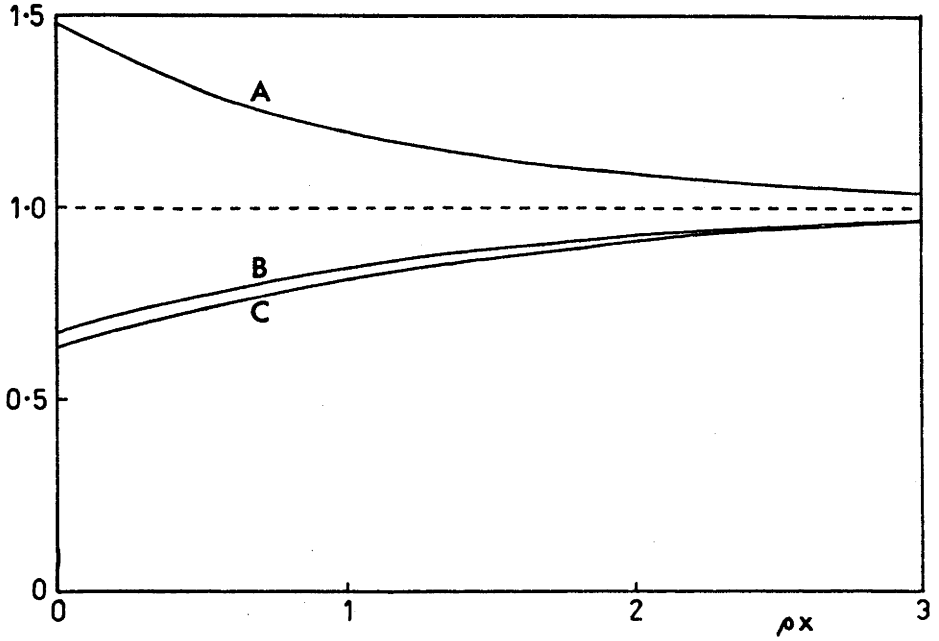

Figure 3.2: Two-particle distribution functions for a one-dimensional plasma with $\tau = 0.4$. Curves A and B are the electron-ion and electron-electron functions for a gas of equal and opposite charges. Curve C is the electron-electron function for a gas of electrons in a uniform neutralizing charge background.

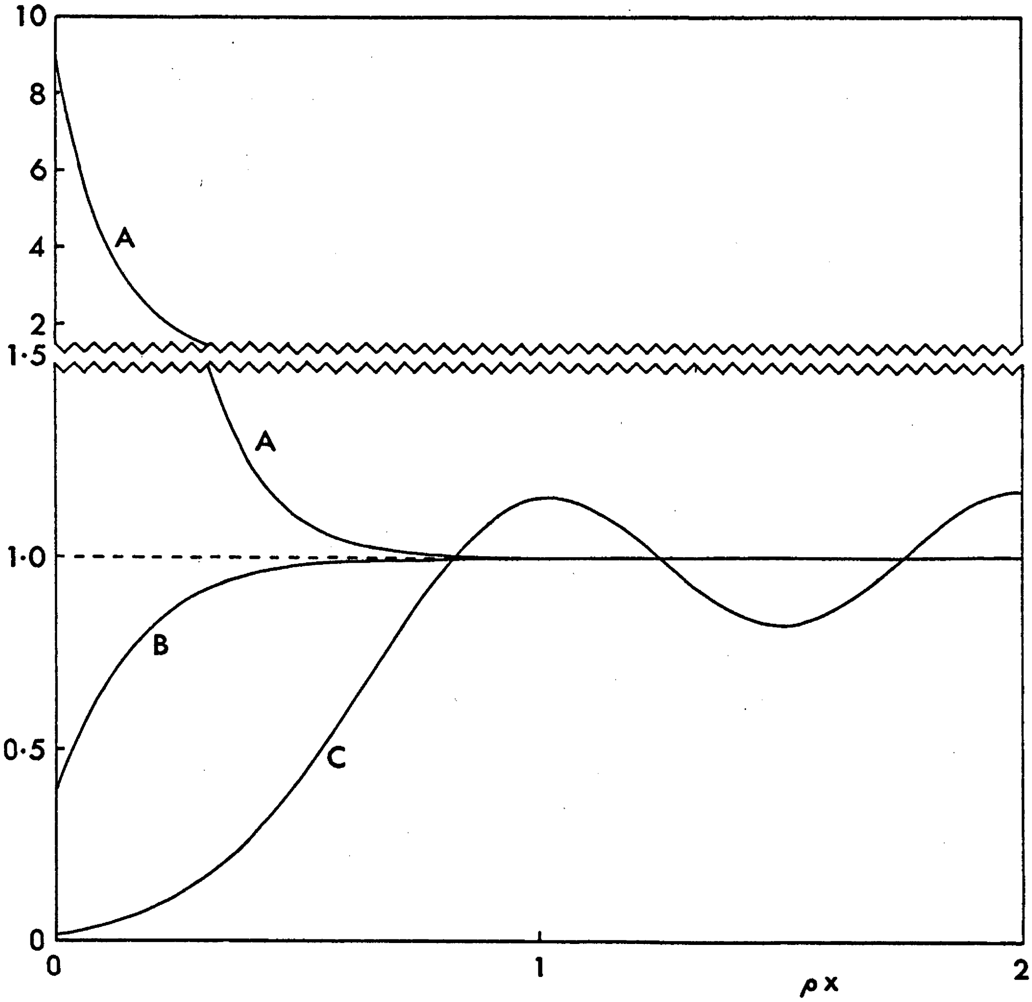

Figure 3.3: Two-particle distribution functions for a one-dimensional plasma with $\tau = 2.0$. Curves A and B are the electron-ion and electron-electron functions for a gas of equal and opposite charges. Curve C is the electron-electron function for a gas of electrons in a uniform neutralizing charge background.

Equation (3.30a) is the result of the Debye-Huckel theory (Debye and Huckel, 1923) and shows that at high temperatures the system behaves as a perfect gas, whereas (3.30b) shows that at low temperatures the behaviour is that of a perfect gas, not of density ρ, but of density $\rho/2$. This may be explained physically by noting that at low temperatures the ions and electrons may be expected to arrange themselves in pairs, forming a gas of neutral atoms.

3. The gas of electrons moving in a uniform background of positive charge

3.1 Discussion of possible methods

As has been pointed out in the introduction to this chapter, it is of interest to consider not only a system of discrete ions and electrons, but also one of electrons moving in a uniform neutralising charge background. There are no less than three possible approaches to such a system and each has its own advantages and disadvantages.

Firstly, there is the method used by Bohm and Pines (1952), Abe (1959) and others, namely to consider a gas of electrons interacting via a potential which has the same Fourier transform $\bar{v}(s)$ as the Coulomb potential, except that $\bar{v}(0)$ is set equal to zero. While this procedure is convenient when applying the prototype graph expansion of Mayer (1950), it does not lend itself to the present techniques and will not be considered further.

Secondly, if η is allowed to tend to zero in the equations of section 2 relating to the discrete charge system, the electrons may be regarded as moving in a neutralising cloud of infinitely fine ion 'dust'. It is shown in section 3.2 that in this limit the ion-ion and electron-ion distribution functions are constant, so that the 'dust' is of uniform density and therefore equivalent to a uniform charge background. This approach yields both the thermodynamic properties and the two-electron function.

Thirdly, the charge background may be explicitly introduced into the model, causing each electron to move in a harmonic potential well centred on the mid-point of the line segment. It will be shown in section 3.3 that the thermodynamic properties of this system may be obtained exactly and are identical with those derived by the second approach. However, this method has the disadvantage that the distribution functions are not translationally invariant.

3.2 The 'dust-cloud' approach

Before taking the limit of η zero in the equations of section 2, care must be taken to avoid a divergence of the canonical partition function arising from the integrations over ion coordinates, which are now physically meaningful only in so far as they are a means of spreading the ions over all available space. It is therefore necessary to divide the partition function by a factor $(2\pi m\varkappa T)^{M/2}A^{M}$, m being the mass of each ion. In addition a term $\sigma^2 A/24$ must be subtracted from the total potential energy to ensure that its minimum value when the ions are uniformly spaced be zero. Together these corrections have the effect of subtracting a term $(\rho_i \varkappa T - \sigma^2/24)$ from the pressure and a term $(M\varkappa T/2 + \sigma^2 A/24)$ from the total internal energy, so that using the relations (3.20) to express the results in terms of the electron density ρ_e, the equations (3.17), (3.18) and (3.19) for the thermodynamic properties become:

$$P / \varkappa T = \lambda_o - \rho_e/\eta + \sigma^2/24\varkappa T \quad , \qquad (3.31)$$

$$\rho_e = \eta \, w \frac{\partial}{\partial w} \lambda_o /(1+\eta) \qquad (3.32)$$

and

$$U / N\varkappa T = \tfrac{1}{2} + \frac{T}{\rho_e} \frac{\partial}{\partial T} \lambda_o - \sigma^2/ 24\rho_e \varkappa T \quad , \qquad (3.33)$$

N being the number of electrons in the system

The equations for the two-particle functions remain unchanged.

As $\eta \rightarrow 0$, it is apparent from (3.10) that the operator H satisfies the limiting relation:

$$\lim_{\eta \to 0} (H - w/\eta) = H' \quad , \qquad (3.34)$$

where

$$H' = \frac{\sigma^2}{2\varkappa T} \frac{d^2}{dt^2} + w\,(e^{it} - it) \quad . \tag{3.35}$$

The eigenvalue condition becomes that the eigenfunctions $z(t)$ must be Fourier analysable over the interval $(-\infty, \infty)$.

It follows that the limit

$$\mu_r = \lim\,(\lambda_r - w/\eta) \tag{3.36}$$

exists for each eigenvalue λ_r of H, and that the quantities μ_r so defined are the eigenvalues of the operator H'. Substituting

$$\lambda_o = \mu_o + w/\eta \tag{3.37}$$

in the equations (3.31), (3.32) and (3.33), it is found that in the limit of η zero the equations become:

$$P\,/\,\varkappa T = \rho_e + (1 - w\tfrac{\partial}{\partial w})\,\mu_o + \sigma^2/\,24\varkappa T \quad , \tag{3.38}$$

$$\rho_e = w \tag{3.39}$$

and

$$U\,/\,N\varkappa T = \tfrac{1}{2} + \frac{T}{\rho_e}\,\frac{\partial}{\partial T}\,\mu_o - \sigma^2/\,24\rho_e\varkappa T \quad . \tag{3.40}$$

As the ions can no longer be regarded as physical particles, the electron density ρ_e is now the total particle density of the system, so that the suffix e may be ignored and the symbol ρ used synonomously with ρ_e. This is convenient when comparing the properties of the charge-background gas with those of the gas of discrete ions and electrons, as such a comparison should be made when the total particle densities of the two systems are the same.

Adopting this procedure, it is desirable to introduce the dimensionless variables

$$S_r = \mu_r/\rho + \sigma^2/24\rho\kappa T \qquad (3.41)$$

and the parameter τ defined by (3.28), i.e.

$$\tau = (\sigma^2/4\rho\kappa T)^{\frac{1}{2}} \quad , \qquad (3.42)$$

for then it follows from (3.35) and (3.41) that the S_r are the values of S such that the equation

$$(2\tau^2 \frac{d^2}{dt^2} + e^{it} - it + \frac{\tau^2}{6})\, z(t) = S\, z(t) \qquad (3.43)$$

has a solution $z(t)$ which is a Fourier analysable function. S_o, the greatest such value, is therefore dependent only on τ and the equations (3.38), (3.39) and (3.40) may be written:

$$P / \rho\kappa T = 1 + \frac{\tau}{2}\frac{d}{d\tau} S_o \quad , \qquad (3.44)$$

and

$$U / N\kappa T = 1 - \frac{\tau}{2}\frac{d}{d\tau} S_o \quad . \qquad (3.45)$$

Though the equation (3.43) has the advantage of exhibiting S_o as the greatest eigenvalue of a symmetric operator, it is desirable from the point of view of numerical work to transform it to a difference-differential equation by setting

$$y(v) = \exp\left\{ 2\,\tau^2(v-\tfrac{1}{2})^3/3 + (S-\tau^2/6)v\right\} \int_{-\infty}^{\infty} dt\, \exp\left\{it(v-\tfrac{1}{2})\right\}\, z_o(t) \tag{3.46}$$

for then it follows from (3.43) that

$$\frac{d}{dv}\, y(v) = \exp(-S-2\tau^2 v^2)\; y(v+1) \quad . \tag{3.47}$$

This equation has real regular solutions which tend to a limit as v tends to either plus or minus infinity, and if the limit at plus infinity is known, then the solution is completely specified. Normalising $y(v)$ so that this limit is unity, it follows that (3.47) may be written in the integral form:

$$y(v) = 1 - \int_{v}^{\infty} dv'\, \exp(-S-2\tau^2 v'^2)\; y(v'+1) \quad . \tag{3.48}$$

As the Fourier transform of $z(t)$ must be bounded, it follows from (3.46) that

$$\lim_{v \to -\infty} y(v) = 0 \quad , \tag{3.49}$$

and this is an eigenvalue condition on the values of S, as may be seen from figure 3.4, where $y(v)$ is plotted for $\tau = 0.4$ and several values of S. It can also be seen that the greatest eigenvalue S_o is that value of S for which the boundary condition (3.49) is satisfied and $y(v)$ is everywhere positive. As the equation (3.48) can readily be solved numerically, S_o may be determined for each value of τ and the thermodynamic properties evaluated by means of (3.44) and (3.45).

In figure 3.1 $P/\rho\varkappa T$ is plotted against τ, together with the corresponding values obtained in section 2.5 for a system of discrete ions and electrons of equal and opposite charge.

The distribution functions

From (3.25), both $g_{ii}(x)$ and $g_{ei}(x)$ depend on the matrix elements of the operator K_i, i.e. of

$$e^{-i\eta t} \quad .$$

As η tends to zero, this operator clearly tends to unity, so that

$$\exp\left\{ (H-\lambda_o)\ |x| \right\} K_i\ z_o(t) \longrightarrow \exp\left\{ (H-\lambda_o)\ |x| \right\} z_o(t)$$

$$\longrightarrow z_o(t) \quad .$$

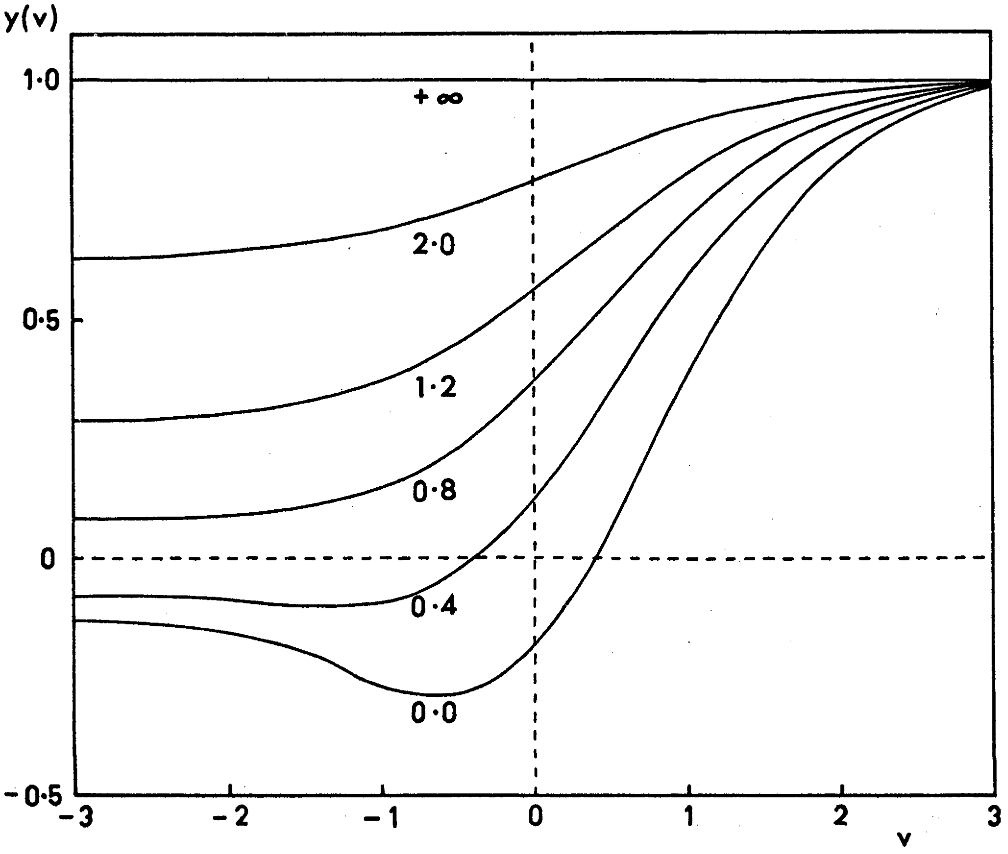

Figure 3.4: The function y(v) (normalized so as to tend to unity as v tends to plus infinity) for $\tau = 0.4$ and $S = +\infty$, 2.0, 1.2, 0.8, 0.4 and 0.0.

Substituting this result in (3.25), it follows that

$$g_{ii}(x) \longrightarrow w_i^2 \,/\, \rho_i^2 \tag{3.50}$$

$$g_{ei}(x) \longrightarrow w_e \, w_i / \rho_e \, \rho_i \int_{-\infty}^{\infty} dt \; z_o(t) \; e^{it} \; z_o(t) \quad , \tag{3.51}$$

so that in this limit both the ion-ion and electron-ion distribution functions are independent of the particle separation, thereby justifying the assumption that the ion-cloud represents a uniform charge background.

The electron-electron function is of course not trivial; using (3.25), (3.34), (3.36) and (3.39), it may be written

$$g_{ee}(x) = \int_{-\infty}^{\infty} dt \; z_o(t) \; e^{it} \; \exp\left\{(H'-\mu_o)\,|x|\right\} \; e^{it} \; z_o(t) \quad . \tag{3.52}$$

To determine this function numerically, it is convenient to define a function $Z(x,t)$ by

$$Z(x,t) = \exp\left\{(H'-\mu_o)\; x\right\} \; e^{it} \; z_o(t) \quad . \tag{3.53}$$

Then in principle $g_{ee}(x)$ may be obtained by evaluating $Z(x,t)$ from the partial differential equation

$$\frac{\partial}{\partial x} Z(x,t) = (H'-\mu_o)\; Z(x,t) \quad , \tag{3.54}$$

together with the boundary condition

$$Z(0,t) = e^{it} \; z_o(t) \quad , \tag{3.55}$$

for then $g_{ee}(x)$, when x is positive, is given by

$$g_{ee}(x) = \int_{-\infty}^{\infty} dt \; z_0(t) \; e^{it} \; Z(x,t) \qquad . \tag{3.56}$$

In practice it is preferable to first apply the transformation (3.46) to $Z(x,t)$, i.e. to define a function $Y(x,v)$ by

$$Y(x,v) = \exp\{2\tau^2(v-\tfrac{1}{2})^3/3 + (S-\tau^2/6)v\} \int_{-\infty}^{\infty} dt \; \exp\{it(v-\tfrac{1}{2})\} \; Z(x,t) \quad , \tag{3.57}$$

for then (3.54) and (3.55) become

$$\left(\frac{1}{\rho}\frac{\partial}{\partial x} + \frac{\partial}{\partial v}\right) Y(x,v) = \exp(-S-2\,\tau^2 v^2)\; Y(x,v+1) \qquad , \tag{3.58}$$

and

$$Y(0,v) = \exp(-S-2\,\tau^2 v^2)\; y_0(v+1) \qquad . \tag{3.59}$$

These two equations completely define $Y(x,v)$ and are quite straightforward to solve numerically. $g_{ee}(x)$ may then be determined from the transformed form of (3.56), only the equation must be presented in a form independent of the normalization of $y_0(v)$, as the condition previously imposed, namely

$$\lim_{v \to +\infty} y_0(v) = 1 \qquad , \tag{3.60}$$

does not correspond with the normalization of $z_0(t)$ required by (3.26). As it can be shown by consideration of (3.35) that

$$\int_{-\infty}^{\infty} dt\ e^{it}\ z_o^2(t) = \int_{-\infty}^{\infty} dt\ z_o^2(t) \quad , \tag{3.61}$$

on transforming (3.56) and the left-hand side of (3.61) $g_{ee}(x)$ is found to be given by:

$$g_{ee}(x) = \frac{\int_{-\infty}^{\infty} dv\ y_o(1+v)\ Y(x,1-v)\ \exp(-2\tau^2 v^2)}{\int_{-\infty}^{\infty} dv\ y_o(1+v)\ y_o(1-v)\ \exp(-2\tau^2 v^2)} \quad . \tag{3.62}$$

The function $g_{ee}(x)$ obtained in this manner is plotted in figures 3.2 and 3.3 for $\tau = 0.4$ and 2.0 respectively. A rather surprising fact emerges from these calculations, namely that the function does not tend to unity when x, the separation between the electrons becomes large; instead it performs undamped oscillations about this value. This behaviour is particularly noticeable at low temperatures, when the amplitude of the oscillations becomes appreciable.

Mathematically this may be understood by a closer inspection of the eigenvalue equation (3.43). If the substitution

$$t \rightarrow t + 2n\pi \quad ,$$

where n is an integer, is made in (3.43), an identical equation is obtained, except that S is replaced by

$$S + 2in\pi \quad .$$

Accordingly, if S_o is the greatest real eigenvalue, $S_o+2in\pi$ is also an eigenvalue, so that the condition that S_o be greater than the real part of any other eigenvalue is violated, and it is this fact which leads to the oscillatory behaviour of $g_{ee}(x)$. Investigation of (3.52) shows that at large particle separations the two-electron function is periodic (of period $1/\rho$) and has maxima at values of x which are integral multiples of $1/\rho$.

Physically this situation is not so unreasonable as it first appears, for the system is no longer a gas with only two-particle interactions. The state of lowest potential energy is that in which the electrons are spaced at equal intervals along the line, and as the one-dimensional Coulomb potential is such that the force on a particle depends only on the total charge on either side of it, the electrons, provided they do not pass one another, oscillate independently about their respective static equilibrium positions. Once one electron is fixed, therefore, all other electrons tend to order themselves so as to be separated from it by an integral multiple of the inter-particle distance $1/\rho$.

This situation is quite different from that of a gas of discrete charges, where each electron tends to coalesce with an ion and then has no effect on any other particle.

Clearly equations such as (1.43), which are meaningful only when the two-particle function tends to a limit for large separations, are not directly applicable to this case. The justification for the use of statistical mechanical formulae derived for a system with only two-particle interaction is that whenever such a difficulty is encountered, η is to be regarded as very small, but finite, and only allowed to tend to zero when the reversal of limit procedures is permissible.

High- and low-temperature approximations

When τ is small, an asymptotic expansion for S_o may be derived from (3.43) by expanding the exponential to second order in t, yielding the well-known equation for the parabolic cylinder functions, and then applying perturbation theory to the remaining terms in the Taylor expansion of the exponential. This procedure shows that:

$$S_o = 1 - \tau + \frac{5}{36}\tau^2 + O(\tau^3) \quad , \qquad (3.63)$$

which from (3.44) implies that

$$P / \rho\varkappa T = 1 - \tfrac{1}{2}\tau + \frac{5}{36}\tau^2 + O(\tau^3) \quad . \qquad (3.64)$$

When τ is large, an expansion for S_o may be derived by solving the integral equation (3.48) by iteration and choosing S so that the boundary condition (3.49) is satisfied. The resulting integrals may be simplified and it is found that

$$\exp(-S_0) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}}\tau + \frac{2}{\pi}\,\tau^2 \int_{2^{-\frac{1}{2}}}^{\infty} dv\, \exp(-2\tau^2 v^2) + 0\{\exp(-2\tau^2)\} \quad . \tag{3.65}$$

Substituting this result in (1,44) it follows that

$$P \,/\, \rho\varkappa T = \tfrac{1}{2} + \tau\, \exp(-\tau^2)/2\pi^{\frac{1}{2}} + 0\{\exp(-2\tau^2)\} \quad . \tag{3.66}$$

The first two terms of the expansion (3.64) are the same as those derived by the Debye-Huckel theory and show that at high temperatures the system behaves as a perfect gas. At low temperatures it is evident from (3.66) that the thermodynamic properties are the same as those of the gas of equal and opposite discrete charges. This behaviour is also that of a system of simple harmonic oscillators, each possessing the 'plasma frequency'

$$(\sigma^2\rho/m)^{\frac{1}{2}} \quad .$$

3.3 The external potential approach

The thermodynamic properties and the two-particle distribution function of a one-dimensional gas of electrons moving in a uniform charge background have been obtained exactly in the previous section. However, the limiting procedure there required is a rather delicate one, so that it is of interest to obtain the results by a more explicit physical picture, namely to consider a system of N electrons of charge $-\sigma$ free to move on the line segment $[0,A]$, together with a uniform distribution of positive charge of magnitude $\rho\sigma$ extending from 0 to A, the particle density being defined in the usual way by

$$\rho = N/A \quad . \tag{3.67}$$

It is apparent that the system is in toto electrically neutral. Also, as the interaction energy of two charges σ_1, σ_2 at x_1, x_2 is

$$-\tfrac{1}{2}\,\sigma_1\,\sigma_2\,|x_1-x_2| \quad ,$$

it is easily verified that the effect of the charge background is to cause each electron to move in a simple harmonic potential well

$$\tfrac{1}{2}\,\sigma^2\,\rho\,(x-A/2)^2$$

centred on the mid-point of the line segment.

If the N electrons have position coordinates $x_1,\ldots,x_N$, the total potential energy E_N of the system is given by

$$2\,E_N\,/\,\sigma^2 = -\sum_{j<k} |x_j-x_k| + \rho\sum_{j}(x_j-A/2)^2 + C \quad , \tag{3.68}$$

where the summations run from 1 to N and C is a term independent of the particle positions.

It is a feature of the statistical mechanics of a system with two-particle interactions that an arbitrary constant may not in general be added to the interaction potential, as this produces a factor of type $\exp(-N^2)$ in the partition function, causing the intensive thermodynamic variables to cease to have a well-defined limit for large N. Thus care must always be taken to choose the additive constant in the potential so that physically meaningful results are obtained. In this case it transpires that the constant C in (3.68) must be given by

$$C = (N-1)N(N+1)/12\rho \quad . \tag{3.69}$$

With this choice of C it follows that when

$$x_1 \leqslant x_2 \leqslant \cdots\cdots \leqslant x_N \quad ,$$

(3.68) may be written

$$E_N = \tfrac{1}{2}\,\sigma^2\,\rho \sum_{j=1}^{N} \left\{ x_j - (2j-1)/2\rho \right\}^2 \tag{3.70}$$

so that the minimum of the total potential energy is zero and is attained when the electrons are spaced along the line at equal intervals $1/\rho$.

As the potential energy does not depend only on the relative coordinates of the electrons, this model clearly cannot yield translation invariant distribution functions. However, it may be expected to provide an adequate description of the thermodynamic properties of the system, so that it is desirable to evaluate the configuration integral

$$Q_N = \frac{1}{N!} \int_0^A \!\!\cdots\!\! \int dx_1 \cdots dx_N \exp(-E_N/\varkappa T) \quad , \qquad (3.71)$$

or rather the function S_o of ρ and T defined by

$$S_o = \lim N^{-1} \log(\rho^N Q_N) \quad , \qquad (3.72)$$

the limit being taken when N and A are large, but ρ, given by (3.67), is constant.

To determine S_o it is convenient to generalise Q_N slightly **and** define

$$Q_N(v) = \frac{1}{N!} \int_0^{(N-\frac{1}{2}+v)/\rho} \!\!\cdots\!\! \int dx_1 \cdots dx_N \exp(-E_N/\varkappa T) \quad , \qquad (3.73)$$

so that $Q_N(\frac{1}{2})$ is the normal configuration integral defined by (3.71).

It is now possible to apply a technique similar to that used in chapter 2, only instead of differentiating the generalised configuration integral with respect to A, N being constant, it is necessary to regard the density ρ as constant and differentiate with respect to v. From (3.73), this is equivalent to multiplying by N/ρ and setting

$$x_N = (N-\tfrac{1}{2}+v)/\rho \qquad . \tag{3.74}$$

x_N must then be greater than or equal to all the other particle coordinates, so substituting (3.74) in the expression (3.70) for the total potential energy, it follows that

$$E_N = E_{N-1} + \sigma^2 v^2/2\rho \qquad . \tag{3.75}$$

Using this result, it readily follows from (3.73) that

$$\frac{d}{dv} Q_N(v) = \exp(-2\tau^2 v^2)\, Q_{N-1}(v+1) \qquad , \tag{3.76}$$

where τ is the dimensionless variable defined by (3.42), i.e. by

$$\tau = (\sigma^2/4\rho\kappa T)^{\frac{1}{2}} \qquad . \tag{3.77}$$

If the function $y(v)$ is defined by

$$y(v) = \sum_{N=0}^{\infty} \rho^N e^{-NS} Q_N(v) \qquad , \tag{3.78}$$

then (3.76) shows that it satisfies the difference-differential equation

$$\frac{d}{dv} y(v) = \exp(-S-2\tau^2 v^2)\, y(v+1) \qquad , \tag{3.79}$$

which is precisely the equation (3.47) encountered when using the dust-cloud approach.

It should be noted that $y(v)$ is not the normal grand partition function, for it is obtained by summing over configuration integrals with different values of N; ρ, rather than A, being constant.

As has been stated in section 3.2, the solution of (3.79) tends to a finite limit as v tends to either plus or minus infinity. If the limit at plus infinity is specified, the solution is uniquely determined. In particular, it is convenient to define the solution which tends to one as v tends to plus infinity to be $y^*(v)$. $y(v)$ is then $y^*(v)$ multiplied by some constant factor.

As v tends to minus infinity, it can be shown that each $Q_N(v)$ tends to a limit which satisfies the inequality

$$\left| \lim_{v \to -\infty} \rho^N Q_N(v) \right| < \frac{1}{N!} (8\tau^2/\pi)^{-N/2} \quad , \tag{3.80}$$

so that as $y(v)$ is known to tend to a limit as v tends to minus infinity, this limit is given by (3.78) and (3.80) to be the sum of an absolutely convergent series and therefore finite. Hence $y(v)$ is given by the equation

$$y(v) = y^*(v)\, y(-\infty)/y^*(-\infty) \quad . \tag{3.81}$$

From (3.72) it follows by the root test for the convergence of a series of positive terms that when $v=\frac{1}{2}$, the right-hand side of (3.78) converges if $S > S_o$, and diverges if $S < S_o$, so that $y(\frac{1}{2})$ becomes infinite when S is equal to S_o. As $y^*(\frac{1}{2})$ and $y(-\infty)$ are always finite, it is apparent from (3.81) that this implies that S_o is the greatest value of S for which $y^*(-\infty)$ vanishes.

As has been shown in chapter 1, the pressure P and the internal energy U of the system are given in terms of the configuration integral Q_N by

$$P/\rho \varkappa T = -\rho \frac{\partial}{\partial \rho} \left(\frac{1}{N} \log Q_N\right) \quad , \tag{3.82}$$

and

$$U/N\varkappa T = \tfrac{1}{2} + T \frac{\partial}{\partial T} \left(\frac{1}{N} \log Q_N\right) \quad , \tag{3.83}$$

so allowing N to tend to infinity, using the equation (3.72), and noting that S_o depends only on the dimensionless parameter τ, it follows that the thermodynamic properties are given by:

$$P/\rho \varkappa T = 1 + \frac{\tau}{2} \frac{d}{d\tau} S_o \quad , \tag{3.84}$$

and

$$U/N\varkappa T = \tfrac{1}{2} - \frac{\tau}{2} \frac{d}{d\tau} S_o \quad . \tag{3.85}$$

Summarising, the thermodynamic properties of a one-dimensional system of electrons moving in a uniform charge background are given by (3.84) and (3.85), where S_o is the greatest value of S such that the solution $y(v)$ of (3.79) tends to zero as v tends to minus infinity. These are precisely the results obtained in section 3.2 and expressed in equations (3.44), (3.45) and (3.47).

4. Discussion of results

Exact expressions have been obtained in this chapter for the thermodynamic properties and distribution functions of both a one-dimensional plasma of discrete electrons and ions, and also one of electrons moving in a uniform charge background. The results for the first case are particularly suitable to numerical investigation when the electrons and ions are of equal and opposite charge.

The equations of state of the two systems are given in figure 3.1 in the form of a plot of $P/\rho\varkappa T$ against the dimensionless parameter τ. It is apparent that the two curves are substantially the same, so that the common procedure of representing a three-dimensional plasma as a gas of electrons moving in a uniform neutralising background of positive charge may be expected to provide a fair approximation to the thermodynamic properties of the real system.

However, this procedure seems unlikely to provide an accurate description of scattering and allied phenomena at low temperatures, for the two-particle functions of the two one-dimensional systems are plotted in figures 3.2 and 3.3 for $\tau = 0.4$ and 2.0 respectively, and it is apparent that the electron-electron functions are of very different character in the second case.

Chapter 4

ONE-DIMENSIONAL GASES WITH HARD CORE REPULSION

1. Introduction

As yet the basic procedure of chapter 2, namely differentiation with respect to A of the configuration integral of the system of particles lying on the line segment $[0, A]$, has been applied only when the interaction potential function $\upsilon(x)$ has derivatives of all orders over the range $(0, \infty)$ and is of course even. This excludes the possibility that $\upsilon(x)$ may contain a hard repulsive core, i.e. may be of the form

$$\begin{aligned} \upsilon(x) &= +\infty , & |x| < b \\ &= \phi(x) , & |x| > b \end{aligned} \quad . \tag{4.1}$$

Potentials of this type are clearly extremely relevant to the consideration of physical systems which contain particles of finite size, particularly when the interaction forces are attractive, as then the size of the particles plays an essential role in ensuring that they do not all coalesce. Further, it is known that when

$$\phi(x) = 0 \tag{4.2}$$

or

$$\phi(x) = - C \exp(-a|x|) \quad , \tag{4.3}$$

the properties of the system are amenable to exact mathematical analysis, the former possibility having been investigated by Tonks (1936) and the latter by Kac (1959), and later by Kac, Uhlenbeck and Hemmer (1963).

It is therefore desirable to attempt to apply the procedure of chapter 2 to systems such as these. In section 2 of this chapter it is shown that application of the technique to the system with interaction potential given by (4.1) and (4.3) leads to an eigenvalue equation, the thermodynamic properties being given by the dependence of the greatest eigenvalue on the fugacity and the temperature. This case is of particular interest, as the method used by Kac (1959) employs the techniques of the theory of stochastic processes and derives the properties in terms of the eigenvalues of an integral equation with a rather complicated kernel, whereas the present procedure involves only the differential calculus and replaces the integral equation by a comparatively simple difference-differential equation.

The extension of the method to include more general forms of the function $\phi(x)$ is also briefly discussed in this section and it is indicated that when $\phi(x)$ satisfies a homogeneous linear differential equation of order p over the range (b,∞), the statistical mechanical properties may be determined in terms of partial difference-differential equations containing at most p variables.

At this stage a difficulty presents itself, for though it remains true that in the limit of A large the grand-partition function behaves as

$$\exp(\lambda_0 A) \quad ,$$

where λ_0 is the greatest eigenvalue of a difference-differential equation, this equation is no longer of the form derived in chapter 2, namely

$$(w\,K + J)\,y = \lambda\,y \tag{4.4}$$

(w being the fugacity and K and J linear operators independent of λ and w). Together with the fact that the general results of chapter 2 were derived on the assumption that the potential function $\upsilon(x)$ has derivatives of all orders over the range $(0,\infty)$, this appears to suggest that they are not applicable when $\upsilon(x)$ contains a hard core.

If this were in fact the case the situation would be very unsatisfactory, particularly as the general results are used to derive the relations (2.118) between the distribution functions and their derivatives with respect to the mean particle density, which relations may be expected to be true for any 'physical' potential. It is therefore instructive to consider the case of a gas of hard rods with no other interaction, as the statistical mechanical properties of this system may be calculated in a very direct manner and compared with the general formalism. In section 3 of this chapter it is shown that though they do not occur explicitly in this working, nevertheless a diagonal matrix H and a symmetric matrix K may be defined such that all the relevant results of chapter 2 are valid in this case. This suggests that though these results may not be the most convenient to use in a given example, they are formally applicable to any one-dimensional gas with two-particle interaction.

2. The thermodynamic properties of a gas of hard rods with exponential attraction

2.1 Derivation of an eigenvalue equation

Consider a system of N particles constrained to lie on the line segment $[0,A]$ and interacting via the potential $\upsilon(x)$ given by (4.1) and (4.3), i.e.

$$\upsilon(x) = +\infty \ , \qquad |x| < b$$

and (4.5)

$$\upsilon(x) = -C\exp(-a|x|) \ , \quad |x| > b \quad .$$

In addition, suppose there acts on the particles an external potential

$$-v\exp\left[-a(A-x)\right] \quad .$$

Then if the particles are situated at $x_1, \ldots, x_N$, the total potential energy of the system may be written $E_N(v,A)$, where

$$E_N(v,A) = \sum_{1 \leqslant j < k \leqslant N} \upsilon(x_j - x_k) - v \sum_{j=1}^{N} \exp\{-a(A-x_j)\} \quad , \tag{4.6}$$

and the configuration integral may be defined as

$$Q_N(v,A) = \frac{1}{N!} \int_0^A \!\!\cdots\!\! \int dx_1 \ldots dx_N \exp\{-E_N(v,A)/\varkappa T\} \quad . \tag{4.7}$$

Consider now the effect of differentiating $Q_N(v,A)$ with respect to A. The symmetry of the integrand of (4.7) ensures that

$$\frac{\partial}{\partial A} Q_N(v,A) = \frac{1}{(N-1)!} \int_0^A \!\!\cdots\!\! \int dx_1 \ldots dx_{N-1} \exp\left\{- \frac{1}{\varkappa T} E_N(v,A)\Big|_{x_N = A}\right\}$$

$$- \frac{1}{N!} \int_0^A \!\!\cdots\!\! \int dx_1 \ldots dx_N \left\{\frac{\partial}{\partial A} E_N(v,A)/\varkappa T\right\} \exp\left\{-E_N(v,A)/\varkappa T\right\}. \tag{4.8}$$

The first term on the right-hand side of this equation is effectively the configuration integral of a system of $(N-1)$ particles with an N th particle fixed at A. As this fixed particle prohibits the others from approaching closer to it than a distance b, the space available to them is no longer the interval $[0,A]$, but rather $[0, A-b]$. When all the $x_1, \ldots, x_N$ lie in this range, it follows from the definition of $\upsilon(x)$ and from the expression (4.6) for the total potential energy that

$$\begin{aligned} E_N(v,A)\Big|_{x_N=A} &= -v + E_{N-1}(v+C,A) \\ &= -v + E_{N-1}\left\{(v+C)e^{-ab},A-b\right\} \quad , \qquad (4.9)\end{aligned}$$

so that the first term becomes

$$e^{v/\varkappa T}\ \frac{1}{(N-1)!}\ \int_0^{A-b}\!\!\cdot\cdot\!\int dx_1\cdot\cdot dx_{N-1}\ \exp\left[-E_{N-1}\left\{(v+C)e^{-ab},A-b\right\}/\varkappa T\right] \quad ,$$

which from (4.7) is

$$e^{v/\varkappa T}\ Q_{N-1}\left\{(v+C)e^{-ab},A-b\right\} \quad .$$

The second term on the right-hand side of (4.8) is readily simplified by noting that

$$\frac{\partial}{\partial A}\ E_N(v,A) = -a\,v\,\frac{\partial}{\partial v}\ E_N(v,A) \quad , \qquad (4.10)$$

so that it may be written

$$-a\,v\,\frac{\partial}{\partial v}\ Q_N(v,A) \quad .$$

Substituting these expressions in (4.7), it follows that the final equation obtained for the derivative of the configuration integral is

$$\frac{\partial}{\partial A}\ Q_N(v,A) = e^{v/\varkappa T}\ Q_{N-1}\left\{(v+C)e^{-ab},A-b\right\} - av\,\frac{\partial}{\partial v}\ Q_N(v,A) \ , \quad (4.11)$$

which if the generalised grand-partition function $f(v,A)$ is defined by

$$f(v,A) = \sum_{N=0}^{\infty} w^N Q_N(v,A) \quad , \qquad (4.12)$$

leads to the equation

$$\frac{\partial}{\partial A} f(v,A) = w\, e^{v/\varkappa T} f\left\{(v+C)e^{-ab}, A-b\right\} - av \frac{\partial}{\partial v} f(v,A) \quad . \qquad (4.13)$$

This equation is of rather similar form to the relation (2.16) derived in chapter 2, namely

$$\frac{\partial}{\partial A} f = H f \quad ,$$

the most significant difference being that the derivative of $f(v,A)$ with respect to A is now determined not only by its values at A, but also by its values at $A-b$. Fortunately this does not affect the separability of the equation with respect to the variables A and v, for it is possible to write the solution in the form

$$f(v,A) = \sum_{m} b_m\, y_m(v) \exp(\lambda_m A) \quad , \qquad (4.14)$$

where the λ_m and $y_m(v)$ are the values of λ and the functions $y(v)$ that simultaneously satisfy the equation

$$\lambda\, y(v) = w\, e^{-\lambda b} e^{v/\varkappa T} y\left\{(v+C)e^{-ab}\right\} - av \frac{d}{dv} y(v) \quad , \qquad (4.15)$$

and the b_m are certain constants determined by the boundary conditions.

A brief consideration of the definitions of $Q_N(v,A)$ and $f(v,A)$ shows that $f(v,A)$ must be a Taylor expandable function of v for all values of A, so that the same must be true of each $y_m(v)$. It turns out that the solution of (4.15) only satisfies this condition for certain values of λ, so that the λ_m form a discrete set of eigenvalues. On thermodynamic grounds it is to be expected that for given w, one of these eigenvalues will be real and greater than the real part of any other. Choosing this to be λ_o, (4.14) shows that when A is large

$$f(v,A) \sim b_o\ y_o(v)\ \exp(\lambda_o A) \quad . \tag{4.16}$$

As the grand-partition function Z^* of the system when there is no external potential is simply $f(0,A)$, it follows that

$$\lim_{A \to \infty} A^{-1} \log Z^* = \lambda_o \tag{4.17}$$

(provided $b_o\ y_o(0)$ is non-zero), so the thermodynamic properties may be derived in the usual way from the dependence of λ_o on w and T, the pressure P being given by

$$P/\varkappa T = \lambda_o \quad , \tag{4.18}$$

the mean particle density ρ by

$$\rho = w \frac{\partial}{\partial w} \lambda_o \tag{4.19}$$

and the total internal energy U by

$$U/N\varkappa T = \tfrac{1}{2} + \frac{T}{\rho} \frac{\partial}{\partial T} \lambda_o \tag{4.20}$$

(N being the number of particles in the system).

2.2 The infinite range phase transition

Kac, Uhlenbeck and Hemmer (1963) have proved that when the parameter C in the above equations is set equal to βa (β being positive) and a allowed to tend to zero, the system exhibits a phase transition, the equation of state in either phase being

$$P/\varkappa T = \rho/(1 - \rho b) - \beta \rho^2/\varkappa T \quad , \tag{4.21}$$

which is of the form derived by van der Waals (1873).

This may also be shown by the present methods, for the eigenvalue equation becomes

$$\lambda\, y(v) = w\, e^{-\lambda b}\, e^{v/\varkappa T}\, y\left\{(v+\beta a)e^{-ab}\right\} - av \frac{d}{dv} y(v) \quad , \tag{4.22}$$

inspection of which indicates that when a is small the solution may be written

$$y(v) = \exp\left\{L(v)/a\right\} \quad , \tag{4.23}$$

where $L(v)$ is a regular function independent of a.

Assuming this to be true, substituting this expression in (4.22) and using the differentiability of $L(v)$, it is obtained that in the limit of a zero

$$\lambda + v\,L'(v) = w\,\exp\left\{-\lambda b + v/\varkappa T + (\beta - bv)L'(v)\right\} \quad . \qquad (4.24)$$

This equation may be put in a more convenient form by setting

$$Y(v) = \frac{\beta - bv}{v}\left\{\lambda + vL'(v)\right\} \qquad (4.25)$$

and

$$X(v) = \frac{\beta - bv}{v}\exp(v/\varkappa T - \lambda\beta/v) \quad , \qquad (4.26)$$

for then it becomes

$$Y(v)\,\exp\left\{-Y(v)\right\} = w\,X(v) \quad . \qquad (4.27)$$

As $X(v)$ is a known function, $Y(v)$ may in principle be determined from (4.27) and then $L'(v)$ from (4.25). However, it is sufficient to consider the general properties of such a solution. As the maximum eigenvalue λ_o must be real, (4.22) shows that $y_o(v)$ may be normalised so as to be everywhere real. In addition to being continuous, $L'(v)$ is therefore also real, and these two conditions can now be shown to be all that is required to determine λ_o in the limit of a zero.

Inspection of (4.26) shows that $X(v)$ has the form sketched in figure 4.1, where it is apparent

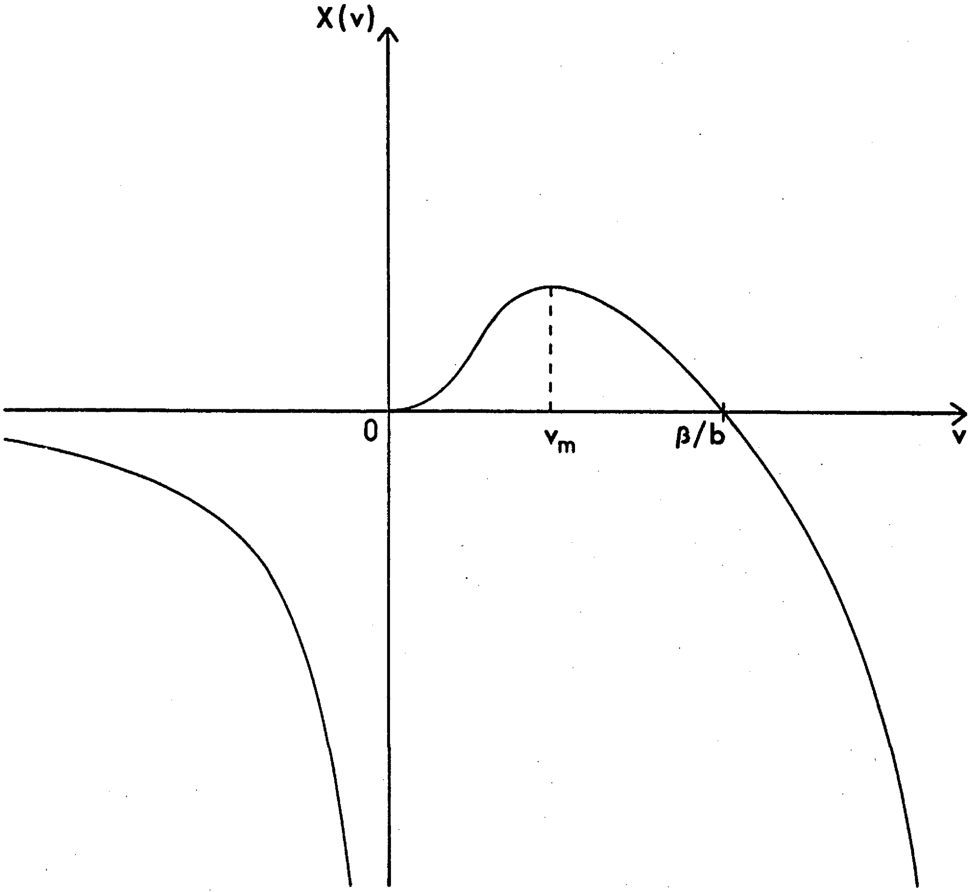

Figure 4.1: The form of the function X(v).

that it is positive only in the range

$$0 < v < \beta/b$$

and there attains its maximum.

(4.27) shows that this maximum value must be e^{-1}/w, for if it is greater there must exist a neighbourhood in which the equation has only complex solutions for $Y(v)$, and if it is less $Y(v)$ can never attain the value 1, which is impossible as, from (4.25),

$$\begin{aligned} Y(v) &\longrightarrow +\infty \qquad \text{as} \quad v \longrightarrow 0^+ \quad , \\ &= 0 \qquad \text{when} \quad v = \beta/b \end{aligned}$$

and must be continuous in between.

The eigenvalue equation is therefore

$$\max X(v) = e^{-1}/w \quad , \tag{4.28}$$

which if v_m is the value of v that maximises $X(v)$ may be written in the form of the two equations

$$\frac{d}{dv} X(v) \Big|_{v=v_m} = 0 \tag{4.29}$$

and

$$X(v_m) = e^{-1}/w \quad . \tag{4.30}$$

The equation of state may now be determined by regarding v_m as the independent variable, for if the temperature T is supposed to be constant,

$$P/\varkappa T = \lambda_o \tag{4.31}$$

and

$$\rho = w \frac{d}{dw} \lambda_o$$

$$= w \frac{d\lambda_o}{dv_m} \Big/ \frac{dw}{dv_m} \quad . \qquad (4.32)$$

But differentiating (4.30) logarithmically with respect to v_m, using (4.29) and noting that $X(v_m)$ depends on λ_o, which is now to be regarded as a function of v_m, it follows that

$$\left\{ \frac{\partial}{\partial \lambda} \log X(v) \Big|_{v=v_m} \right\} \frac{d\lambda_o}{dv_m} = - w^{-1} \frac{dw}{dv_m} \quad , \qquad (4.33)$$

which from the explicit form (4.26) of $X(v)$ can be seen to imply that

$$\frac{\beta}{v_m} \frac{d\lambda_o}{dv_m} = w^{-1} \frac{dw}{dv_m} \quad . \qquad (4.34)$$

Substituting this result in (4.32), it is found that v_m bears a very simple relation to the particle density, namely

$$\rho = v_m / \beta \quad . \qquad (4.35)$$

The equation of state may now be derived by eliminating v_m between (4.35) and the explicit form of (4.29). It is a trivial calculation to verify that

$$P/\varkappa T = \rho/(1 - b\rho) - \beta \rho^2 / \varkappa T \quad , \qquad (4.36)$$

which is the van der Waals equation (4.21) obtained by Kac, Uhlenbeck and Hemmer (1963).

Although this equation is exact when it is applicable, it clearly needs to be modified, for if

$$\varkappa T < 8\beta / 27b \quad , \tag{4.37}$$

there are values of ρ between 0 and b^{-1} for which (4.36) gives

$$\frac{\partial}{\partial \rho} P/\varkappa T < 0 \quad , \tag{4.38}$$

which is thermodynamically impossible. This anomaly may be resolved by consideration of the behaviour of λ_o as a function of w. When

$$\varkappa T > 8\beta / 27b \tag{4.39}$$

λ_o increases monotonically with w, but if the temperature is low enough for the converse inequality (4.37) to hold, the graph takes the form shown in figure 4.2, where it is apparent that for certain values of w, λ_o is a three-valued function. As it is defined to be the greatest possible value for given w, the cusped section of the curve must be ignored and the physically significant graph has a discontinuity in its derivative at a certain point. It is this behaviour that leads to the phase transition, and the resulting isotherm is plotted in figure 4.3.

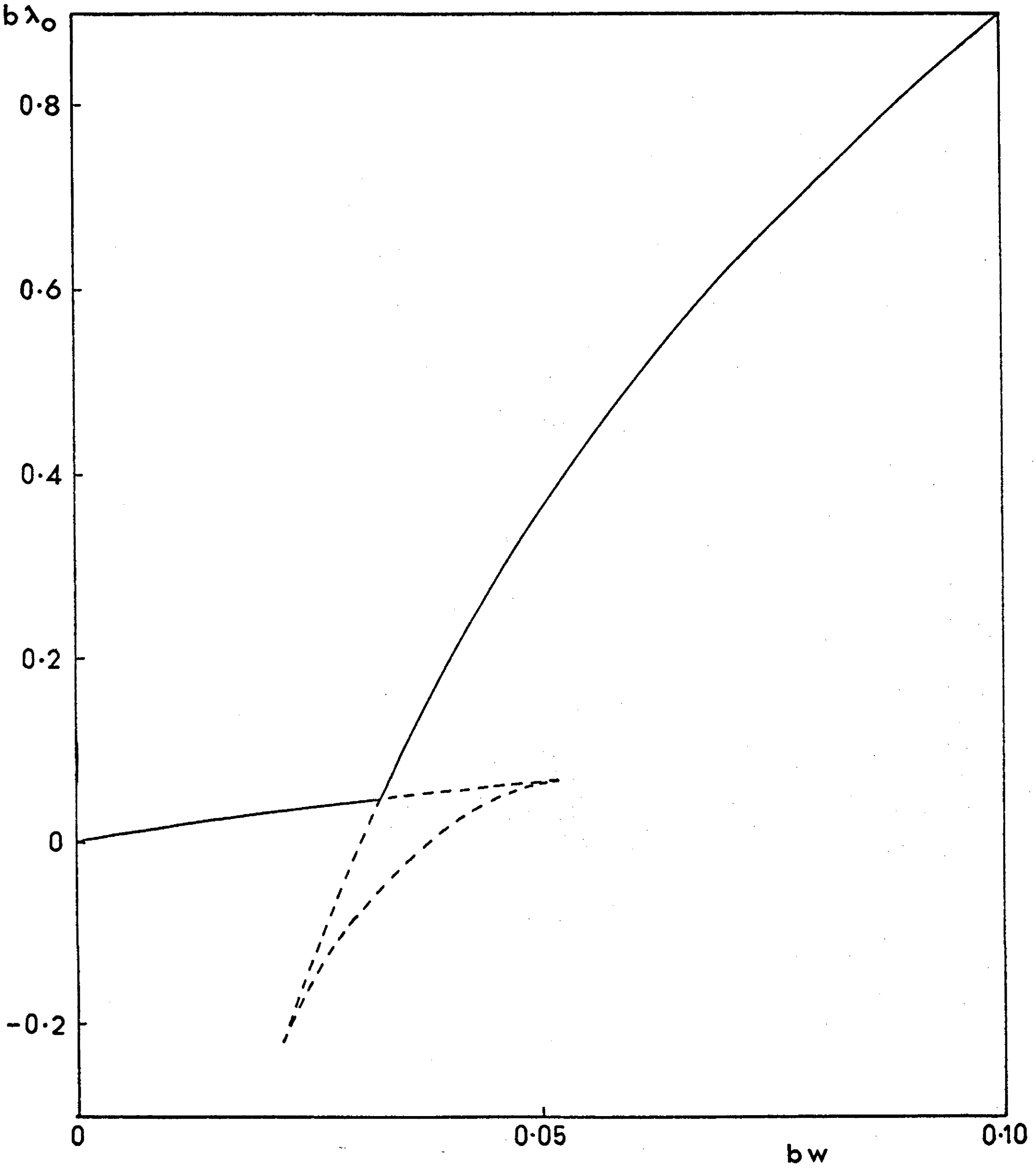

Figure 4.2: The eigenvalue λ_o as a function of the fugacity w for the gas of hard rods with infinite-range exponential attraction ($\beta/b\varkappa T = 343/72$). The broken curves correspond to real eigenvalues which are less than λ_o.

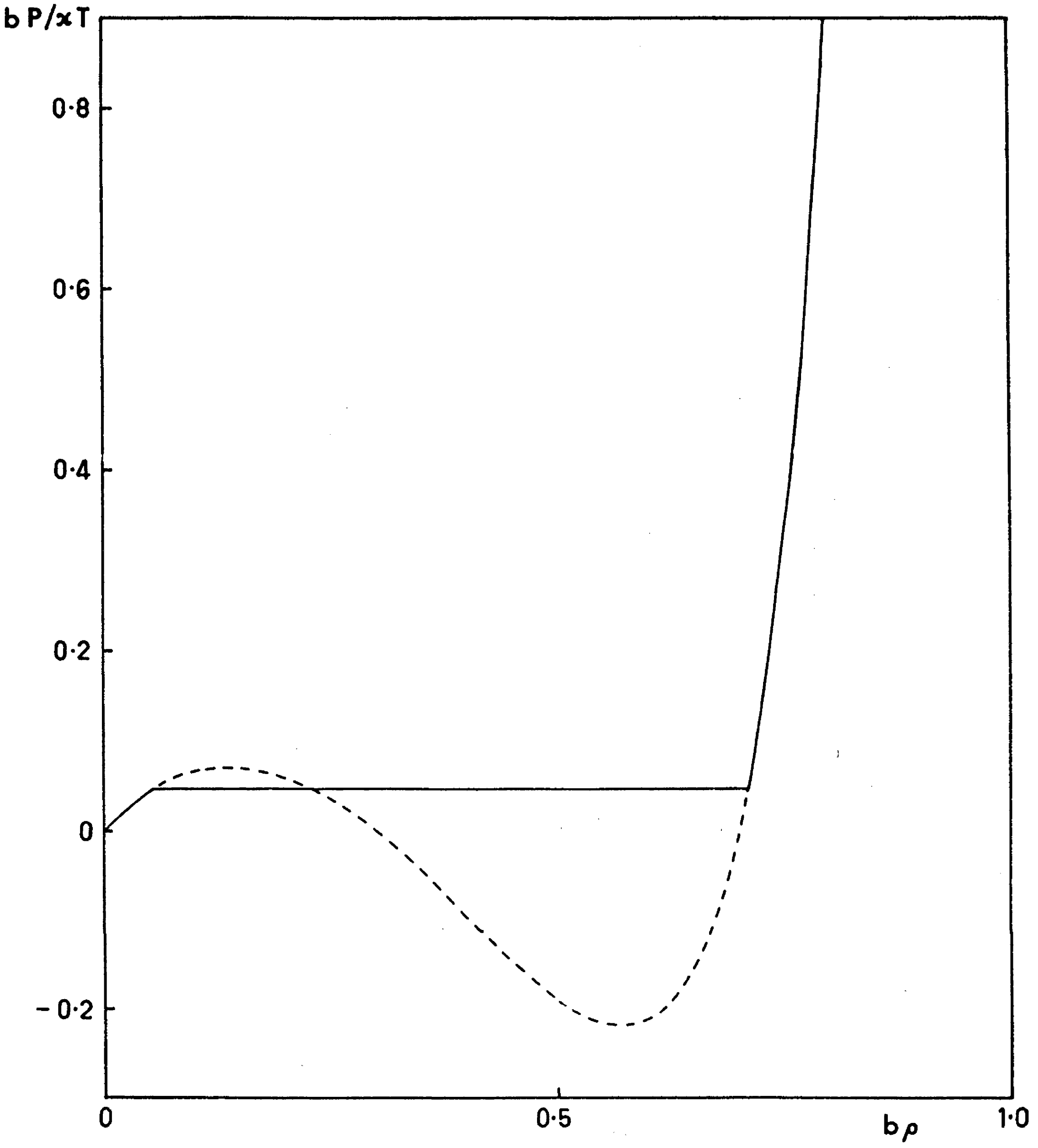

Figure 4.3: A two-phase isotherm for the gas of hard rods with infinite-range exponential attraction ($\beta/b\varkappa T = 343/72$). The broken curve is the unphysical isotherm obtained by applying (4.36) in the transition region.

2.3 The extension to more general potentials

When the interaction potential is of the form (4.1), i.e. when it contains a hard core of radius b together with a potential $\phi(x)$ outside the core, and when $\phi(x)$ is not necessarily given by (4.3), but satisfies a homogeneous linear differential equation of order p, it is quite straightforward to generalise the working of section 2.1 of this chapter, it merely being necessary to introduce an applied external potential of the form

$$v_1 \phi(x) + v_2 \phi'(x) + \dots\dots + v_p \phi^{(p-1)}(x)$$

and to regard $v_1, \dots, v_p$ as arbitrary parameters.

A recurrence relation between the configuration integrals, considered as functions of A and $v_1, \dots, v_p$, may then be established, and this leads to an equation for the generalised grand-partition function $f(A)$ of the form

$$\frac{\partial}{\partial A} f(A) = w K^* f(A-b) + J^* f(A) \quad , \tag{4.40}$$

where K^* and J^* are linear operators involving only the variables $v_1, \dots, v_p$.

This equation is separable, it being possible to write the solution in the form

$$f(A) = \sum_m b_m y_m \exp(\lambda_m A) \quad , \tag{4.41}$$

where the λ_m and y_m are the eigenvalues and eigenfunctions respectively of the equation

$$\lambda\, y = w\, e^{-\lambda b} K^* y + J^* y \quad . \tag{4.42}$$

On thermodynamic grounds one of these eigenvalues must be real and greater than the real part of any other, so choosing this to be λ_o, (4.41) shows that when A is large the grand-partition function is proportional to $\exp(\lambda_o A)$. The thermodynamic properties are then given by (4.18), (4.19) and (4.20).

The calculation of the distribution functions follows similar lines to those of section 3 of chapter 2, but is rather complicated by the fact that the eigenfunctions of (4.42) for given w are not linearly independent. Nevertheless it is possible to define an operator K such that the distribution functions are given by (2.29).

If H is defined as a diagonal matrix with elements λ_m, it follows that the formulae (2.25) to (2.29) for the statistical mechanical properties are valid when the interaction contains a hard core. To complete the identification of the present results with those of chapter 2, it is only necessary to establish the relations (2.103) and (2.104) between the matrix elements of H and K and their derivatives with respect to fugacity.

In general this is a rather difficult problem, but in the next section it is shown that when $\upsilon(x)$ consists of a hard core with no other interaction, the matrices H and K may be written down explicitly and the relations verified.

3. The gas of non-interacting hard rods

3.1 Derivation of the r-particle grand-partition function

The properties of a one-dimensional gas of hard rods of length b constrained to lie on the line-segment $[0,A]$ are of course well-known, the thermodynamic properties having been derived by Tonks (1936) and the distribution functions by Salsburg, Zwanzig and Kirkwood (1953). If the r-particle grand-partition function Z_r^* is defined by

$$Z_r^* = \sum_{N=r}^{\infty} \frac{w^N}{(N-r)!} \int_0^A \cdots \int dx_{r+1} \dots dx_N \exp(-E_N/\varkappa T) \quad , \tag{4.43}$$

where

$$E_N = \sum_{1 \leqslant j < k \leqslant N} \upsilon(x_j - x_k) \tag{4.44}$$

and

$$\begin{aligned} \upsilon(x) &= +\infty , & |x| &< b \\ &= 0 & |x| &> b \quad , \end{aligned} \tag{4.45}$$

the integral on the right-hand side may be calculated explicitly.

If

$$A > x_1 > \cdots > x_r > 0$$

and p_1 particles lie between A and x_1, p_2 between x_1 and x_2, etc., the contribution to the integral arising from this configuration can be seen to be

$$c_{p_1 \cdots p_{r+1}} = (A-x_1-p_1 b)^{p_1} (x_1-x_2-b-p_2 b)^{p_2} \cdots$$

$$\cdots(x_{r-1}-x_r-b-p_r b)^{p_r} (x_r-p_{r+1} b)^{p_{r+1}} \quad , \qquad (4.46)$$

provided all the bracketed expressions are positive. Should one be negative, $c_{p_1 \cdots p_{r+1}}$ vanishes.

As the number of ways in which such an arrangement can occur is

$$\frac{(N-r)!}{p_1! \cdots p_{r+1}!}$$

it follows that

$$Z_r^* = w^r \sum_{p_1 \cdots p_{r+1}} \frac{w^{p_1+\cdots+p_{r+1}}}{p_1! \cdots p_{r+1}!} c_{p_1 \cdots p_{r+1}} \quad , \qquad (4.47)$$

where the summation, originally over all values of N not less than r and those non-negative values of the p_j such that

$$p_1 + \cdots + p_{r+1} = N-r \quad , \qquad (4.48)$$

may now be regarded as being over all non-negative values of the p_j, (4.48) being a definition of N, rather than a restriction on their values.

As $c_{p_1 \cdot\cdot p_{r+1}}$ is factorisable, the same is true of the summation on the right-hand side of (4.47), so that Z_r^* may be written

$$Z_r^* = w^r \, L(x_r+b) \, L(x_{r-1}-x_r) \cdots\cdots \, L(x_1-x_2) \, L(A-x_1+b) \qquad , \quad (4.49)$$

where

$$L(x) = \sum_{p=0}^{\infty} \frac{w^p}{p!} \left\{x-(p+1)b\right\}^p \, \epsilon\left\{x-(p+1)b\right\} \qquad , \qquad (4.50)$$

the function $\epsilon(x)$ being defined by

$$\begin{aligned} \epsilon(x) &= 0 \quad , \quad x < 0 \\ &= 1 \quad , \quad x \geqslant 0 \quad . \end{aligned} \qquad (4.51)$$

The normal grand-partition function is simply

$$Z_o^* = L(A + 2b) \qquad . \qquad (4.52)$$

3.2 The thermodynamic properties and distribution functions

As yet the working appears to be quite different from the general formulation of chapter 2. The first clue as to their connection is afforded by an attempt to derive the thermodynamic properties from Z_o^*, for then it is necessary to evaluate

$$\lim_{A \to \infty} A^{-1} \log Z_o^* \quad .$$

The known existence of this limit suggests that Z_o^*, considered as a function of A, may be written as a sum of exponentials. If this is so, the same must be true of $L(x)$.

Investigation of the Laplace transform of $L(x)$ shows that this is in fact the case, and that

$$L(x) = \sum_m R_m \exp(\lambda_m x) \quad , \tag{4.53}$$

where the R_m and λ_m are defined by the identity

$$\sum_m \frac{R_m}{\lambda - \lambda_m} \equiv \frac{1}{\lambda\ e^{\lambda b} - w} \quad . \tag{4.54}$$

The λ_m are therefore the roots of the equation

$$\lambda\ e^{\lambda b} = w \quad . \tag{4.55}$$

Consideration of these roots shows that as w is positive there is only one real root, and this is greater than the real part of any of the complex roots. Choosing this to be λ_o, it follows that when A is large

$$Z_o^* \sim R_o \ \exp\{\lambda_o(A + 2b)\} \quad , \tag{4.56}$$

so that in the usual way the equation of state is given by

$$P/\varkappa T = \lambda_o \tag{4.57}$$

and

$$\rho = w \frac{d}{dw} \lambda_o \quad . \tag{4.58}$$

Using the fact that λ_o satisfies the equation (4.55), it is readily obtained that

$$P/\varkappa T = \rho/(1 - \rho b) \quad , \tag{4.59}$$

which is the equation of state derived by Tonks (1936).

The r-particle distribution function is known from section 2.3 of chapter 1 to be

$$n(x_1,\ldots,x_r) = Z_r^* \,/\, Z_o^* \quad , \tag{4.60}$$

where the right-hand side is to be evaluated when $A-x_1$ and x_r are large, so that surface effects are neglected. In this limit it follows from (4.49) and the asymptotic behaviour of $L(x)$ that

$$Z_r^* \sim w^r \; R_o^2 \; \exp\{\lambda_o(A+2b+x_r-x_1)\} \prod_{j=1}^{r-1} L(x_j-x_{j+1}) \quad , \tag{4.61}$$

so substituting this expression in (4.60) and using (4.56), the distribution function is found to be

$$n(x_1,\ldots,x_r) = R_o \exp\{\lambda_o(x_r-x_1)\} \prod_{j=1}^{r-1} L(x_j-x_{j+1}) \quad . \tag{4.62}$$

To establish the connection between this result and the general formulae of chapter 2, it is only necessary to substitute the form (4.53) of $L(x)$, giving

$$n(x_1,\dots,x_r) = \sum_{m_1\dots m_{r-1}} R_o\, R_{m_1} \dots R_{m_{r-1}}$$

$$\exp\left\{\lambda_o (x_r - x_1) + \sum_{j=1}^{r-1} \lambda_{m_j} (x_j - x_{j+1})\right\} , \qquad (4.63)$$

which, if a set of matrix elements $K_{m,n}$ are defined by

$$K_{m,n} = (R_m\, R_n)^{\frac{1}{2}} , \qquad (4.64)$$

is precisely the equation (2.29).

It is now apparent that a diagonal matrix H with elements

$$H_{m,n} = \lambda_m\ \delta_{m,n} \qquad (4.65)$$

and a symmetric matrix K may be defined such that the statistical mechanical properties of this system are given by the general results of chapter 2. To complete the link it only remains to note that the identity (4.54) may be used to establish the relations

$$\frac{d}{dw}\ \lambda_m = R_m \qquad (4.66)$$

and

$$\frac{d}{dw}\ R_m = 2\, R_m \sum_{n \neq m} \frac{R_n}{\lambda_m - \lambda_n} , \qquad (4.67)$$

which from the definition (4.64) of the $K_{m,n}$ imply that

$$\frac{d}{dw}\lambda_m = K_{m,m} \tag{4.68}$$

and

$$\frac{d}{dw}K_{m,n} = \sum_{\ell \neq m} \frac{K_{m,\ell}K_{\ell,n}}{\lambda_m - \lambda_\ell} + \sum_{\ell \neq n} \frac{K_{m,\ell}K_{\ell,n}}{\lambda_n - \lambda_\ell} \ . \tag{4.69}$$

These last two relations are precisely the equations (2.103) and (2.104) derived in chapter 2 for the derivatives of the matrix elements with respect to the fugacity w, so that all the exact general formulae of chapter 2 apply to the gas of non-interacting hard rods.

4. Discussion of results

Two distinct conclusions may be drawn from the results of this chapter: firstly, that the procedure of differentiating the configuration integral of a one-dimensional gas with respect to its 'volume' A is capable of yielding exact expressions for the statistical mechanical properties when the interaction potential consists of a hard core with an interaction outside it that satisfies a homogeneous linear differential equation of finite order; and secondly, that the general formulae of chapter 2 expressing the properties in terms of the eigenvalues of an operator H and the matrix elements of an associated operator K apply even when the condition originally imposed, namely that the potential function have derivatives of all orders over the range $(0,\infty)$, is violated.

The first result implies that the thermodynamic properties of systems such as a one-dimensional plasma with charges of finite size and a gas of hard rods with exponential attraction can be obtained exactly. The second of these examples is of particular interest, as Kac, Uhlenbeck and Hemmer (1963) have shown that it exhibits a phase transition when the range of the attraction is allowed to become infinite. In section 2.2 this transition has been investigated and found to be associated with the crossing of the two greatest eigenvalues of the operator H at some critical value of the fugacity. This behaviour of the eigenvalues may be expected to be responsible for any one-dimensional phase transition. Unfortunately such transitions must always be of an artificial character, as it is known that they cannot occur for any 'physical' potential (Landau and Lifshitz, 1958; van Hove, 1950).

Chapter 5

LATTICE GASES

1. Introduction

It is sometimes convenient when considering the statistical mechanics of a gas of particles to suppose not that they can occupy any position in a given spatial domain, but that they can only lie on a certain discrete set of sites in a lattice. Such a procedure is obviously relevant to the discussion of a crystalline solid, but may also be supposed to include the normal continuum gas as a limiting case when the sites are uniformly spaced and the density of sites is much greater than the density of particles.

The mathematical analysis of the grand-partition function of such a gas is of different character to that of a continuum gas in so far as attention is necessarily diverted from the behaviour of the particles to that of the sites. This change of emphasis is illustrated by the fact that in section 3 of this chapter it is shown that it is possible to transform the grand-partition function to an integral over a set of variables associated with the sites. This transformation has the property that the interaction between the particles no longer occurs in the form of a matrix $\underline{V}$, with elements $V_{j,k}$ representing the interaction potential between a particle at the j th site with one at the k th, but in the form of the inverse matrix $\underline{V}^{-1}$.

In section 4 it is shown that for a certain class of interactions of considerable physical interest the inverse matrix is of a much simpler form than the original, only the diagonal and one-off diagonal elements being non-zero. The calculation of the grand-partition function in such a case therefore follows very similar lines to that of the partition function of an Ising lattice (Ising, 1925), where each site interacts only with its nearest neighbours. It is possible to determine the thermodynamic properties exactly in the one-dimensional case, but in two or higher dimensions the problem becomes one of calculating the asymptotic behaviour of the maximum eigenvalue of an m-fold operator in the limit of m large. Unfortunately the resemblance to the Ising model is not sufficiently close to enable the methods used by Onsager (1944) and Kaufman (1949) to be applicable.

2. The grand-partition function of a lattice gas

When considering a D-dimensional lattice it is necessary to use D integers to specify each site. Clearly a large number of geometric types of array are possible, but the simplest, and the one that will be considered here, is the D-dimensional analogue of the rectangular lattice, with sites at the points

$$\begin{aligned} x_1 &= j_1 u_1 \quad , & j_1 &= 1,\ldots,m_1 \quad , \\ x_2 &= j_2 u_2 \quad , & j_2 &= 1,\ldots,m_2 \quad , \\ &\ldots & &\ldots \\ x_D &= j_D u_D \quad , & j_D &= 1,\ldots,m_D \quad , \end{aligned} \qquad (5.1)$$

where $u_1,\ldots,u_D$ are constants specifying the spacing of the lattice. Such a lattice may be said to have sides of length

$$\begin{aligned} A_1 &= m_1 u_1 \quad , \\ A_2 &= m_2 u_2 \quad , \\ &\ldots \\ A_D &= m_D u_D \quad , \end{aligned} \qquad (5.2)$$

and is confined in a volume

$$A_1 \ldots A_D = m_1 \ldots m_D \, u_1 \ldots u_D \quad . \qquad (5.3)$$

In the following work the symbols j and k will be used to represent the ordered sets $(j_1,\ldots,j_D)$ and $(k_1,\ldots,k_D)$, so that the j th site is that which has position coordinates given by (5.1), and similarly the k th site has coordinates

$$x_\alpha = k_\alpha u_\alpha \quad , \qquad \alpha = 1,\ldots,D \quad .$$

Suppose that N particles are distributed so that N_j lie on the j th site. Then as the interaction energy between a particle on the j th site and one on the k th is $V_{j,k}$, the total potential energy is

$$E = \tfrac{1}{2} \sum_{j} \sum_{k} N_j V_{j,k} N_k - \tfrac{1}{2} \sum_{j} V_{j,j} N_j \quad , \qquad (5.4)$$

where the summations over j and k in this and all subsequent equations of this section range over all ordered sets $(j_1, \ldots, j_D)$ and $(k_1, \ldots, k_D)$ such that

$$1 \leqslant j_\alpha \leqslant m_\alpha$$

and

$$1 \leqslant k_\alpha \leqslant m_\alpha \quad , \quad \alpha = 1, \ldots, D \quad .$$

The second term on the right-hand side of (5.4) occurs as self-energy terms are to be neglected.

As the probability of such an arrangement of the particles is

$$\frac{N!}{\prod_j N_j!} \quad ,$$

the canonical partition function may be defined as

$$Q_N = (u_1 \ldots u_D)^N \sum_{N_j} \frac{N!}{\prod_j N_j!} \exp(-E/\varkappa T) \quad , \qquad (5.5)$$

where the summation is over all non-negative values of the N_j such that

$$\sum_j N_j = N \tag{5.6}$$

and the factor $(u_1 \cdot\cdot u_D)^N$ is introduced to ensure that in the limit of the density of sites becoming infinite Q_N reduces to the configuration integral of the continuum case.

The grand-partition function may now be defined as

$$Z^* = \sum_{N=0}^{\infty} \frac{w^N}{N!} Q_N \quad , \tag{5.7}$$

w being the fugacity, and the thermodynamic properties obtained in the manner indicated in section 2.3 of chapter 1, the pressure P being given by

$$P/\varkappa T = (u_1 \cdot\cdot u_D)^{-1} \lim_{\substack{m_1 \to \infty \\ \cdots\cdots \\ m_D \to \infty}} (m_1 \cdot\cdot m_D)^{-1} \log Z^* \quad , \tag{5.8}$$

the mean particle density ρ by

$$\rho = w \frac{\partial}{\partial w} P/\varkappa T \quad , \tag{5.9}$$

and the total internal energy U of the N-particle system by

$$U/N\varkappa T = D/2 + \rho^{-1} T \frac{\partial}{\partial T} P/\varkappa T \quad . \tag{5.10}$$

3. The transformation of the grand-partition function

To transform the grand-partition function Z^* into a more convenient form it should first be noted that from the definition (5.5) of Q_N, (5.7) may be written

$$Z^* = \sum_{N_j} \frac{(u_1 \cdot\cdot u_D \; w)^{\sum_j N_j}}{\prod_j N_j!} \exp(-E/\varkappa T) \quad , \qquad (5.11)$$

where the summation is now over all non-negative values of the N_j, (5.6) being a definition of N, rather than a restriction on their values.

Also, as $V_{j,k}$ can for a system with no external forces depend only on $j-k$, i.e. on the ordered set $(j_1-k_1, \ldots, j_D-k_D)$, all the $V_{j,j}$ are equal, so that from (5.4) and (5.6),

$$E = \tfrac{1}{2}\, \underline{N}' \, \underline{V} \, \underline{N} - \tfrac{1}{2} N V_{j,j} \quad , \qquad (5.12)$$

where $\underline{N}$ is an $m_1 \ldots m_D$ -dimensional vector with elements N_j and an obvious matrix notation has been adopted (though no summation convention).

Substituting this expression for E in (5.11), it follows that

$$Z^* = \sum_{N_j} \frac{(u_1 \cdot\cdot u_D \; w')^{\sum_j N_j}}{\prod_j N_j!} \exp(-\, \underline{N}' \, \underline{V} \, \underline{N} \, / \, 2\varkappa T) \quad , \qquad (5.13)$$

where

$$w' = w \exp(V_{j,j} / 2\varkappa T) \quad . \tag{5.14}$$

The trick required to transform this equation for the grand-partition function into a more useful form was noticed by Edwards (1959), who pointed out that as $\underline{V}$ is a symmetric matrix,

$$\exp(-\underline{N}'\underline{V}\,\underline{N}/2\varkappa T) = \frac{\int_{-\infty}^{\infty}\!\cdot\!\cdot\!\int \prod_j (dt_j)\, \exp(-\tfrac{1}{2}\varkappa T\; \underline{t}'\underline{V}^{-1}\underline{t} + i\,\underline{N}'\underline{t})}{\int_{-\infty}^{\infty}\!\cdot\!\cdot\!\int \prod_j (dt_j)\, \exp(-\tfrac{1}{2}\varkappa T\; \underline{t}'\underline{V}^{-1}\underline{t})} \tag{5.15}$$

(as may be seen by applying the change of variables

$$\underline{t} = \underline{s} + i\,\underline{V}\,\underline{N} / \varkappa T \tag{5.16}$$

in the integral which is the numerator of the right-hand side).

It is therefore possible to replace the term

$$\exp(-\,\underline{N}'\,\underline{V}\,\underline{N} / 2\varkappa T)$$

in (5.13) by the right-hand side of (5.15), and this has the advantage that the summations over the N_j may be performed, the final result being

$$Z^* = X(w) / X(0) \quad , \tag{5.17}$$

where

$$X(w) = \int_{-\infty}^{\infty}\!\cdot\!\cdot\!\int \prod_j (dt_j)\, \exp(-\,I + u_1 \cdot\cdot u_D\, w' \sum_j e^{it_j}) \quad , \tag{5.18}$$

I being defined by

$$I = \tfrac{1}{2}\varkappa T \, \underline{t}' \, \underline{V}^{-1} \, \underline{t} \quad . \tag{5.19}$$

The above method of transforming the grand-partition function is closely related to the work of Edwards (1959), Edwards and Lenard (1962), and Kac and Helfand (1963), but has the advantage that it requires neither a functional integration nor sophisticated statistical techniques.

In general (5.18) is no less difficult to evaluate than the original form (5.13) of the grand-partition function, but it will be shown that for a certain type of potential of considerable physical interest the matrix $\underline{V}^{-1}$ assumes a very simple form, enabling the limit

$$\lim_{m_D \to \infty} \; m_D^{-1} \log Z^*$$

to be determined explicitly.

4. Application to a 'wave-equation' potential

4.1 Discussion of the potential

One of the gaseous systems of obvious physical relevance is the plasma, in which the particles interact via the Coulomb potential, which for a D-dimensional system is

$$\upsilon(\underline{x}) = \frac{C}{(2\pi)^D} \int_{-\infty}^{\infty} \frac{d\underline{v}}{\underline{v}^2} \; \exp(i \; \underline{v}\cdot\underline{x}) \tag{5.20}$$

($\underline{x}$ and $\underline{v}$ being D-dimensional vectors).

Unfortunately the direct analysis of this system is complicated by the need to consider particles of more than one type (both positively and negatively charged), together with the fact that if a lattice gas with such an interaction is treated by the above methods the quadratic form I is found not to be positive definite, so that the integral (5.18) diverges. These difficulties may be overcome, but for the present purposes it is convenient to generalise the potential $\upsilon(\underline{x})$ and define it not by (5.20), but by

$$\upsilon(\underline{x}) = \frac{C}{(2\pi)^D} \int_{-\infty}^{\infty} \frac{d\underline{v}}{a^2 + \underline{v}^2} \exp(i\, \underline{v}\cdot\underline{x}) \quad . \qquad (5.21)$$

$\upsilon(\underline{x})$ is now a repulsive potential of short range and depends only on the radial distance between the interacting particles. Quite aside from the question of plasmas, this is a very interesting case to study, as the probable existence of a phase transition in a two- or three-dimensional gas of hard spheres (Alder and Wainwright, 1960) suggests that a similar transition may occur in this system.

The reason for the title of this section is that $\upsilon(\underline{x})$ satisfies the decaying wave equation for a point source, namely

$$(\nabla^2 - a^2)\ \upsilon(\underline{x}) = -\, C\ \delta(\underline{x}) \quad , \qquad (5.22)$$

where ∇^2 is the usual div grad operator and $\delta(\underline{x})$ the D-dimensional Dirac delta function. The simplifications in $\underline{V}^{-1}$ that will become apparent may be ascribed directly to this fact.

As yet the discussion of this potential has been implicitly concerned with the case when the interacting particles are free to occupy any position within a given domain. From the point of view of representing such a continuum gas of large volume by a lattice it is clearly not necessary, nor need it be desirable, to suppose that the interaction energy $V_{j,k}$ between two particles situated on sites j and k a vector distance $\underline{x}$ apart be given exactly by $\upsilon(\underline{x})$, rather it is sufficient that this should be so in the limit of the lattice being of dense spacing and large overall dimensions. For the lattice previously defined the most suitable choice of $V_{j,k}$ which satisfies this condition is

$$V_{j,k} = \frac{C}{A_1 \cdot\cdot A_D} \sum_{p_1=1}^{m_1} \cdots \sum_{p_D=1}^{m_D} h_p^{-1} \exp\left\{2\pi i \sum_{\alpha=1}^{D} p_\alpha (j_\alpha - k_\alpha)/m_\alpha\right\}, \quad (5.23)$$

where p represents the ordered set of integers $(p_1, \ldots, p_D)$ and

$$h_p = a^2 + 2 \sum_{\alpha=1}^{D} u_\alpha^{-2} \left\{1 - \cos(2\pi p_\alpha / m_\alpha)\right\} . \quad (5.24)$$

This form has the advantage that it incorporates explicitly the very natural condition that $\underline{V}$ be a cyclic matrix. It is of course a very straightforward procedure to invert such a matrix, in fact it can be seen that

$$(\underline{V}^{-1})_{j,k} = \frac{u_1 \cdots u_D}{m_1 \cdots m_D\, C} \sum_{p_1=1}^{m_1} \cdots \sum_{p_D=1}^{m_D} h_p \exp\left\{2\pi i \sum_{\alpha=1}^{D} p_\alpha (j_\alpha - k_\alpha)/m_\alpha\right\} , \quad (5.25)$$

which from the form (5.24) of h_p implies that

$$(\underline{V}^{-1})_{j,k} = \frac{u_1 \cdots u_D}{C} \left\{ a^2 \delta_{j,k} + \sum_{\alpha=1}^{D} u_\alpha^{-2} R^{(\alpha)}_{j,k} \right\} , \quad (5.26)$$

where

$$\delta_{j,k} = \delta_{j_1,k_1} \cdots \delta_{j_D,k_D} \quad (5.27)$$

and

$$R^{(\alpha)}_{j,k} = \delta_{j_1,k_1} \cdots \delta_{j_{\alpha-1},k_{\alpha-1}} W_{j_\alpha,k_\alpha} \delta_{j_{\alpha+1},k_{\alpha+1}} \cdots \delta_{j_D,k_D} , \quad (5.28)$$

the W_{j_α,k_α} being elements of the m_α by m_α cyclic matrix with 2 on the diagonal, -1 on the first off-diagonal, and zero on all other positions.

$\underline{V}^{-1}$ therefore has the remarkable property that its elements $(\underline{V}^{-1})_{j,k}$ vanish if any of the j_α, k_α differ by more than 1 (to modulus m_α). The quadratic form I given by (5.19) can now be evaluated and is found to be

$$I = \frac{\varkappa T\, u_1 \cdot\cdot u_D}{2\,C} \sum_{j_1=1}^{m_1} \cdots \sum_{j_D=1}^{m_D} \left\{ a^2\, t^2_{j_1,\ldots,j_D} + u_1^{-2}(t_{j_1,\ldots,j_D} - t_{j_1-1,j_2,\ldots,j_D})^2 + \ldots + u_D^{-2}(t_{j_1,\ldots,j_D} - t_{j_1,\ldots,j_{D-1},j_D-1})^2 \right\}, \tag{5.29}$$

where the cyclic convention is adopted that if any index j_α appears to become zero it is to be set equal to m_α.

It is now possible to determine the asymptotic behaviour of the integral $X(w)$ defined by (5.18) when m_D is large in terms of an integral equation in $m_1 \cdot\cdot m_{D-1}$ variables. For the sake of clarity of presentation it seems best to abandon the consideration of a system of arbitrary dimensionality at this stage and consider explicitly the one- and two-dimensional systems.

4.2 Reduction of the one-dimensional case to an eigenvalue problem

When $D = 1$, the expression (5.29) reduces to

$$I = \frac{\varkappa T\, u}{2C} \sum_{j=1}^{m} \left\{ a^2 t_j^2 + u^{-2}(t_j - t_{j-1})^2 \right\} , \tag{5.30}$$

and $X(w)$ is, from (5.18), given by

$$X(w) = \int_{-\infty}^{\infty}\!\!\cdots\!\int dt_1 \cdots dt_m \ \exp\left\{- I + u\, w' \sum_{j=1}^{m} e^{it_j}\right\} \qquad (5.31)$$

(dropping the suffix 1 relating to the dimensionality of the system).

To determine the asymptotic behaviour when m is large it is convenient to define a function $K(t,t';w)$ by

$$K(t,t';w) = \exp\left\{- Y(t,t') + u\, w' \left[G(t)+G(t')\right]\right\} , \qquad (5.32)$$

where

$$Y(t,t') = \frac{\varkappa T\ u}{4C} \left\{ a^2(t^2 + t'^2) + 2\, u^{-2}(t-t')^2\right\} \qquad (5.33)$$

and

$$G(t) = e^{it}/\, 2 \quad . \qquad (5.34)$$

(5.31) may then be written

$$X(w) = \int_{-\infty}^{\infty}\!\!\cdots\!\int dt_1 \cdots dt_m \ K(t_1,t_2;w)\ K(t_2,t_3;w) \ \ldots\ K(t_m,t_1;w) \ , \qquad (5.35)$$

which is essentially the trace of the m th power of $K(t,t';w)$, considered as a matrix with continuous indices t and t'. It must therefore follow that

$$X(w) = \sum_{r} \left\{\mu_r(w)\right\}^m \quad , \qquad (5.36)$$

where the $\mu_r(w)$ are the eigenvalues of the integral equation

$$\int_{-\infty}^{\infty} dt' \; K(t,t';w) \; z(t') \;=\; \mu(w) \; z(t) \quad , \tag{5.37}$$

subject to the boundary condition that

$$z(t) \longrightarrow 0 \qquad \text{as} \qquad t \longrightarrow \pm\infty \quad . \tag{5.38}$$

While the detailed investigation of these eigenvalues is undoubtedly of interest, it is sufficient for the present purposes to note that as the limit (5.8) must exist and be positive there is an eigenvalue which is real and positive and greater than the modulus of any other (when w is zero this is certainly true). Choosing this to be $\mu_o(w)$ it follows from (5.17) and (5.36) that when m is large

$$z^* \sim \left\{ \mu_o(w) \; / \; \mu_o(0) \right\}^m \quad , \tag{5.39}$$

so that the thermodynamic properties are from (5.8) given by

$$P/\varkappa T \;=\; u^{-1} \left\{ \log \mu_o(w) \; - \; \log \mu_o(0) \right\} \quad , \tag{5.40}$$

together with (5.9) and (5.10). As the solution of the integral equation (5.37) is well within the capacity of present numerical techniques these equations may be regarded as an exact solution of the problem.

It remains to investigate the case of most interest, namely when the spacing u of the lattice sites tends to zero, so that the system is essentially a continuum gas. To do this it is necessary to write the eigenvalue equation in a differential form by use of the identity

$$\int_{-\infty}^{\infty} dt' \, K^*(t,t') \, z(t') \equiv B^{-1} \exp(J^*) \, z(t) \quad , \tag{5.41}$$

where

$$K^*(t,t') = \exp\left\{-\frac{b^2}{1-\beta^2} \left[\tfrac{1}{2}(1+\beta^2)(t^2+t'^2) - 2\beta \, t \, t'\right]\right\} , \tag{5.42}$$

$$J^* = -\tfrac{1}{2} (\log \beta) \left\{ \frac{1}{b^2} \frac{d^2}{dt^2} - b^2 t^2 + 1 \right\} \tag{5.43}$$

and

$$B = b\left\{\pi(1-\beta^2)\right\}^{-\frac{1}{2}} \quad , \tag{5.44}$$

provided

$$0 < \beta < 1 \quad . \tag{5.45}$$

(This identity may be proved by showing that it is true for any eigenfunction of J^*.)

As $K(t,t';0)$ is of the same form as $K^*(t,t')$, and as, from (5.32),

$$K(t,t';w) = e^{uw'G(t)} \, K(t,t';0) \, e^{uw'G(t')} \quad , \tag{5.46}$$

it is possible to choose the constants β and b so as to write the equation (5.37) in the form

$$e^{uw'G(t)} \; e^{J^*} \; e^{uw'G(t)} \; z(t) = B\,\mu(w)\,z(t) \quad . \tag{5.47}$$

On determining β and b and supposing u to be small, a rather interesting fact emerges, namely that J^* may be written

$$J^* = u\,J + O(u^2) \quad , \tag{5.48}$$

where

$$J = \tfrac{1}{2}\left\{\frac{C}{\varkappa T}\,\frac{d^2}{dt^2} - \frac{a^2\varkappa T}{C}\,t^2 + a\right\} \quad . \tag{5.49}$$

On substituting this expression in (5.47) it becomes apparent that the limit

$$\lambda_r(w) = \lim_{u \to 0} u^{-1} \log\{B\,\mu_r(w)\} \tag{5.50}$$

exists for any value of r and is itself an eigenvalue of the equation

$$(w'\,e^{it} + J)\;z(t) = \lambda(w)\,z(t) \tag{5.51}$$

(using the definition (5.34) of $G(t)$).

$\lambda_o(w)$ must then be real and greater than the real part of any other $\lambda_r(w)$; and as $\lambda_o(0)$ can be shown to be zero, it follows from (5.40) that the thermodynamic properties are in this limit given by

$$P/\varkappa T = \lambda_o(w) \quad , \tag{5.52}$$

together with (5.9) and (5.10).

It is gratifying that these are precisely the results obtained in section 5.1 of chapter 2 for a one-dimensional continuum gas with interaction potential

$$\upsilon(x) = \frac{C}{2\pi} \int_{-\infty}^{\infty} \frac{dv}{a^2 + v^2} \exp(ivx) \quad , \tag{5.53}$$

$$= \frac{C}{2\,a} \exp(-\,a|x|) \quad . \tag{5.54}$$

4.3 The two-dimensional system

The working of the previous sub-section may be followed through in an exactly analogous manner for a two-dimensional system, the main difference being the increased complexity of notation, for now to determine the asymptotic behaviour when the number m_2 of rows of the lattice becomes large it is necessary to consider not just two single variables t and t', but two m_1-fold sets of quantities $t_1, \ldots, t_{m_1}$ and $t_1', \ldots, t_{m_1}'$ relating to the sites on adjacent rows.

If the m_1-dimensional vectors $\underline{t}$ and $\underline{t}'$ are used to denote these sets, and the functions

$$Y(\underline{t},\underline{t}') = \frac{\varkappa T\ u_1 u_2}{4\ C} \sum_{j=1}^{m_1} \Big\{ a^2(t_j^2 + t_j'^2) + 2\ u_2^{-2}(t_j - t_j')^2 + u_1^{-2}(t_j - t_{j-1})^2 + u_1^{-2}(t_j' - t_{j-1}')^2 \Big\} \quad , \tag{5.55}$$

$$G(\underline{t}) = \tfrac{1}{2} \sum_{j=1}^{m_1} e^{it_j} \tag{5.56}$$

and

$$K(\underline{t},\underline{t}';w) = \exp\Big\{ - Y(\underline{t},\underline{t}') + u_1 u_2 w' \big[G(\underline{t}) + G(\underline{t}') \big] \Big\} \tag{5.57}$$

defined, it then follows from (5.18) and (5.29) that

$$X(w) = \int\!\!\cdot\cdot\!\!\int_{-\infty}^{\infty} d\underline{t}_1 \cdots d\underline{t}_2\ K(\underline{t}_1,\underline{t}_2;w)\ K(\underline{t}_2,\underline{t}_3;w)\ \ldots\ K(\underline{t}_{m_2},\underline{t}_1;w) \quad . \tag{5.58}$$

The asymptotic behaviour of Z^* is therefore again given by

$$Z^* \sim \big\{ \mu_o(w) \ / \ \mu_o(0) \big\}^{m_2} \tag{5.59}$$

when m_2 is large, the $\mu_r(w)$ being in this case the eigenvalues of the integral equation

$$\int\!\!\cdot\cdot\!\!\int_{-\infty}^{\infty} d\underline{t}'\ \ K(\underline{t},\underline{t}';w)\ z(\underline{t}') = \mu(w)\ z(\underline{t}) \quad , \tag{5.60}$$

and $\mu_o(w)$ is chosen to be that eigenvalue which is real and greater than the modulus of any other.

To investigate the behaviour when the lattice is of sufficiently dense spacing to represent a continuum gas, it is convenient at this stage to consider the behaviour of $\mu_o(w)$ when u_2 tends to zero. This may be done by noting that by an extension of the procedure used in section 4.2 the eigenvalue equation (5.60) may be written as

$$e^{u_1 u_2 w' G(\underline{t})} \cdot e^{J^*} \cdot e^{u_1 u_2 w' G(\underline{t})} \, z(\underline{t}) = B \, \mu(w) \, z(\underline{t}) \, , \qquad (5.61)$$

where B is a constant (independent of w), and J^* a differential operator. When u_2 is small, J^* can be shown to be of the form

$$J^* = m_1 u_1 u_2 \, J + O(u_2^2) \, , \qquad (5.62)$$

where

$$J = \frac{1}{2\, m_1 u_1^2} \sum_{j=1}^{m_1} \left\{ \frac{C}{\varkappa T} \frac{\partial^2}{\partial t_j^2} - \frac{\varkappa T}{C} \left[a^2 u_1^2 t_j^2 + (t_j - t_{j-1})^2 \right] + f \right\} \, , \qquad (5.63)$$

the constant f being defined by

$$f = m_1^{-1} \sum_{j=1}^{m_1} \left\{ a^2 u_1^2 + 2 \left(1 - \cos\frac{2\pi j}{m_1}\right) \right\}^{\frac{1}{2}} \, . \qquad (5.64)$$

It therefore follows from (5.61) and (5.62) that the limit

$$\lambda_r(w) = (m_1 u_1)^{-1} \lim_{u_2 \to 0} u_2^{-1} \log\{B\ \mu_r(w)\} \qquad (5.65)$$

exists for any value of r and is an eigenvalue of the equation

$$\left\{ J + m_1^{-1} w' \sum_{j=1}^{m_1} e^{it_j} \right\} z(\underline{t}) = \lambda(w)\ z(\underline{t}) \qquad (5.66)$$

(using the definition (5.56) of $G(\underline{t})$).

The behaviour of the maximum eigenvalue $\lambda_o(w)$ of (5.66) in the limit of m_1 large therefore completely determines the thermodynamic properties of the system, which is now a gas confined to lie on lines parallel to the x_2 axis, the spacing between which is u_1. As $\lambda_o(0)$ can be shown to be zero, the pressure P is from (5.8), (5.59) and (5.65) given by

$$P/\varkappa T = \lambda_o(w) \quad , \qquad (5.67)$$

and the particle density and total internal energy by (5.9) and (5.10).

5. Discussion of results

The form (5.17) of the grand-partition function is clearly extremely useful for considering the statistical mechanical properties of a gas with interaction potential given by (5.21). Although in one dimension the method appears slightly cumbersome when compared with the 'differentiation with respect to volume' approach used in the previous chapters, it has the advantage of being more readily extended to higher dimensions.

In two dimensions the problem becomes one of determining the greatest eigenvalue of the equation (5.66). It is interesting to note that with suitable choice of units the form of the operator J is such that this problem is the same as that of determining the lowest energy level of a one-dimensional quantum mechanical system of particles $1,\ldots,m_1$, each moving in a complex potential well of the form

$$\frac{\varkappa T}{2\,C}\, a^2\, t^2 - w'\, e^{it}$$

and with an attractive harmonic interaction potential between the first and second, second and third, third and fourth, etc., particles.

In particular, it is desired to determine the asymptotic behaviour of the greatest eigenvalue when the column spacing u_1 is small and the extension $u_1 m_1$ of the system in the x_1 direction is large. Unfortunately there appears to be no obvious way of accomplishing this, though the 'nearest neighbour' property suggests that if further progress towards the exact solution of the problem can be made, the equation (5.66), or some equivalent expression, is the appropriate starting point.

Various approximation procedures suggest themselves, the most obvious being a variational approach with a trial function $z(\underline{t})$ which is the exponential of an arbitrary quadratic and linear form in the t_j's. However, this is found to yield the 'ring approximation' (Mayer, 1950) discussed in section 5.2 of chapter 2, which approximation may be derived by more elementary means.

Chapter 6

THE DIRECT CORRELATION FUNCTIONS AND THEIR DERIVATIVES WITH RESPECT TO DENSITY

1. Introduction

In chapter 1 the well-known distribution functions of a statistical mechanical system of particles have been defined. The usefulness of these functions lies in their obvious physical interpretation and explicit mathematical definition, but from the point of view of numerical work they suffer from quite serious disadvantages, notably their slow (usually oscillatory) approach to their asymptotic values at large particle separations and the fact that as these values are non-zero the functions cannot be Fourier analysed (a device which is frequently useful in considering the integral equations which relate them).

The second difficulty may be overcome by using the Ursell-Mayer or 'cluster' functions (Mayer and Montroll, 1951; page 203 of M. Green, 1961; page 78 of Uhlenbeck, 1963), which are defined in terms of the distribution functions and have the property that they tend to zero when the distance between any two particles becomes large. However, in general the rate of convergence is rather poor and for this reason alone the proof in this chapter of the existence of many-particle analogues of the two-particle Ornstein-Zernike direct correlation function (Ornstein and Zernike, 1914; page 82 of Rosenfeld, 1951) is of particular interest, as it is known that this function is considerably more regular and rapidly convergent than the corresponding cluster function. It may be expected that this is also true of its many-particle analogues (the direct correlation functions) and indeed it appears that the r-particle direct correlation function of a one-dimensional gas of hard rods vanishes exactly when the distance between any two of the r particles exceeds the range of the interaction potential, which is a striking demonstration of this property.

One other interesting point which will be proved in this chapter is the existence of relations between the distribution, cluster and direct correlation functions respectively and their derivatives with respect to the mean particle density of the gas. In the last case the relation is of a particularly simple form and suggests that if some approximate closure of the equations can be made by expressing the three-particle direct correlation function in terms of the two-particle, the resulting equations would be very easy to handle as they would predict the behaviour of the gas at one density in terms of its behaviour at another. With this end in view a superposition approximation is suggested.

2. Definition of the problem

Consider a system of N identical particles confined within a volume V and with an interaction potential $\upsilon(x-y)$ acting between any pair of particles at points x and y (in three dimensions x and y are to be interpreted as vectors). Then the total potential energy of the gas is

$$E = \sum_{1\leqslant j<k\leqslant N} \upsilon(x_j-x_k) \quad . \tag{6.1}$$

As this chapter is concerned throughout with the behaviour of a gas at some fixed temperature, it is convenient to introduce the function $u(x)$ and the quantity E' defined by

$$u(x) = \upsilon(x) / \varkappa T \tag{6.2}$$

and

$$E' = E / \varkappa T \quad . \tag{6.3}$$

(6.1) then clearly implies that

$$E' = \sum_{1\leqslant j<k\leqslant N} u(x_j-x_k) \quad . \tag{6.4}$$

The equations (1.33) and (1.42) for the configuration integral Q_N and the j-particle distribution function $n(x_1,..,x_j)$ of the gas can now be written:

$$Q_N = \int_V \cdots \int dx_1 \cdots dx_N \exp(-E') \qquad (6.5)$$

and

$$n(x_1, \ldots, x_j) = \frac{N!}{(N-j)!\, Q_N} \int_V \cdots \int dx_{j+1} \cdots dx_N \exp(-E') \quad , \qquad (6.6)$$

where x_k is the position coordinate of the k th particle and the integrations range over the domain V. (6.6) is to be evaluated in the limit when N and V are large, but the particle number density

$$\rho = N / V \qquad (6.7)$$

is finite.

Clearly $n(x_1, \ldots, x_j)$ and all other statistical mechanical quantities are functions of ρ. It is the object of the next four sections to obtain explicit expressions for the derivatives of some of these with respect to ρ.

3. The functional formalism

Suppose an arbitrary external potential $\varkappa T\ U(x)$ is superimposed on the system described above. Then the statistical mechanical quantities of the modified system, in addition to being functions of the density ρ, are functionals of the function $U(x)$. In order to exhibit this dependence explicitly, all such functionals will be represented by underlined symbols.

It will be found that these functionals can be expanded as Taylor series with respect to U(x) or other functionals of U(x), the 'coefficients' of the series being independent of U(x) and related to the distribution functions defined above. These and all other quantities which are not dependent on U(x) will be represented by symbols which are not underlined.

It is convenient to define the quantities

$$\underline{b}(x_1,\ldots,x_j) = \frac{N!}{(N-j)!\,Q_N} \int_V \!\cdots\! \int dx_{j+1}\ldots dx_N \exp\left\{-E' - \sum_k U(x_k)\right\} , \tag{6.8}$$

where the summation in the exponent ranges from 1 to N and again it is to be understood that N and V are large, but ρ, given by (6.7), is finite. Clearly (6.8) defines a set of one-, two-, three-, etc. particle functionals of U(x). In addition, when j=0 it is to be regarded as defining a quantity $\underline{b}$ which is independent of all particle positions but is still a functional of U(x).

As the following equations will contain many integrations over functions of position coordinates, the notation U_j will be used to denote $U(x_j)$, and similarly for other functions. In the case of functions of more than one variable, the number of variables will be sufficiently indicated by the number of suffixes. In addition, the notation

$$\int dj$$

will be used to denote integration over the variable x_j.

If $\underline{F}(x)$ is defined by

$$\underline{F}(x) = \exp\left\{-U(x)\right\} - 1 \quad , \tag{6.9}$$

then separating the factor

$$\exp\left\{-\sum_{k=1}^{j} U(x_k)\right\}$$

from the integrand of (6.8) and eliminating the function $U(x)$ from the remainder by (6.9), (6.8) may be written:

$$\underline{b}^*_{1,..,j} = \frac{N!}{(N-j)!\ Q_N} \int_V \cdot\cdot\int d(j+1)\,..\,dN\ e^{-E'} \prod_{k=j+1}^{N} (1+\underline{F}_k) \quad , \tag{6.10}$$

where

$$\underline{b}^*_{1,..,j} = \underline{b}_{1,..,j}\ \exp(U_1+\cdots+U_j) \quad . \tag{6.11}$$

Expanding the $(N-j)$-fold product and using the equation (6.6) for the distribution functions, it is readily seen from (6.10) that

$$\underline{b}^*_{1,..,j} = \sum_{k=j}^{\infty} \frac{1}{(k-j)!} \int\cdot\cdot\int d(j+1)\,..\,dk\ \underline{F}_{j+1}\cdot\cdot\underline{F}_k\ n_{1,..,k} \quad , \tag{6.12}$$

where the integrations in this and all subsequent equations of this chapter range not over V, but over all space. The first term of the summation is $n_{1,\ldots,j}$, as follows if the operator

$$\int\cdot\cdot\int d(j+1)\ldots dk\ \underline{F}_{j+1}\ldots\underline{F}_k$$

is defined to be unity when $k=j$, for any function $\underline{F}$. This convention will be adhered to in the subsequent equations.

It is now evident that the distribution functions occur as 'coefficients' in the Taylor expansions of the functionals $\underline{b}^*_{1,\ldots,j}$ with respect to $\underline{F}(x)$. It is in fact possible to adopt this rather than (1.42) as their definition, and this general technique of functional Taylor expansions will be employed to define the direct correlation functions.

When

$$U(x) = u(x-y_1) + \ldots + u(x-y_k) \quad , \qquad (6.13)$$

it is possible to give an explicit definition of the $\underline{b}(x_1,\ldots,x_j)$ in terms of the distribution functions, for the negative exponent

$$E' + \sum_{\ell=1}^{N} U(x_\ell)$$

in the definition (6.8) becomes

$$\sum_{1 \leqslant \ell < m \leqslant N+k} u(x_\ell - x_m) \quad - \quad \emptyset \qquad ,$$

where

$$x_{N+\ell} \equiv y_\ell \qquad (1 \leqslant \ell \leqslant k)$$

and

$$\emptyset = \sum_{1 \leqslant \ell < m \leqslant k} u(y_\ell - y_m) \qquad . \tag{6.14}$$

(6.8) is therefore reminiscent of the definition of the (j+k) -particle distribution function in terms of an (N+k) -particle system. In fact it can be shown from (6.6) to imply that

$$\underline{b}(x_1,\ldots,x_j) = \frac{N!\; Q_{N+k}}{(N+k)!\; Q_N}\, n(x_1,\ldots,x_j,y_1,\ldots,y_k) \quad e^{\emptyset} \qquad . \tag{6.15}$$

As it can be shown from the definition (1.38) of the concentration activity coefficient and the relation (1.60) between that and the fugacity w that when N and V are large

$$w = N\, Q_{N-1} \,/\, Q_N$$

(Q_{N-1} and Q_N both being evaluated for a system of volume V), it follows from (6.15) that

$$\underline{b}(x_1,\ldots,x_j) = w^{-k}\, n(x_1,\ldots,x_j,y_1,\ldots,y_k) \quad e^{\emptyset} \qquad , \tag{6.16}$$

when $U(x)$ is given by (6.13).

4. The derivatives of the distribution functions with respect to density

It has been shown in section 7 of chapter 2 that the distribution functions of a general one-dimensional gas satisfy the relations

$$(\mu\ \rho \frac{\partial}{\partial \rho} - j)\ n_{1,..,j} = \int d(j+1)\ (n_{1,..,j+1} - \rho\ n_{1,..,j})\quad , \qquad (6.17)$$

where μ is the quantity defined by (1.39), i.e.

$$\mu^{-1} = \frac{\partial}{\partial \rho}\ P/\varkappa T \quad . \qquad (6.18)$$

It is reasonable to suppose that this is the case in any number of dimensions and in fact it is not difficult to produce a convincing, if not rigorous, proof by the present methods, for if k is set equal to 1, 2, 3, etc. in (6.13) and these values of $U(x)$ substituted into the set of equations (6.12), then using (6.11) and (6.16) a doubly infinite set of equations for the singly infinite set of distribution functions is obtained. Not surprisingly, these equations completely determine the distribution functions (and the fugacity), as may be seen by solving them in the form of a virial expansion (expansion in powers of the density). It is therefore reasonable to suppose that if the equations are differentiated with respect to the mean particle density they then completely determine the derivatives of the distribution functions, so that if they are satisfied by the values given by (6.17), this relation is thereby proved correct.

Adopting this procedure and differentiating (6.12) with respect to ρ, multiplying by $\mu\ \rho$, and using (6.17), it is found that

$$(\mu\ \rho \frac{\partial}{\partial \rho} - j)\ \underline{b}^*_{1,\dots,j} =$$

$$\sum_{k=j+1}^{\infty} \frac{1}{(k-j-1)!} \int\cdots\int d(j+1)\dots dk\ \underline{F}_{j+1}\cdots\underline{F}_k\ n_{1,\dots,k}$$

$$+ \sum_{k=j}^{\infty} \frac{1}{(k-j)!} \int\cdots\int d(j+1)\dots d(k+1)\ \underline{F}_{j+1}\cdots\underline{F}_k (n_{1,\dots,k+1} - \rho\ n_{1,\dots,k}) \quad . \tag{6.19}$$

Each of the series on the right-hand side of this equation may be manipulated into a form where it is the integral of a series of the type occurring in (6.12). Summing these series by (6.12), expressing the functionals $\underline{b}^*_{1,\dots,j}$ in terms of the $\underline{b}_{1,\dots,j}$ by (6.11) and using the definition (6.9) of $\underline{F}(x)$, all the exponential terms cancel out, leaving

$$(\mu\ \rho \frac{\partial}{\partial \rho} - j)\ \underline{b}_{1,\dots,j} = \int d(j+1)\ (\underline{b}_{1,\dots,j+1} - \rho\ \underline{b}_{1,\dots,j}) \quad . \tag{6.20}$$

The simplicity of this equation and its formal resemblance to (6.17) are quite gratifying. It is now sufficient to show that when $U(x)$ is given by (6.13), (6.20) is equivalent to (6.17).

To show this, suppose all the $\underline{b}_{1,..,j}$ are given by (6.16) for some fixed value of k. Then substituting these values into (6.20), the terms e^{ϕ} cancel out, giving

$$w^{k}\left(\mu\rho\frac{\partial}{\partial\rho} - j\right)w^{-k}n_{1,..,j+k} = \int d(j+k+1)\,\left(n_{1,..,j+k+1} - \rho\, n_{1,..,j+k}\right) \quad . \tag{6.21}$$

As

$$w^{k}\,\mu\,\rho\,\frac{\partial}{\partial\rho}\,w^{-k} = \mu\,\rho\,\frac{\partial}{\partial\rho} - k\,\rho\,\mu\,\left(\frac{\partial}{\partial\rho}\log w\right) \quad , \tag{6.22}$$

using the relation (1.62), i.e.

$$\mu\,\rho\,\left(\frac{\partial}{\partial\rho}\log w\right) = 1 \quad , \tag{6.23}$$

it follows that

$$w^{k}\,\mu\,\rho\,\frac{\partial}{\partial\rho}\,w^{-k} = \mu\,\rho\,\frac{\partial}{\partial\rho} - k \quad . \tag{6.24}$$

Substituting this result in (6.21), the relation (6.17) is obtained, only with j replaced by j+k. Accordingly the values of the derivatives given by (6.17) satisfy the equations obtained from (6.12) and (6.16) and so must be correct.

When k=1, using the definition (1.45) of g(x) and the fact that

$$n(x) = \rho \quad , \tag{6.25}$$

equation (6.17) yields

$$\mu = 1 + \rho \int dx \left\{ g(x) - 1 \right\} \quad , \qquad (6.26)$$

which is a well-known relation expressing the isothermal compressibility in terms of the two-particle distribution function (page 67 of H.S. Green, 1960).

5. The cluster functions

The technique of considering the properties of a gas acted on by an arbitrary external potential $U(x)$ as functionals of $U(x)$ has been used by Percus (1962) to obtain a very elegant derivation of the Percus-Yevick approximation. As yet the formalism of this chapter has differed slightly from that of Percus, in so far as the functionals $\underline{b}(x_1,..,x_j)$ and $\underline{b}^*(x_1,..,x_j)$ have been considered, rather than the distribution functions $\underline{n}(x_1,..,x_j)$ of the modified system, which may be defined by:

$$\underline{n}(x_1,..,x_j) = \underline{b}(x_1,..,x_j) \, / \, \underline{b} \quad . \qquad (6.27)$$

The reason for this is that a Taylor expansion of the functionals $\underline{n}(x_1,..,x_j)$ with respect to $\underline{F}(x)$ inevitably leads to a consideration of the cluster functions and functionals $h(x_1,..,x_j)$ and $\underline{h}(x_1,..,x_j)$ defined by

$$h_1 = n_1 \quad , \tag{6.28a}$$

$$h_{1,2} = n_{1,2} - n_1 n_2 \quad , \tag{6.28b}$$

$$h_{1,2,3} = n_{1,2,3} - n_1 n_{2,3} - n_2 n_{3,1} - n_3 n_{1,2} + 2\, n_1 n_2 n_3 \,, \tag{6.28c}$$

etc.

and (similarly)

$$\underline{h}_1 = \underline{n}_1 \quad , \tag{6.29a}$$

$$\underline{h}_{1,2} = \underline{n}_{1,2} - \underline{n}_1\, \underline{n}_2 \quad , \tag{6.29b}$$

etc.

(c.f. references quoted in section 1), for which the relation (6.16) has no simple counterpart.

However, having established the relations (6.17) between the distribution functions and their derivatives with respect to density it is now convenient to abandon the functionals $\underline{b}(x_1,..,x_j)$ and $\underline{b}^*(x_1,..,x_j)$ and to consider instead the cluster functionals $\underline{h}(x_1,..,x_j)$ and the related quantities $\underline{h}^*(x_1,..,x_j)$ defined by

$$\underline{h}^*_{1,..,j} = \underline{h}_{1,..,j} \exp\,(U_1+..+U_j) \quad , \tag{6.30}$$

for by a method similar to that of H.S. Green (1961) it may be shown that

$$\underline{h}^*_{1,..,j} = \sum_{k=j}^{\infty} \frac{1}{(k-j)!} \int\!..\!\int d(j+1)..dk\ \underline{F}_{j+1}..\underline{F}_k\ h_{1,..,k} \ . \tag{6.31}$$

Also, it can be shown from (6.17) and the definitions (6.28) of the cluster functions that

$$(\mu \, \rho \frac{\partial}{\partial \rho} - j) \, h_{1,..,j} = \int d(j+1) \, h_{1,..,j+1} \quad , \qquad (6.32)$$

so that differentiating (6.31) with respect to ρ and using (6.32) it follows in a manner analogous to the derivation of (6.20) that

$$(\mu \, \rho \frac{\partial}{\partial \rho} - j) \, \underline{h}_{1,..,j} = \int d(j+1) \, \underline{h}_{1,..,j+1} \qquad (6.33)$$

(which obviously reduces to (6.32) when the function $U(x)$ is identically zero).

In addition to the effect of differentiating $\underline{h}(x_1,..,x_j)$ with respect to density, it will be necessary in the next section to consider the increments $\delta\underline{h}(x_1,..,x_j)$ induced in the cluster functionals by changing $U(x)$ to $U(x) + \delta U(x)$, the density being kept constant. Using (6.30), (6.31) and the definition (6.9) of $\underline{F}(x)$, these are found to be:

$$\delta\underline{h}_{1,..,j} = - \underline{h}_{1,..,j} \, (\delta U_1 + .. + \delta U_j) - \int d(j+1) \, \delta U_{j+1} \, h_{1,..,j+1} \quad . \qquad (6.34)$$

6. The direct correlation functions

6.1 Definition and proof of symmetry

Percus (1962) showed that the two-particle Ornstein-Zernike direct correlation function $c(x,y)$ (Ornstein and Zernike, 1914), which may be regarded as defined by

$$\rho^2 \, c(x,y) = h(x,y) - \rho \int dz \, h(x,z) \, c(z,y) \quad , \qquad (6.35)$$

occurs as the first coefficient in the Taylor expansion of $\underline{Y}(x)-1$, where

$$\underline{Y}(x) = \rho^{-1} \, \underline{h}(x) \, \exp\{U(x)\} \quad , \qquad (6.36)$$

considered as a functional, not of $U(x)$ or $\underline{F}(x)$, but of

$$\underline{s}(x) = \underline{h}(x) - \rho \quad . \qquad (6.37)$$

It was on precisely this observation that the derivation of the P.Y. equation rested.

It should be emphasized here that $\underline{Y}(x)$ is to be regarded as both a functional of $\underline{s}(x)$ and a function of ρ. For given ρ, $\underline{s}(x)$ is arbitrary only in so far as it is free to assume any of the values obtained by varying $U(x)$.

Though the dependence of $\underline{Y}(x)$ on $\underline{s}(x)$ may be suitable for obtaining approximations, it is equally true that $c(x,y)$ occurs as the first coefficient in a Taylor expansion of $\log \underline{Y}(x)$ with respect to $\underline{s}(x)$, and it seems that this expansion is of greater fundamental interest, for if

$$\log \underline{Y}_1 = \sum_{k=2}^{\infty} \frac{1}{(k-1)!} \int \cdot\cdot \int d2 \cdot\cdot dk \; \underline{s}_2 \cdot\cdot \underline{s}_k \; c_{1,\cdot\cdot,k} \quad , \qquad (6.38)$$

it will be shown that the functions $c(x_1, \cdot\cdot, x_k)$ may be chosen to be symmetric with respect to all the variables $x_1, \cdot\cdot, x_k$. There is no a priori reason why this should be so, and it is certainly not true of the coefficients obtained by expanding $\underline{Y}(x)$. To prove this symmetry property, note that each $c(x_1, \cdot\cdot, x_k)$ may be chosen to be symmetric with respect to all but the first variable, and that when this is done it is uniquely defined by (6.38). It is then convenient to introduce a functional $\underline{c}(x,y)$ defined by

$$\underline{c}_{1,2} = \sum_{k=2}^{\infty} \frac{1}{(k-2)!} \int \cdot\cdot \int d3 \cdot\cdot dk \; \underline{s}_3 \cdot\cdot \underline{s}_k \; c_{1,\cdot\cdot,k} \quad . \qquad (6.39)$$

In the limit of $U(x)$ zero $\underline{s}(x)$ vanishes, so that $\underline{c}(x,y)$ reduces to the direct correlation function $c(x,y)$.

Incrementing $U(x)$ by $\delta U(x)$ in (6.38), if $\delta \log \underline{Y}(x)$ and $\delta \underline{s}(x)$ are the corresponding increments of $\log \underline{Y}(x)$ and $\underline{s}(x)$, it follows from (6.39) that

$$\delta \log \underline{Y}_1 = \int d2 \; \delta \underline{s}_2 \; \underline{c}_{1,2} \quad . \qquad (6.40)$$

As

$$\delta \underline{s}_2 \;=\; \delta \underline{h}_2 \quad , \tag{6.41}$$

substituting the value of $\delta \underline{h}_2$ given by (6.34) in (6.40) and re-arranging the orders of integration:

$$\delta \log \underline{Y}_1 = - \int d2 \; \delta U_2 \, (\underline{h}_2 \, \underline{c}_{1,2} + \int d3 \; \underline{c}_{1,3} \, \underline{h}_{3,2}) \quad . \tag{6.42}$$

But the increment of $\log \underline{Y}(x)$ may be obtained directly from the definition (6.36) together with (6.34), in fact

$$\delta \log \underline{Y}_1 = - \frac{1}{\underline{h}_1} \int d2 \; \delta U_2 \, \underline{h}_{1,2} \quad , \tag{6.43}$$

so that comparing (6.42) and (6.43), as $\delta U(x)$ is an arbitrary function

$$\underline{h}_{1,2} \,/\, \underline{h}_1 = \underline{h}_2 \, \underline{c}_{1,2} + \int d3 \; \underline{c}_{1,3} \, \underline{h}_{3,2} \quad . \tag{6.44}$$

This equation may be regarded as defining the functional $\underline{c}(x,y)$. It is readily seen by solving by iteration and noting that

$$\underline{h}(x,y) \;=\; \underline{h}(y,x) \tag{6.45}$$

that $\underline{c}(x,y)$ is also a symmetric function, i.e.

$$\underline{c}(x,y) \;=\; \underline{c}(y,x) \quad . \tag{6.46}$$

As this property holds for all values of the function $U(x)$, (6.39) shows that $c(x_1,\ldots,x_k)$ is symmetric with respect to interchange of x_1 and x_2. As it has been defined to be symmetric with respect to the variables $x_2,\ldots,x_k$, it follows that it is symmetric with respect to all the variables. The set of functions $c(x_1,\ldots,x_k)$ is therefore a physically useful set for considering a system of identical particles, and in analogy with the two-particle function it is convenient to term them the direct correlation functions.

6.2 <u>The derivatives with respect to density</u>

Using the equations (6.32) previously obtained for the derivatives of the cluster functions with respect to density, it is possible to establish similar, but simpler, relations for the derivatives of the direct correlation functions.

To do this, first note that from (6.32) and (6.37),

$$\mu\,\rho\,\left(\frac{\partial}{\partial\rho}\,\underline{s}_2 + 1\right) = \underline{h}_2 + \int d3\,\underline{h}_{2,3} \quad , \tag{6.47}$$

so that multiplying by $\underline{c}_{1,2}$, integrating over x_2 and re-arranging the order of integration in the second term on the right-hand side:

$$\mu\,\rho\int d2\,\left(\frac{\partial}{\partial\rho}\,\underline{s}_2 + 1\right)\underline{c}_{1,2} = \int d2\,\left(\underline{h}_2\,\underline{c}_{1,2} + \int d3\,\underline{c}_{1,3}\,\underline{h}_{3,2}\right) \quad , \tag{6.48}$$

which from (6.44) clearly leads to

$$\int d2 \left(\frac{\partial}{\partial\rho} \underline{s}_2 + 1\right) \underline{c}_{1,2} = \frac{1}{\mu\rho\underline{h}_1} \int d2\ \underline{h}_{1,2} \quad . \tag{6.49}$$

The derivative of $\log \underline{Y}(x)$ with respect to density is given by (6.33) and (6.36) to be

$$\frac{\partial}{\partial\rho} \log \underline{Y}_1 = \frac{1-\mu}{\mu\,\rho} + \frac{1}{\mu\rho\underline{h}_1} \int d2\ \underline{h}_{1,2} \quad , \tag{6.50}$$

and it is a standard result (Percus and Yevick, 1958), obtainable from (6.26) and (6.35), that

$$\mu^{-1} = 1 - \rho \int d2\ c_{1,2} \quad . \tag{6.51}$$

μ and $\underline{h}(x,y)$ may now be eliminated from (6.49), (6.50) and (6.51) to yield:

$$\frac{\partial}{\partial\rho} \log \underline{Y}_1 = \int d2\ \underline{c}_{1,2} \frac{\partial}{\partial\rho} \underline{s}_2 + \int d2\ (\underline{c}_{1,2} - c_{1,2}) \quad . \tag{6.52}$$

This relation, together with the expansions (6.38) and (6.39), enables the derivatives of the direct correlation functions with respect to density to be determined, for differentiating (6.38) with respect to ρ and using (6.39), it is found that

$$\frac{\partial}{\partial\rho} \log \underline{Y}_1 = \int d2\ \underline{c}_{1,2} \frac{\partial}{\partial\rho} \underline{s}_2$$
$$+ \sum_{k=2}^{\infty} \frac{1}{(k-1)!} \int\cdots\int d2..dk\ \underline{s}_2..\underline{s}_k \frac{\partial}{\partial\rho} c_{1,..,k} \quad . \tag{6.53}$$

Expanding the second term in the right-hand side of (6.52) by (6.39) and subtracting (6.53), it follows that

$$\sum_{k=2}^{\infty} \frac{1}{(k-1)!} \int\cdot\cdot\int d2 \cdot\cdot dk\ \underline{s}_2 \cdot\cdot \underline{s}_k \left(\frac{\partial}{\partial \rho} c_{1,\ldots,k} - \int d(k+1)\ c_{1,\ldots,k+1}\right) = 0 \quad . \qquad (6.54)$$

As $U(x)$ and hence $\underline{s}(x)$ are arbitrary functions, this equation can only be satisfied if

$$\frac{\partial}{\partial \rho} c_{1,\ldots,k} = \int d(k+1)\ c_{1,\ldots,k+1} \qquad (6.55)$$

for all integral values of k greater than one.

The simplicity of this relation is striking. The rather annoying term μ which occurs in the analogous formulae for the distribution and cluster functions has disappeared. In principle (6.55) should give a very direct method of obtaining the virial expansion if the functions $c(x_1,\ldots,x_k)$ can be determined at infinite dilution. However, the lack of an explicit definition is a weakness here, as each direct correlation function must be obtained in terms of the cluster functions by Taylor expanding $\underline{s}(x)$ and $\log \underline{Y}(x)$ with respect to $\underline{F}(x)$, substituting the expansions in (6.38) and equating coefficients. Such a procedure is impractical for all but very small values of k.

6.3 The one-particle direct correlation function

By analogy with the distribution and cluster functions it is reasonable to suppose that a one-particle direct correlation function $c(x)$ may be meaningfully defined. In view of the translational invariance of all functions relating to the behaviour of a gas of particles with interaction dependent only on the distance between interacting particles, such a function must in fact be a constant and may be expected to have some thermodynamic significance.

From (6.55), $c(x)$ must satisfy the equation

$$\frac{\partial}{\partial\rho} c(x) = \int dy\, c(x,y) \quad , \qquad (6.56)$$

which from (6.51) implies that

$$\frac{\partial}{\partial\rho} c(x) = (\mu-1) / \mu\,\rho \quad . \qquad (6.57)$$

However, it is known from (1.60) and (1.62) that the quantity μ and the concentration activity coefficient γ, considered as functions of the density ρ at constant temperature, satisfy the relation

$$\mu\,\rho \frac{\partial}{\partial\rho} \log(\rho\gamma) = 1 \quad , \qquad (6.58)$$

which may be written

$$\frac{\partial}{\partial\rho} \log\gamma = (1-\mu) / \mu\,\rho \quad . \qquad (6.59)$$

Comparing (6.57) and (6.59), it is apparent that a suitable choice of $c(x)$ is

$$c(x) = - \log \gamma \quad , \qquad (6.60)$$

so the one-particle direct correlation function is the negative logarithm of the concentration activity coefficient.

7. A superposition approximation

The above results are in a sense purely formal, since they do not provide a closed system of equations for determining the thermodynamic properties of the gas. However, this is by no means a new situation, and as the direct correlation functions tend to zero very rapidly when the distance between any two particles becomes greater than the range of the interaction potential it seems reasonable to suppose they should prove useful in numerical work. Further, if a closure can be made of the equations for the derivatives of either the distribution, cluster or direct correlation functions with respect to density, notably by some approximate relation expressing one of the three-particle functions in terms of the two-particle, the resulting equations would be quite simple to handle, as the values of the two-particle functions at one density would predict their values at an adjacent density. This situation is quite different from that encountered when using one of the Percus-Yevick (Percus, 1962), hypernetted chain (Meeron, 1960) and Born-Green-Kirkwood (Born and Green, 1946) approximations, each of which has to be solved by some sort of iterative procedure for each value of the density.

One obvious procedure is to use the Kirkwood superposition approximation (Kirkwood, 1935) for the three-particle distribution function, together with the equations obtained by setting $j=1$ and 2 in (6.17). However, in view of the known regularity of the direct correlation functions and the simplicity of the equations (6.55) compared with (6.17) and (6.32), it seems more desirable to seek a relation between $c_{1,2,3}$ and $c_{1,2}$.

For a one-dimensional gas of hard rods it can be shown that $c(x_1,\ldots,x_k)$ vanishes exactly when the distance between any two of the position coordinates $x_1,\ldots,x_k$ exceeds the range of the interaction potential, so that the superposition approximation

$$c_{1,2,3} = c_{1,2}\, c_{2,3}\, c_{3,1} \tag{6.61}$$

may be expected to be accurate at moderately large particle separations for any short-range potential. Further, (6.61) is exactly true everywhere when the gas is infinitely dilute.

In the context of the present procedure the approximation (6.61) is very attractive, for on eliminating $c_{1,2,3}$ between it and the exact relation

$$\frac{\partial}{\partial \rho} c_{1,2} = \int d3 \; c_{1,2,3} \tag{6.62}$$

(obtained by setting $k=2$ in (6.55)), the equation

$$\frac{\partial}{\partial \rho} \log c_{1,2} = \int d3 \; c_{1,3} \, c_{3,2} \tag{6.63}$$

is obtained. Together with the boundary condition that

$$c(x,y) = \exp\{-\upsilon(x-y)/\varkappa T\} - 1 \tag{6.64}$$

when $\rho=0$, this equation completely determines the two-particle direct correlation function and is extremely simple to solve numerically.

If $c(x,y)$ is calculated in this manner, the thermodynamic properties of the gas, in particular its equation of state, may be derived from it by any one of a number of exact relations. Clearly the most straightforward is simply (6.51), which from the definition (6.18) of μ may be written

$$\frac{\partial}{\partial \rho} P/\varkappa T = 1 - \rho \int d2 \; c_{1,2} \quad . \tag{6.65}$$

Alternatively, if the function $g(x)$ defined by (1.45), i.e.

$$g(x-y) = \rho^{-2} \, n(x,y) \quad , \tag{6.66}$$

is obtained from $c(x,y)$ by the relation

$$g(x-y) - 1 = c(x,y) + \rho \int dz\ c(x,z)\ \left[g(z-y) - 1\right] \qquad (6.67)$$

(which is equivalent to (6.35)), then the pressure P may be derived from it by the relation (1.47), i.e.

$$P\ /\ \rho\varkappa T = 1 - \frac{\rho}{2\varkappa TD} \int dx\ \left[x\cdot\nabla\ \upsilon(x)\right]\ g(x) \qquad (6.68)$$

(D being the dimensionality of the space).

Both these procedures yield the first three virial coefficients correctly, but the second, though considerably more complicated, has the advantage that it is capable of giving the 'ring approximation' (c.f. section 5.2 of chapter 2) which is the basis of the Debye-Huckel theory.

It should be noticed that the arguments which lead to the superposition approximation (6.61) equally suggest the more general equation

$$c_{1,2,3} = \sigma(\rho)\ c_{1,2}\ c_{2,3}\ c_{3,1} \quad , \qquad (6.69)$$

where $\sigma(\rho)$ is independent of the particle positions but may depend on the density ρ (and also on the temperature T), subject to the condition that

$$\sigma(0) = 1 \quad . \qquad (6.70)$$

If $c_{1,2}$ is regarded as depending not on ρ, but on the related parameter

$$\rho^{*} = \int_{0}^{\rho} d\rho' \, \sigma(\rho') \quad , \qquad (6.71)$$

then the equation for $c_{1,2}$ obtained from (6.62) and (6.69) is simply

$$\frac{\partial}{\partial \rho^{*}} \log c_{1,2} = \int d3 \, c_{1,3} \, c_{3,2} \quad , \qquad (6.72)$$

so that the evaluation of the direct correlation function is no more difficult than formerly.

It should then be possible to determine the function $\sigma(\rho)$ by requiring that the pressure P determined from both (6.65) and (6.68) be the same. Admittedly this amounts to an increase in the complexity of the approximation procedure, but the numerical analysis is well within the scope of present computing techniques and may be expected to yield quite accurate results.

8. Discussion of results

The sets of relations (6.17) and (6.32) between the distribution and cluster functions and their derivatives with respect to particle density have been established. On defining the direct correlation functions by (6.38) they are found to satisfy similar, but simpler, relations. The possibility of a closure of these equations by means of a superposition approximation for the three-particle direct correlation function has been discussed.

It should be stressed that the aim of this approximation is not to obtain a correction to the Percus-Yevick or hypernetted chain approximations (though this may be done, resulting in quite unmanageable equations), but to utilize the procedural simplicity of directly calculating statistical mechanical properties at one density in terms of those at an adjacent density.

References

R. Abe, Progress of Theor. Phys., 22, 213 (1959)

B.J. Alder and T.E. Wainwright, J. Chem. Phys., 33, 1439 (1960)

G.A. Baker, Phys. Rev., 122, 1477 (1961)

M.E. Baur and L.H. Nosanow, J. Chem. Phys., 37, 153 (1962)

M. Born and H.S. Green, Proc. Roy. Soc. (London), A 118, 10 (1946)

P. Debye and E. Huckel, Zeitschrift fur Physik, 24, 185 (1923)

S.F. Edwards, Phil. Mag., 4, 1171 (1959)

S.F. Edwards and A. Lenard, J. Math. Phys., 3, 778 (1962)

O.C. Eldridge and M. Feix, Phys. Fluids, 5, 1076 (1962)

J.W. Gibbs, 'Elementary Principles in Statistical Mechanics' (Dover reprint, 1960) 1902

H.S. Green, 'The Molecular Theory of Fluids' (North-Holland, 1952)

H.S. Green, Handbuch der Physik, 10, 1 (1960)

H.S. Green, Nuclear Fusion, 1, 69 (1961)

M. Green, 'Lectures in Theoretical Physics' (Interscience, 1961)

D. ter Haar, 'Elements of Statistical Mechanics' (Constable, 1955)

L. van Hove, Physica, 16, 137 (1950)

E. Ising, Z. Physik, 31, 253 (1925)

M. Kac, Phys. Fluids, 2, 8 (1959)

M. Kac and E. Helfand, J. Math. Phys., 4, 1078 (1963)

M. Kac, G.E. Uhlenbeck and P.C. Hemmer, J. Math. Phys., 4, 216 (1963)

B. Kaufman, Phys. Rev., 76, 1232 (1949)

J.G. Kirkwood, J. Chem. Phys., 3, 300 (1935)

L.D. Landau and E.M. Lifshitz, 'Statistical Physics' (Pergamon, 1958)

A. Lenard, J. Math. Phys., 2, 682 (1961)

A. Lenard, J. Math. Phys., 4, 533 (1963)

J.E. Mayer, J. Chem. Phys., 18, 1426 (1950)

J.E. Mayer and E. Montroll, J. Chem. Phys., 9, 2 (1941)

E. Meeron, J. Math. Phys., 1, 192 (1960)

National Bureau of Standards, 'Tables relating to Mathieu Functions' (Columbia, 1951)

L. Onsager, Phys. Rev., 65, 117 (1944)

L.S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam, 17, 793 (1914)

J.K. Percus, Phys. Rev. Letters, 8, 462 (1962)

J.K. Percus and G.J. Yevick, Phys. Rev., 110, 1 (1958)

D. Pines and D. Bohm, Phys. Rev., 85, 338 (1952)

A.B. Pippard, 'Elements of Classical Thermodynamics' (Cambridge University Press, 1957)

S. Prager, Advances in Chemical Physics, 4, 201 (1962)

L. Rosenfeld, 'Theory of Electrons' (North-Holland, 1951)

G.S. Rushbrooke, 'Introduction to Statistical Mechanics', (Oxford University Press, 1949)

E.E. Salpeter, Annals of Physics, 5, 183 (1958)

Z.W. Salsburg, R.W. Zwanzig and J.G. Kirkwood, J. Chem. Phys., 21, 1098 (1953)

E. Schrodinger, 'Statistical Thermodynamics' (Cambridge University Press, 1957)

L. Tonks, Phys. Rev., 50, 955 (1936)

G.E. Uhlenbeck, 'Statistical Physics' (Benjamin, 1963)

J.D. van der Waals, Dissertation Leiden (1873)