THE VAN DER WAALS LIMIT AND RELATED TOPICS IN STATISTICAL MECHANICS

by

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General Abstract

This thesis is devoted to the study of a model of the fluid state which is a precise formulation and generalization of the well known model proposed by van der Waals in 1873. In certain special cases other authors have calculated exactly the thermodynamic properties of such fluids, and obtained essentially the van der Waals equation.

The main new result of the thesis is the extension of this calculation to cover the general case of the model. It is shown in particular that (i) the thermodynamic functions are given by a variational principle ; (ii) the pressure is a continuous function of the density (which agrees with the well known properties of real fluids); (iii) in some special cases of the model, the van der Waals equation is not satisfied and the system behaves more like a solid than a fluid.

The general problem of phase transitions in the model is also considered, and some criteria for their absence are derived.

A detailed abstract is given at the beginning of each of the Parts I to IV of the thesis.

Preface

The work presented in this thesis is original except where the work of other authors is explicitly refferred to. Some of the work is due to Professor Oliver Penrose :

(i) In Part I, Prof. Penrose helped me with the proofs of the variational formulae, although the formulae themselves are my own invention.

(ii) In Part II, I use an unpublished inequality (2.10) due to Prof. Penrose. The proof of this inequality presented in the thesis, and its application to the van der Waals model are mainly my own work.

(iii) In Part III, the basic idea, namely the use of (2.1), is due to Prof. Penrose, while the final results and the method are mainly my own.

(iv) In Part IV, the work is entirely my own.

The thesis consists of a general introduction and four Parts. Each Part is self contained, and written in a form which is intended to be suitable for publication in a journal. Parts I and II have been accepted for publication (jointly with Prof. Penrose) in 'Communications in Mathematical Physics', and Part III is shortly to be submitted to the same journal.

I am greatly indebted to Prof. Penrose for giving me the

opportunity to work under his supervision, for suggesting the research topic, and for his continual help and encouragement.

Also, I gratefully acknowledge a Research Fellowship awarded to me on 1/10/'69 by the Royal Commission for the Exhibition of 1851.

I certify the above statement of originality.

Contents

PART III. DEVIATION FROM THE VAN DER WAALS - MAXWELL THEORY

PART IV. VAN KAMPEN'S EQUATION AND SOME OF ITS CONSEQUENCES

GENERAL INTRODUCTION

I. The van der Waals - Maxwell (VDWM) Equation.

We begin by discussing the equation which led to the work in this thesis. The VDWM equation [1][2][3] is an approximate relation between the pressure p, temperature T and volume per particle v of a simple fluid in equilibrium in a closed container. The equation describes the fluid in its pure liquid state and its pure gas state, as well as states which are mixtures of liquid and gas in equilibrium. It therefore provides a qualitative picture of the phenomenon of boiling.

The VDWM equation is

$$p = MC[kT/(v-b) - a/v^2] \qquad (1.1)$$

where k is Boltzmanns constant (positive)[2], while a and b are positive constants which depend on the fluid under consideration. The operation MC, called the Maxwell construction, consists of replacing a loop (see Fig.1) in the function $kT/(v-b) - a/v^2$ by a horizontal straight line segment (representing a constant pressure), in such a way that the areas formed by the curve above and below the segment are equal.

Referring to Fig.1, the part of the graph where $b < v < v_1$ (high density) describes the fluid in its pure liquid state. The part where $v > v_2$ (low density) describes the pure gas state. The horizontal portion where $v_1 \leq v \leq v_2$ describes the transition between liquid and gas, where the system is a mixture of these two phases. In this latter

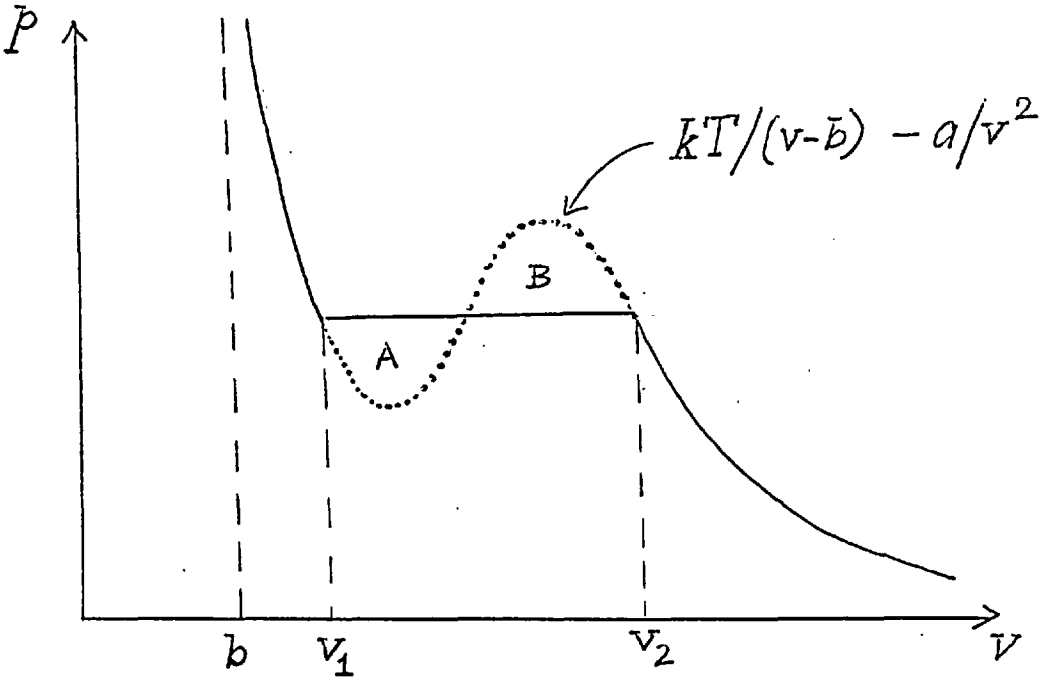

Fig.1. The VDWM equation (continuous line) for $T<T_c$. The areas A and B are equal.

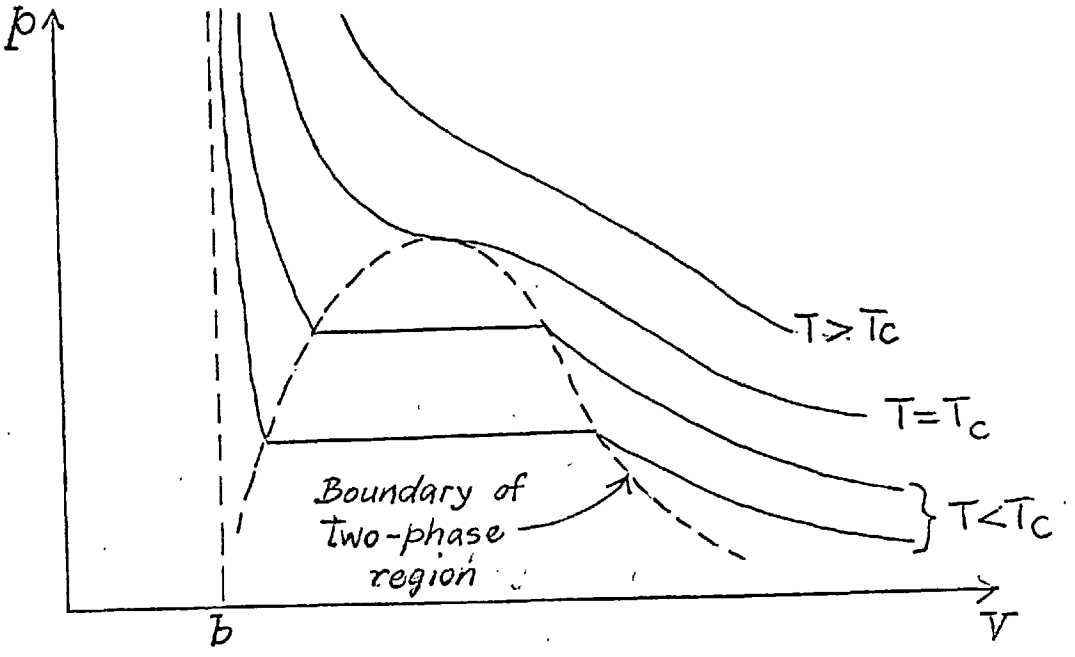

Fig.2. Isotherms of the VDWM equation.

region of the graph, the pressure is constant (for a given temperature), in agreement with the well known properties of fluids.

The form of the curve for p depends of course on the temperature. One finds that p has no straight line segment for $T \geq T_c$ where

$$T_c = \frac{8a}{27bk} \tag{1.2}$$

which is called the critical temperature (see Fig.2). In this case there is no phase transition from liquid to gas. Hence these phases are no longer distinguishable, and there is just one phase which can only be described as a fluid. All this is in qualitative agreement with experiment.

A further property of the VDWM equation is that it agrees quantitatively with experiment when $v >> v_2$ (dilute gas) for a suitable choice of a and b. The agreement is otherwise poor however.

The simplicity of the VDWM equation and its qualitative and partial quantitative agreement with experiment has made it a very useful equation. This usefulness is enhanced by the fact that it has a theoretical justification : it can be derived from a molecular model of the fluid state. The history of this derivation divides into two distinct periods :
The old theory (pre 1900) of van der Waals and Maxwell,

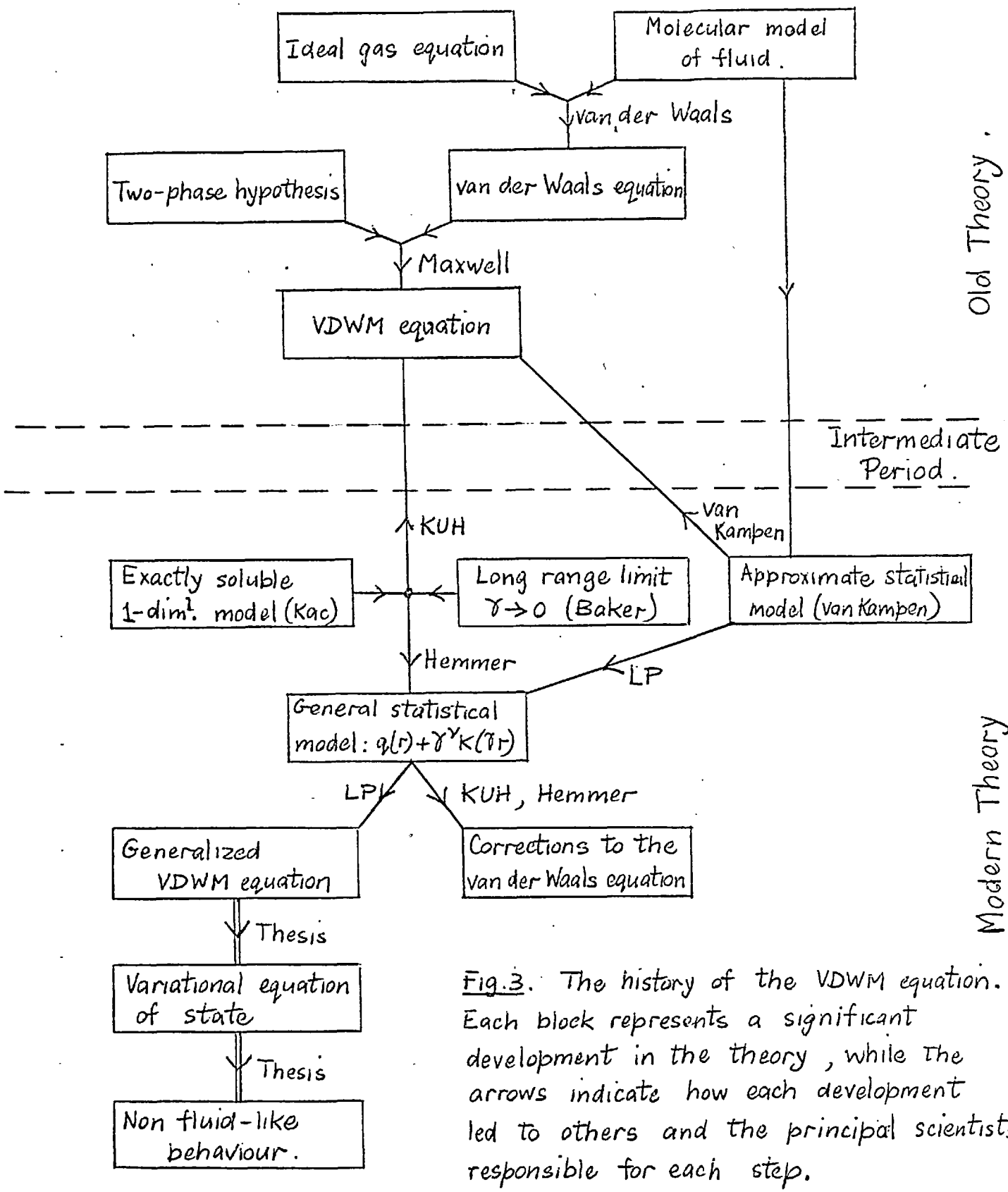

Fig.3. The history of the VDWM equation. Each block represents a significant development in the theory, while the arrows indicate how each development led to others and the principal scientists responsible for each step.

The modern theory (post 1960) derived by Kac, Hemmer, Lebowitz, Penrose, Uhlenbeck and others.

The intermediate period (1900 - 1960 approximately) saw the developement of the theory of statistical mechanics upon which the modern theory of the VDWM equation is based. These theories are illustrated in Fig.3 and discussed in the following sections.

II. The Old Theory of the VDWM Equation

The first equation of state for a gas was the ideal gas law

$$p = kT/v \qquad (2.1)$$

which combined the experimental laws of Boyle (1662), Charles (1787) (or Gay-Lussac 1802) and Avogadro (1811). The equation was, much later, derived theoretically by Maxwell [4] and others using the kinetic theory of gases [2] and the assumptions that (i) the molecules are of negligible volume and that (ii) interactions or collisions between them are negligible.

Further experimental work with gases showed marked deviations from the ideal gas law. A better agreement with experiment was obtained from

$$p = kT/(v-b) \qquad (2.2)$$

where b was an experimentally determined positive constant

for a given gas. This was used by Clausius among others. The equation had a theoretical justification. The molecules were imagined not to be points but to each have an effective volume b. Hence v was replaced in (2.1) by the available volume per particle (v-b), giving (2.2).

The next major advance was the attainment of lower temperatures (e.g. Thilorier (1835) obtained -110^{o}c) which enabled many more gases to be liquefied. This led to the belief that any gas could be liquefied at sufficiently low temperatures. To explain this liquefaction it was thought that there must be attractive forces between the molecules. More direct evidence of these forces was obtained from the experiments of J.P.Joule and W.Thomson (Lord Kelvin)(1852-1862) resulting in the so called Joule Thomson effect [1].

It was van der Waals [1](1873) who first included these attractive forces in the equation of state (2.2) in a satisfactory way. By a well known argument [1,2] he deduced that the attractive force between molecules should reduce the pressure on the container walls by a term proportional to $1/v^2$. He thus arrived at the van der Waals equation

$$p = kT/(v-b) - a/v^2 \qquad (2.3)$$

where a is a positive constant. Van der Waals also showed that his equation agreed well with experimental results for

gases at sufficiently low densities. The achievement of van der Waals is assessed by E.H.Kennard [2] (p.208) in his well known book 'Kinetic Theory of Gases', where he states :

.....'like every important advance in physics, the equation had forerunners which went a long way toward accomplishing the same thing. Clausius, for example, introduced the term b, and Hirn wrote p+a for p. The advance made by van der Waals over his predecessors was twofold : first of all, he made the change from a to a/v^2, and then he discussed the equation in comparison with experimental data and showed that in certain cases it fitted well. Both of these steps were important. We can probably say with safety, however, that, if van der Waals had not proposed the equation, some one else presently would have done so ; it was, so to speak, in the air. In scientific work in general the individual scientist seems to determine when and in what form an advance shall come rather than to determine what advances shall ultimately be made.'

The experiments of T.Andrews (1869) showed that during liquefaction (or boiling) the pressure follows curves of the form shown in Fig.2. It was Maxwell [3] who showed how the van der Waals equation could be modified to give such curves. He considered the system to be a mixture of a gas phase and a

liquid phase, each obeying the van der Waals equation, and used the equilibrium condition that the two phases must have equal pressures and chemical potentials. This led him to the VDWM equation (1.1).

III. The Intermediate Period. Development of Statistical Mechanics

Early attempts to improve on the VDWM equation or to make its derivation more rigorous met with little success. Work on this problem led instead to the development of equilibrium statistical mechanics, primarily by Boltzmann (1896)[4] and Gibbs (1902)[5]. This theory shows[3] how to calculate in principle the exact pressure of a system of N particles (a fluid for example) given its temperature T, volume V, and the potential energy function $\varphi(r)$ for two interacting particles at distance r. Formally one can express this as

$$P = f(N,V,T,\varphi) \qquad (3.1)$$

The potential φ was known to be repulsive (positive) at short distances (small r) and attractive (negative) for large distances (large r)(see Fig.4). However, the exact form of φ was not (and is still not) precisely known. Also, the formula (3,1) was far too complex to make direct calculations of pressure.

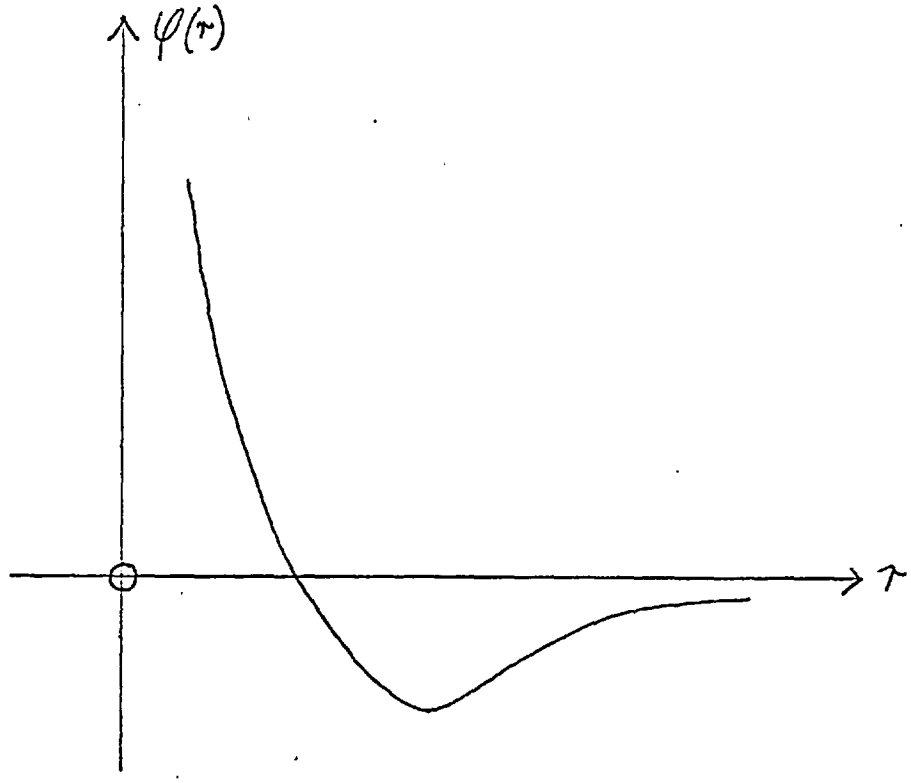

Fig. 4. Typical interaction potential for a fluid.

The next major advance was the theory of virial expansions primarily due to Mayer [6], which showed how to express (3.1) in a series of the form

$$p = \frac{kT}{v} + a_2/v^2 + a_3/v^3 + \ldots , \qquad (3.2)$$

a form proposed originally by H.K.Onnes (1901). Here $v \equiv \frac{V}{N}$ is the volume per particle and $a_2, a_3, \ldots$ depend on T and the potential $\varphi(r)$.

The virial expansion (3.2) showed excellent agreement with experiment for gases, but unfortunately attempts to apply it to the liquid state, and to construct a theory of the gas-liquid transition from it, were unsuccessful. The reason for this failure was provided by the theory of Lee and Yang (1952) [7,8]. This theory shows that (3.2) does not converge for the liquid state, and that a value v_t of v where a phase transition occurs does not necessarily coincide with a value v_d of v where the series (3.2) diverges.

To the present day there is no theory of the liquid state with anything like the completeness of the Mayer theory of gases. The great difficulties with the liquid state has forced research into several indirect lines of approach to the problem. One line of approach was the construction of simplified artificial models of a fluid. The most famous of these is the lattice gas : in a special two-dimensional case

the pressure of this system can be calculated exactly and shows a gas-liquid transition. This calculation was first made by Onsager (1944)[9] for the analogous Ising magnet, and later applied to fluids by Lee and Yang (1952)[8]. Apart from the usefulness of the exact result, the Onsager solution proved for the first time that statistical mechanics, as expressed by (3.1), could by itself yield a complete theory of the liquid state and the gas-liquid transition.

Another approach to the equation of state was through the so called two body distribution $n_2(r)$ of Ornstein and Zernike (1914)[10]. If this function is known the pressure can be calculated exactly. Attempts to calculate $n_2(r)$ led to various approximate integral equations. Among these are the equations of Yvon, Born and Green [11], Kirkwood[12], Percus and Yevick [13] and the HNC equation [14]. Unfortunately, the errors in these equations are difficult to evaluate so that the significance of the results obtained form them is not clear.

Yet another approach has been to concentrate on general properties of the pressure as predicted by (3.1), rather than attempting exact calculations. It is found that the pressure has simple properties only in the limit in which the volume V of the container and the number N of particles tends to infinity in such a way that $v \equiv V/N$ remains constant. This is the so called Thermodynamic limit. This limit is applied to the

general formula (3.1) and the resulting thermodynamic pressure can be written formally as

$$p(v,T) = \lim_{\substack{N,V\to\infty \\ V/N\to v}} f(N,V,T,\varphi) \qquad (3.3)$$

The existence of this very important limit was proved by Van Hove (1949)[15], Ruelle (1963)[16] and Fisher (1964)[17] for a large class of two-body potentials φ including those which occur in real fluids. Also $p(v,T)$ was shown to be a non-increasing function of v, which agrees with experiment. More recently Dobrushin and Minlos (1967)[18] and Penrose (1967)[19] have proved that p is a continuous function of v, again in agreement with experiment. The most important result of this kind is the general theory of phase transitions developed by Yang and Lee (1952)[7], which has resulted in much recent research [20 - 28].

IV. The Modern Theory of the VDWM Equation

Recently, Kac, Uhlenbeck and Hemmer (KUH) (1963)[29] considered an idealized one-dimensional system in which the interaction potential $\varphi(r,\gamma)$, depending on a positive parameter γ, is given by (see Fig.5)

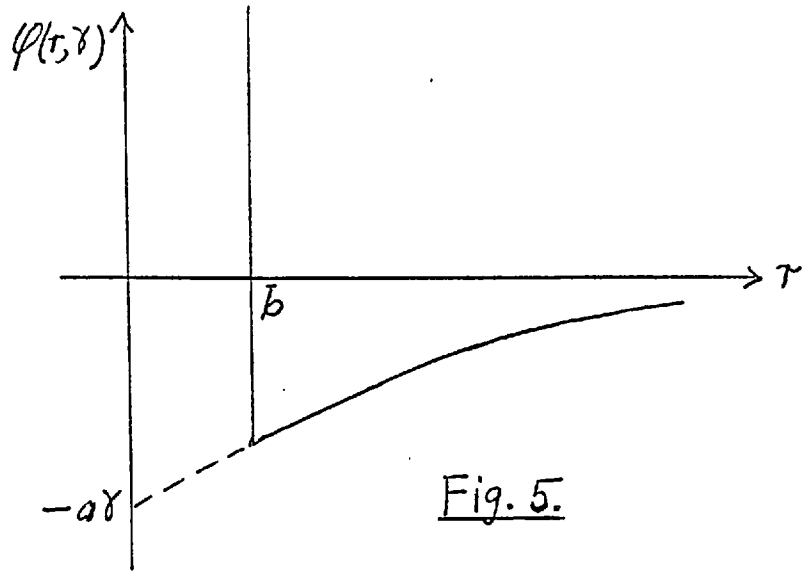

Fig. 5.

$$\varphi(r,\gamma) \equiv \begin{cases} \infty \text{ for } r < b, \\ -a\gamma e^{-\gamma r} \text{ for } r \geq b , \end{cases} \tag{4.1}$$

where a and b are positive constants. The definition (4.1) implies that the particles have a hard core and an attractive 'tail'. This is qualitatively the same as the expected form of φ for real fluids, shown in Fig.4.

The parameter γ plays a vital role in the theory : γ itself is a measure of the strength of the attraction, while γ^{-1} is a measure of the range of this attraction.

The form (4.1) of φ was chosen because, from a method found by Kac (1959)[30], it enables the thermodynamic pressure (3.3) to be calculated exactly. The dependence on γ is chosen so that as $\gamma \to 0$ (called the van der Waals limit)[1]

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[1] Considered earlier by Baker (1962)[31] for magnetic systems.

the original assumptions of van der Waals become more and more nearly satisfied. Indeed, one easily finds from (4.1) that

$$\lim_{\gamma \to 0} \varphi(r,\gamma) = 0 \quad \text{for} \quad r \geqq b \tag{4.2}$$

so that the attraction vanishes, although its range becomes infinite, in this limit. One also finds that

$$\lim_{\gamma \to 0} \int_0^\infty dr\, \varphi(r,\gamma) = -\int_0^\infty ds\, ae^{-s} = -a \tag{4.3}$$

This means that the potential energy of a single particle, interacting with any number of other particles (each with a hard core), remains finite when $\gamma \to 0$. (If the limit (4.3) were zero we would expect the effects of the attractive tail to vanish when $\gamma \to 0$; if the limit (4.3) were infinite we would expect something catastrophic to happen when $\gamma \to 0$).

The results of KUH can be expressed, with the notation of (1.1), in the form

$$\lim_{\gamma \to 0} p(v,T,\gamma) = MC[kT/(v-b) - a/v^2] \tag{4.4}$$

where $p(v,T,\gamma)$ is the thermodynamic pressure (3.3) corresponding to the potential (4.1). The right side of (4.4) is precisely the VDWM pressure (1.1). This provided, for the first time, a rigorous formulation of the VDWM equation and gave a precise mathematical interpretation to the constants a and b.

This gives a new and deeper significance to the old VDWM theory. Also the complicated formalism of statistical mechanics becomes a little less forbidding when one knows that it can yield such simple and old established results.

It should be noted that the rigourous proof of the existence of the thermodynamic pressure $p(v,T)$ is essential to the modern theory of the VDWM equation. Without it, the result (4.4) could not even be formulated, let alone proved.

The result (4.4) has been generalized by Lebowitz and Penrose (LP) (1966)[32], by a method based on the work of van Kampen (1944)[33]. They showed that the restriction to one dimensional systems, and to the potential (4.1), is not necessary. They found, for certain classes of potentials $\varphi(r,\gamma)$, including those with an attractive tail, that the van der Waals limit of the pressure has the form

$$\lim_{\gamma\to 0} p(v,T,\gamma) = MC[p^{o}(v,T) - a/v^{2}] \qquad (4.5)$$

where p^{o} is the thermodynamic pressure for a general system of particles with hard cores.

Another developement is the expansion of $p(v,T,\gamma)$ in powers of γ, obtained by KUH[29] and Hemmer [34]. The first term of this expansion is the van der Waals equation, while other terms give corrections which in principle describe the behaviour of real fluids.

V. The Thesis

The work of LP leaves several questions unanswered. They proved (4.5) for a certain class of functions $\varphi(r,\gamma)$, but for functions not in this class they could prove very little. This leads us to ask

(i) does (4.5) hold for all functions $\varphi(r,\gamma)$, and

(ii) if not, what happens when (4.5) does not hold ?

In this thesis we provide some answers to these questions. We consider question (ii) first and show that, for a very general class of functions $\varphi(r,\gamma)$, the van der Waals limits of the 'free energy'[3] and the so called'grand canonical pressure'[3] exist and are given by a variational principle. We answer question (i) by showing that the free energy is sometimes less than that corresponding to (4.5), which proves that (4.5) does <u>not</u> always hold. We show that when (4.5) does not hold the density of the system is non-uniform, and very probably periodic, so that the system resembles a solid more than a fluid.

We also answer some questions of a more technical nature. We show (Part II) that the pressure

$$p(v,T,0+) \equiv \lim_{\gamma \to 0} p(v,T,\gamma)$$

is a continuous function of v, (even when (4.5) does not hold). If this result, which is by no means obvious, were not true,

the model we are considering would be very unphysical.

In Part IV we show that the notions of uniqueness and degeneracy, associated with phase transitions in other models, have a counterpart in the present model. We find that some methods of treating this problem already exist in the standard literature of non-linear integral equations.

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(References to Parts I-IV are given at the end of the appropriate Part.)

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Part I.

A VARIATIONAL PRINCIPLE

(As mentioned in the preface, each of the Parts I, II and III is written in a form which is intended to be suitable for publication in a journal. Consequently there is some repetition of definitions and results. Each Part has its own numbering for equations and references, and makes no reference to equations in any other Part. There are slight differences of notation between the General Introduction and the following Parts and between the Parts themselves, but this is always made clear).

Abstract.

We consider the thermodynamic pressure $p(\mu,\gamma)$ of a classical system of particles with the two-body interaction potential $q(\underset{\sim}{r}) + \gamma^{\nu}K(\gamma\underset{\sim}{r})$, where ν is the number of space dimensions, γ is a positive parameter, and μ is the chemical potential. The temperature is not shown in the notation. We prove rigorously, for hard-core potentials $q(\underset{\sim}{r})$ and for a very general class of functions $K(\underset{\sim}{s})$, that the limit $\gamma \to 0$ of the pressure $p(\mu,\gamma)$ exists and is given by

$$\sup_{n\in\mathcal{R}} \lim_{|D|\to\infty} \frac{1}{|D|}\left[\int_D d\underset{\sim}{y}\left\{\mu n(\underset{\sim}{y}) - a^{o}[n(\underset{\sim}{y})]\right\} - \frac{1}{2}\int_D d\underset{\sim}{y}\int_D d\underset{\sim}{y}'\, n(\underset{\sim}{y})n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}')\right]$$

where the limit and the supremum can be interchanged. Here $\mathcal{R}$ is a certain class of non-negative, Riemann integrable functions, D is a cube of volume $|D|$, and $a^{o}(\rho)$ is the free energy density of a system with $K = 0$ and density ρ. A similar result is proved for the free energy.

I. Introduction.

Many authors have considered the equilibrium statistical mechanics of a system of identical particles which have a two-body interaction potential of the form

$$v(\underset{\sim}{r},\gamma) = q(\underset{\sim}{r}) + \gamma^{\nu} K(\gamma \underset{\sim}{r}) \qquad (1.1)$$

where $\underset{\sim}{r}$ is the vector distance between a pair of particles, γ is a positive parameter and ν is the number of dimensions. [redacted]. The function $q(\underset{\sim}{r})$ is called the short range or reference potential and the term $\gamma^{\nu}K(\gamma\underset{\sim}{r})$ is called the long range or Kac potential, whose range is proportional to γ^{-1}. Some of these authors [1-4] have considered the limiting values of the thermodynamic functions and correlation functions in the limit $\gamma \to 0$; others [3,5-7] have derived expansions of these functions in powers of γ. We shall be dealing with the former problem. In particular, we shall generalize the results of LEBOWITZ and PENROSE [4] (henceforth referred to as LP), to a wider class [redacted] of Kac potentials. [redacted] Both the paper of LP and the present one are [redacted] motivated to some extent by the work of VAN KAMPEN [8].

The main result of LP was to prove rigorously, for a certain class of Kac potentials (including, for example, non-positive Kac potentials) [redacted], that the free energy density $a(\rho,\gamma)$ of a system with the potential (1.1) and density ρ has the limit

$$a(\rho,0+) \equiv \lim_{\gamma\to 0} a(\rho,\gamma) = CE[a^0(\rho) + \tfrac{1}{2}\alpha\rho^2] \qquad (1.2)$$

where[1] $\alpha \equiv \int d\underset{\sim}{s}\, K(\underset{\sim}{s})$, $a^0(\rho)$ is the free energy density of a system (called the reference system) with two-body potential $q(\underset{\sim}{r})$, and CE $f(\rho)$, called the convex envelope of the function $f(\rho)$, is defined for arbitrary f as the maximal convex function not exceeding $f(\rho)$. They deduced that the limit $\pi(\rho,0+)$ of the pressure $\pi(\rho,\gamma) \equiv \rho\, \partial/\partial\rho\, a(\rho,\gamma) - a(\rho,\gamma)$ is given by the Maxwell construction (or equal area rule) [4] applied to the function

$$\pi^0(\rho) + \tfrac{1}{2}\alpha\rho^2 \qquad (1.3)$$

where $\pi^0(\rho)$ is the pressure of the reference system. This strongly resembles Maxwell's modification of the van der Waals equation of state, and is identical to it in the one dimensional case if the reference system consists of hard rods [3]. Consequently, the limit $\gamma \to 0$ is known as the van der Waals limit.

The result (1.2) can also be formulated in terms of the pressure $p(\mu,\gamma)$ expressed as a function of the chemical potential μ. We then find

$$p(\mu,0+) \equiv \lim_{\gamma\to 0} p(\mu,\gamma) = \max_{\rho} [\mu\rho - a^0(\rho) - \tfrac{1}{2}\alpha\rho^2] \qquad (1.4)$$

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[1] When the range of an integral is not specified, it is over all of ν-dimensional space.

To deduce this from (1.2) we use the general relationship (see [10])

$$p(\mu,\gamma) = \max_{\rho} [\mu\rho - a(\rho,\gamma)] \qquad (1,5)$$

and note (as can be seen from Fig. 1) that

$$\max_{\rho} [\mu\rho - CE\ f(\rho)] = \sup_{\rho} [\mu\rho - f(\rho)] \qquad (1.6)$$

for any function f. [illegible] Now taking the limit $\gamma \to 0$ of (1.5) and using (1.2) and (1.6) we obtain (1.4). The interchange of the maximum and the limit is justified[2] by the fact [4] that $a(\rho,\gamma)$ tends uniformly to its limit on a suitable interval of values of ρ. Alternatively equation (1.4) can be deduced from first principles by using the method of LP in the grand ensemble. [illegible].

For a more general class of Kac potentials, LP obtained upper and lower bounds on $a(\rho,0+)$, but they did not prove for these potentials that the limits $a(\rho,0+)$ and $p(\mu,0+)$ exist. In the present paper we provide such proofs and obtain expressions for the limit functions. We also include the effects of an external potential of the form $\psi(\gamma x)$.

[2] See reference [10], section 10.

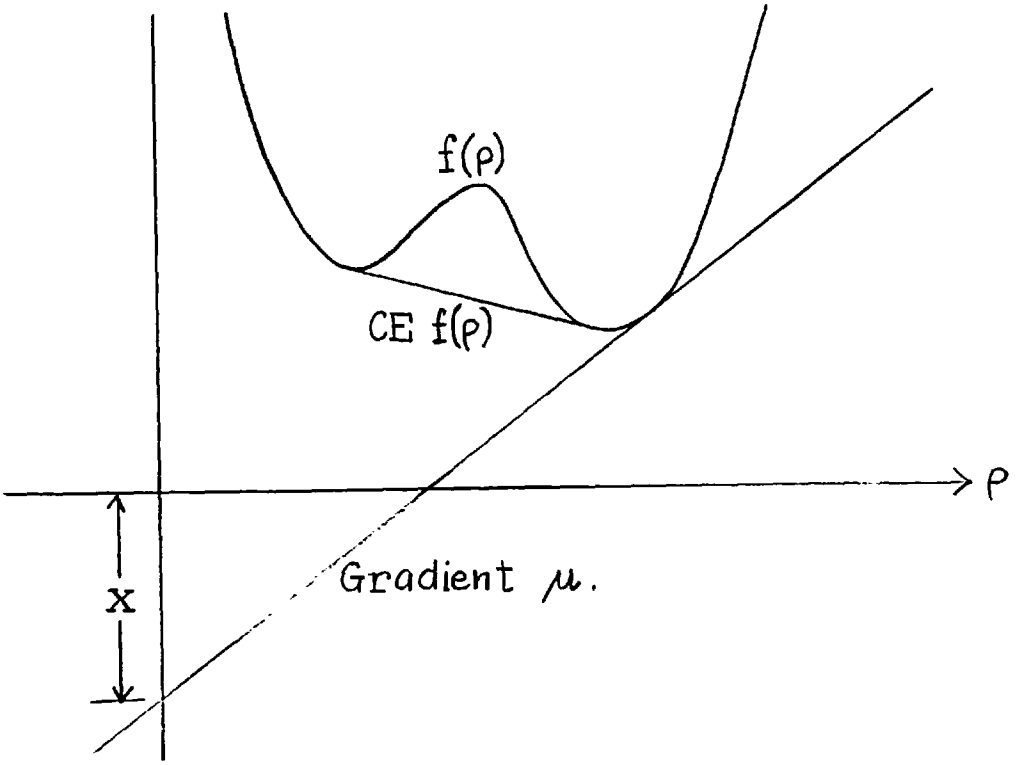

Fig 1. Both sides of (1·6) are equal to the distance x.

Results
II. Definitions and Outline of Method.

We confine our attention for the moment to the pressure $p(\mu,\gamma)$, since the method and the main result are considerably simpler for this function. The free energy will be dealt with in section VI.

The function $p(\mu,\gamma)$, called the pressure in the grand ensemble, can be defined by the thermodynamic limit [10]

$$p(\mu,\gamma) \equiv \lim_{|\Omega|\to\infty} P(\mu,\Omega,\gamma) \tag{2.1}$$

where Ω is a cube of volume $|\Omega|$ and

$$P(\mu,\Omega,\gamma) \equiv \frac{1}{\beta|\Omega|} \log \Xi(\mu,\Omega,\gamma) \tag{2.2}$$

β being the reciprocal temperature and Ξ the grand partition function, defined by

$$\Xi(\mu,\Omega,\gamma) \equiv \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,\Omega,\gamma) \tag{2.3}$$

Here, $Z(N,\Omega,\gamma)$ is the partition function for N particles in Ω, defined for $N=0$ by $Z(0,\Omega,\gamma) \equiv 1$ and for $N \geq 1$ by

$$Z(N,\Omega,\gamma) \equiv \frac{1}{N!\Lambda^{\nu N}} \int_{\Omega} d\underset{\sim}{x}_1 \cdots \int_{\Omega} d\underset{\sim}{x}_N \exp(-\beta V_N) \tag{2.4}$$

where Λ is the thermal wavelength [10], $V_1 \equiv \psi(\gamma \underset{\sim}{x}_1)$ and

$$V_N \equiv \sum_{1\leq a<b\leq N} v(\underset{\sim}{x}_a - \underset{\sim}{x}_b, \gamma) + \sum_{1\leq a\leq N} \psi(\gamma \underset{\sim}{x}_a) \tag{2.5}$$

for $N \geq 2$, with $v(\underset{\sim}{r},\gamma)$ defined by (1.1) and $\psi(\gamma\underset{\sim}{x})$ a periodic external potential whose period is proportional to γ^{-1}. The potential ψ provides, among other things, a way of calculating the correlation functions in the van der Waals limit by functional differentiation; this calculation we hope to present in a future publication.

The conditions to be satisfied by the interaction potentials q and K are

$$q(\underset{\sim}{r}) = q(-\underset{\sim}{r}), \qquad K(\underset{\sim}{s}) = K(-\underset{\sim}{s}), \tag{2.6}$$

$$\left.\begin{aligned} &q(\underset{\sim}{r}) = \infty \text{ for } |\underset{\sim}{r}| < r_0 \\ &|q(\underset{\sim}{r})| < C|\underset{\sim}{r}|^{-\nu-\varepsilon} \text{ for } |\underset{\sim}{r}| \geq r_0 \end{aligned}\right\} \tag{2.7}$$

$|K(\underset{\sim}{s})| < k(|\underset{\sim}{s}|)$ for all $\underset{\sim}{s}$, where $k(t)$ is a non-increasing function such that $\int d\underset{\sim}{s}\, k(|\underset{\sim}{s}|)$ is finite, and $|K(\underset{\sim}{s})| < \bar{K}$ for all $\underset{\sim}{s}$, (2.8)

$K(\underset{\sim}{s})$ is continuous almost everywhere, (2.9)

where $\bar{K}$, C, r_0 and ε are positive constants. Condition (2.7) implies that the particles have a ν-dimensional spherical hard core of diameter r_0. The function ψ satisfies the conditions

$\psi(\underset{\sim}{y})$ is periodic over an infinite cubic lattice with unit cell J, (2.10)

$|\psi(\underset{\sim}{y})| < \bar{\psi}$, a positive constant, for all $\underset{\sim}{y}$, (2.11)

$\psi(\underset{\sim}{y})$ is continuous almost everywhere. (2.12)

In the case $\psi = 0$ it was shown by DOBRUSHIN [9] that the conditions (2.6,7,8) ensure the existence of $p(\mu,\gamma)$.

It is not difficult to extend the argument of DOBRUSHIN and prove that the thermodynamic limit also exists if a periodic external potential, bounded below, is present. We shall not give this proof here.

Our first result is

Theorem 1. Under conditions (2.6-12), the van der Waals limit $p(\mu,0+)$ of the pressure $p(\mu,\gamma)$ exists and is given by

$$p(\mu,0+) = \lim_{|D|\to\infty} \sup_{n\in\mathcal{R}} F(n,\mu,D) \tag{2.13}$$

or equivalently by

$$p(\mu,0+) = \sup_{n\in\mathcal{R}} F(n,\mu,\infty) \tag{2.14}$$

The convergence of $p(\mu,\gamma)$ to $p(\mu,0+)$ is uniform on any closed interval of values of μ. The functionall $F(n,\mu,D)$ is defined to be

$$\frac{1}{|D|}\int_D d\underset{\sim}{y}\left\{\mu n(\underset{\sim}{y}) - \psi(\underset{\sim}{y})n(\underset{\sim}{y}) - a^0[n(\underset{\sim}{y})]\right\} - \frac{1}{2|D|}\int_D d\underset{\sim}{y}\int_D d\underset{\sim}{y}' n(\underset{\sim}{y})n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}') \tag{2.15}$$

and $F(n,\mu,\infty)$ is defined by

$$F(n,\mu,\infty) \equiv \lim_{|D|\to\infty} F(n,\mu,D) \tag{2.16}$$

The limits in (2.13) and (2.16) are taken over any ascending[3] sequence of [redacted] ν-dimensional cubes D (of volume $|D|$) whose sides are multiples of λ and are parallel to those of J. The set $\mathcal{R}$ comprises all functions n which are Riemann integrable on every bounded region of ν-dimensional space, satisfy $0 \leqq n(\underset{\sim}{y}) \leqq \rho_c$ where ρ_c is the close packing density [13] for spheres of diameter r_0,

[3] A sequence of sets $E_1, E_2, E_3 \ldots$ is ascending if $E_1 \subset E_2 \subset E_3 \ldots$

and are periodic[4], with a unit cell that need not be Ω.

All the integrals in (2.15), and henceforth, are taken as Lebesgue integrals. The formal similarity between the result (2.14) (in the case $\psi = 0$) and the equation of state (1.4) is apparent. In particular they are identical if there is a function n independent of $\underset{\sim}{y}$ which maximizes $F(n,\mu,\infty)$. [redacted].

Our method of proof of theorem 1 is similar to the method used by LP. Starting from (2.4), we divide the cube Ω into a number of cells of volume ω, obtain upper and lower bounds on $P(\mu,\gamma,\Omega)$ in terms of Ω, γ and ω, and then take the succession of limits (called the LP triple limit)

$$\text{first } |\Omega|\to\infty, \text{ then } \gamma\to 0 \text{ and finally } \omega\to\infty \qquad (2.17)$$

of these bounds. We also use an additional operation which consists of restricting the density ρ of the particles thus :

$$\rho \leqq \rho' \quad \text{where} \quad \rho' < \rho_c \ , \qquad (2.18)$$

and finally taking the limit $\rho' \to \rho_c$ after the LP triple limit.

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[4] i.e. we can find ν linearly independent vectors $\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_\nu$ such that $n(\underset{\sim}{y}+\underset{\sim}{k}_\lambda) = n(\underset{\sim}{y})$ for $\lambda = 1\ldots\nu$ and for all $\underset{\sim}{y}$.

When this sequence of limits has been taken, the upper and lower bounds coincide and are given by (2.14) or (2.13).

III. Properties of $F(n,\mu,D)$ and $F(n,\mu,\infty)$.

Before proving theorem 1, we derive some properties of the functionals defined therein. We prove firstly that $F(n,D)$ and $F(n,\infty)$ exist[5] (or have value $-\infty$), and that they both have a supremum for $n \in \mathcal{R}$. Secondly we prove the equivalence of (2.13) and (2.14). Finally, for later use in the proof of theorem 1, we show that $F(n,D)$ is continuous with respect to n in a certain sense.

To show that $F(n,D)$ exists, we note from (2.15) that it is the sum of four integrals. The first, second and last integrals exist because products of integrable functions are integrable. To study the third integral we define, for any ρ' satisfying $0 < \rho' < \rho_c$,

$$a^o_{\rho'}(\rho) \equiv \begin{cases} a^o(\rho) & \text{for } 0 \leqq \rho \leqq \rho' \\ a^o(\rho') & \text{for } \rho' \leqq \rho \leqq \rho_c . \end{cases} \tag{3.1}$$

Since $a^o_{\rho'}(\rho)$ is uniformly continuous function[10] of ρ in the closed interval $[0,\rho_c]$, it follows [11] that $a^o_{\rho'}[n(\underset{\sim}{y})]$ is measurable. Consider, for a given n, the sequence of functions

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[5] We omit the dependence of F on μ in this section.

$$f_{\rho'}(\underset{\sim}{y}) \equiv a^{o}_{\rho'}[n(\underset{\sim}{y})] - a^{o}(\rho_{o}) \tag{3.1}$$

where ρ_o is a value of ρ where $a^o(\rho)$ attains its minimum. The functions $f_{\rho'}$ are non-negative, measurable and, since a^o is convex, form a non-decreasing (as ρ' increases) sequence for $\rho' \geq \rho_o$. Now defining

$$f(\underset{\sim}{y}) \equiv \lim_{\rho' \to \rho_c} f_{\rho'}(\underset{\sim}{y}) = a^{o}[n(\underset{\sim}{y})] - a^{o}(\rho_{o}) \tag{3.3}$$

we deduce from Lebesgues' monotone convergence theorem [11] that $\int_D d\underset{\sim}{y}\, f(\underset{\sim}{y})$ either exists or is infinite. It follows that $\int_D d\underset{\sim}{y}\, a^o[n(\underset{\sim}{y})]$ either exists or is infinite. We have proved that $F(n,D)$ either exists or is equal to $-\infty$ (depending on the choice of n) for all $n \in \mathcal{R}$. In particular, F is finite if $n(\underset{\sim}{y})$ is bounded away from ρ_c.

Next we show that $F(n,\infty)$ exists, and if n has the unit cell Γ

$$F(n,\infty) = \frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\left\{\mu n(\underset{\sim}{y}) - a^{o}[n(\underset{\sim}{y})] - \tfrac{1}{2}n(\underset{\sim}{y})\int d\underset{\sim}{y}'\, n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}')\right\}$$

$$- \lim_{|D|\to\infty}\frac{1}{|D|}\int_D d\underset{\sim}{y}\; n(\underset{\sim}{y})\psi(\underset{\sim}{y}) \tag{3.4}$$

To prove this we note firstly that the limit on the right side exists because of the periodicity of n and ψ. Secondly, we consider the difference

$$\delta(D) \equiv \frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\; n(\underset{\sim}{y})\int d\underset{\sim}{y}'\, n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}') - \frac{1}{|D|}\int_D d\underset{\sim}{y}\; n(\underset{\sim}{y})\int_D d\underset{\sim}{y}'\, n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}') \tag{3.5}$$

between the quadratic terms in the expressions (2.15) and (3.4) for $F(n,\infty)$. Now D can be expressed as a union of regions congruent to the unit cell Γ together with a region σ whose volume $|\sigma|$ is of order $|D|^{1-1/\nu}$ (proportional to the surface area of D). Hence we can, by (2.8) and the periodicity of n, replace Γ by D in the first term on the right side of (3.5) if we add a correction of order $|D|^{-1/\nu}$. This correction has the upper bound $\rho_c^2 |\sigma| |D|^{-1} \int d\underset{\sim}{s} |K(\underset{\sim}{s})|$. We now have

$$|\delta(D)| = \frac{1}{|D|} \left| \int_D d\underset{\sim}{y}\, n(\underset{\sim}{y}) \int_{D^c} d\underset{\sim}{y}'\, n(\underset{\sim}{y}') K(\underset{\sim}{y}-\underset{\sim}{y}') \right| + O(|D|^{-1/\nu})$$

$$\leq \rho_c^2 \frac{1}{|D|} \int_D d\underset{\sim}{y} \int_{D^c} d\underset{\sim}{y}' \, |K(\underset{\sim}{y}-\underset{\sim}{y}')| + O(|D|^{-1/\nu}) \qquad (3.6)$$

where D^c is the complement of D. By the argument applied by LP to their equation (2.15), the first term on the right side vanishes when $|D| \to \infty$. Thirdly, we note that the terms in (2.15) involving μn and $a^o(n)$ tend to the corresponding terms in (3.4) because of the periodicity of n. This completes the proof of (3.4).

The fact that $F(n,D)$ and $F(n,\infty)$ have suprema follows from the inequality

$$F(n,D) \leq \rho_c |\mu| + \rho_c \overline{\psi} - a^o(\rho_o) + \frac{1}{2} \rho_c^2 \int d\underset{\sim}{s} |K(\underset{\sim}{s})| , \qquad (3.7)$$

which in turn follows from (2.15) and (2.11).

To prove the equivalence of (2.13) and (2.14) we need

Lemma 1. If $\mathcal{R}_\Gamma$ is the subclass of $\mathcal{R}$ consisting of functions with unit cell Γ, and Γ is a cube whose sides are parallel to and are multiples of those of J (the unit cell of ψ), then we can find an $\varepsilon(\Gamma) > 0$ such that $\varepsilon(\Gamma) \to 0$ as $|\Gamma| \to \infty$ and

$$\left|F(n,\Gamma) - F(n,\infty)\right| < \varepsilon(\Gamma) \tag{3.8}$$

for all $n \in \mathcal{R}_\Gamma$. Here $|\Gamma|$ means the volume of Γ.

Proof. The terms involving μn and $a^o(n)$ in the expression (2.15) for $F(n,\Gamma)$ are identical to the corresponding terms in the expression (3.4) for $F(n,\infty)$. By an argument like that leading to (3.6), we deduce that difference between the quadratic terms in $F(n,\Gamma)$ and in $F(n,\infty)$ is bounded by an amount $\varepsilon(\Gamma)$ independent of n and tending to zero as $|\Gamma| \to \infty$. Also, because $n(\underset{\sim}{y})\psi(\underset{\sim}{y})$ has unit cell Γ, we deduce that

$$\lim_{|D|\to\infty} \frac{1}{|D|}\int_D d\underset{\sim}{y}\; n(\underset{\sim}{y})\psi(\underset{\sim}{y}) = \frac{1}{|\Gamma|}\int_\Gamma d\underset{\sim}{y}\; n(\underset{\sim}{y})\psi(\underset{\sim}{y}) \tag{3.9}$$

i.e. the terms involving ψ in $F(n,\Gamma)$ and $F(n,\infty)$ are equal. This completes the proof of (3.8).

It follows from (3.8) that

$$\sup_{n\in\mathcal{R}_\Gamma} F(n,\Gamma) \leqq \sup_{n\in\mathcal{R}_\Gamma} F(n,\infty) + \varepsilon(\Gamma) \quad . \tag{3.10}$$

We can replace $\mathcal{R}_\Gamma$ by $\mathcal{R}$ on the left side because $F(n,\Gamma)$ depends only on the values of $n(\underset{\sim}{y})$ for $\underset{\sim}{y}$ in Γ, and on the right side because $\mathcal{R}_\Gamma \subset \mathcal{R}$. Taking the limit $|\Gamma| \to \infty$ of the resulting inequality gives

$$\limsup_{|D|\to\infty} \sup_{n\in\mathcal{R}} F(n,D) \leqq \sup_{n\in\mathcal{R}} F(n,\infty) \tag{3.11}$$

provided that every D is related to J as specified in theorem 1. The reverse of this inequality also holds because $F(n,\infty) \equiv \lim_D F(n,D) \leqq \liminf_D \sup_n F(n,D)$ for all n. This proves the equivalence of (2.13) and (2.14) and the existence of the limit on the right side of (2.13).

Finally, we show that the functional $F(n,D)$ is continuous in n. For any ρ' satisfying $0 < \rho' < \rho_c$, let $\mathcal{R}(\rho')$ be the subclass of $\mathcal{R}$ consisting of functions n which are bounded above by ρ'. We then have

Lemma 2. The functional $F(n,D)$ is continuous with respect to n, [illegible] for $n \in \mathcal{R}(\rho')$, in the following sense : for any $\varepsilon > 0$ we can find a $\delta > 0$ such that, for $n_1 \in \mathcal{R}(\rho')$ and $n_2 \in \mathcal{R}(\rho')$,

$$\frac{1}{|D|}\int_D d\underset{\sim}{y}\left|n_1(\underset{\sim}{y}) - n_2(\underset{\sim}{y})\right| < \delta \tag{3.12}$$

implies $$\left|F(n_1,D) - F(n_2,D)\right| < \varepsilon \tag{3.13}$$

Further, the continuity is uniform in both n and D. (In the language of modern analysis, F is continuous on a subspace of the metric space L_1.)

Proof. From (3.12) we have

$$\left|\frac{1}{|D|}\int_D d\underset{\sim}{y}[n_2(\underset{\sim}{y}) - n_1(\underset{\sim}{y})]\mu\right| < |\mu|\delta \tag{3.14}$$

and from (2.11)

$$\left|\frac{1}{|D|}\int_D d\underset{\sim}{y}[n_2(\underset{\sim}{y}) - n_1(\underset{\sim}{y})]\psi(\underset{\sim}{y})\right| < \overline{\psi}\,\delta \tag{3.15}$$

We also have

$$n_2(\underset{\sim}{y})n_2(\underset{\sim}{y}') - n_1(\underset{\sim}{y})n_1(\underset{\sim}{y}')$$

$$= [n_2(\underset{\sim}{y}) - n_1(\underset{\sim}{y})][n_2(\underset{\sim}{y}') + n_1(\underset{\sim}{y}')] + n_1(\underset{\sim}{y})n_2(\underset{\sim}{y}') - n_1(\underset{\sim}{y}')n_2(\underset{\sim}{y}) \tag{3.16}$$

Multiplying by $K(\underset{\sim}{y}-\underset{\sim}{y}')$ and integrating we find, since $n_1(\underset{\sim}{y}) + n_2(\underset{\sim}{y}) < 2\rho_c$, that

$$\left| \frac{1}{2|D|} \int_D d\underset{\sim}{y} \int_D d\underset{\sim}{y}' K(\underset{\sim}{y}-\underset{\sim}{y}')[n_2(\underset{\sim}{y})n_2(\underset{\sim}{y}') - n_1(\underset{\sim}{y})n_1(\underset{\sim}{y}')] \right|$$

$$< \frac{\rho_c}{|D|} \int_D d\underset{\sim}{y} \left|[n_2(\underset{\sim}{y}) - n_1(\underset{\sim}{y})]\right| \int_D d\underset{\sim}{y}' \left|K(\underset{\sim}{y}-\underset{\sim}{y}')\right|$$

$$< \rho_c \delta \int d\underset{\sim}{s} \left|K(\underset{\sim}{s})\right| . \qquad (3.17)$$

Since $a^o(\rho)$ is uniformly continuous in the closed interval $[0,\rho']$, it follows that for the given δ we can find a positive number $\sigma(\delta)$ such that (i) for all ρ_1 and ρ_2 in $[0,\rho']$, $|\rho_1 - \rho_2| < \sqrt{\delta}$ implies $|a^o(\rho_1) - a^o(\rho_2)| < \sigma(\delta)$, and (ii) $\sigma(\delta) \to 0$ as $\delta \to 0$. For a given n_1 and n_2, we can express D as the sum of two parts $D_<$ and $D_>$, where $|n_1 - n_2| < \sqrt{\delta}$ for $\underset{\sim}{y} \in D_<$ and $|n_1 - n_2| \geqq \sqrt{\delta}$ for $\underset{\sim}{y} \in D_>$. Then we have

$$\left| a^o[n_1(\underset{\sim}{y})] - a^o[n_2(\underset{\sim}{y})] \right| \leqq \begin{cases} \sigma(\delta) & \text{for } \underset{\sim}{y} \in D_< \\ 2M & \text{for } \underset{\sim}{y} \in D_> , \end{cases} \qquad (3.18)$$

where $$M \equiv \sup_{0 \leqq \rho \leqq \rho'} a^o(\rho). \qquad (3.19)$$

But (3.12) implies

$$|D_>| \sqrt{\delta} < \int_{D_>} d\underset{\sim}{y} |n_1 - n_2| \leqq \int_D d\underset{\sim}{y} |n_1 - n_2| < |D| \delta \qquad (3.20)$$

[illegible], so that $|D_>| < |D|\sqrt{\delta}$. It follows from (3.16) and (3.18) that

$$\int_D d\underset{\sim}{y} \left| a^0[n_1(\underset{\sim}{y})] - a^0[n_2(\underset{\sim}{y})] \right| \leq [\sigma(\delta) + 2M\sqrt{\delta}]|D| \qquad (3.21)$$

Finally, from (3.14, 15, 20, and 21) we have

$$|F(n_1,D) - F(n_2,D)| < |\mu|\delta + \bar{\psi}\delta + \rho_c\delta \int d\underset{\sim}{s}|K(\underset{\sim}{s})| + \sigma(\delta) + 2M\sqrt{\delta}$$
$$\rightarrow 0 \quad \text{as} \quad \delta \rightarrow 0 , \qquad (3.22)$$

which proves the lemma[6].

IV. Lower Bound on the Pressure.

The main part or the proof of theorem 1 now consists of proving the statement (2.13). To do this we show in the present section that the right side of (2.13) is a lower bound on $p(\mu,0+)$, and in the following section that it is an upper bound.

Finding a lower bound on $P(\mu,\Omega,\gamma)$ is equivalent to finding a lower bound on the partition function $Z(N,\Omega,\gamma)$. To obtain such a lower bound, we follow LP and divide Ω into M smaller cubical regions $\omega_1 \ldots \omega_M$, each of volume ω, so that $|\Omega| = M\omega$. We shall find a sucession of lower bounds, firstly in terms of the occupation numbers of these cells, secondly in terms of step functions and finally in terms of

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[6] The same argument proves that $F(n,D)$ is upper semi-continuou for $n \in \mathcal{R}$.

functions in $\mathcal{R}$. Let ω_i' be a subcube of ω_i, concentric with and similarly oriented to ω_i and of volume ω' where $\omega' < \omega$. Now, following LP, we obtain from the definition (2.4

$$Z(N,\Omega,\gamma) > \frac{\Lambda^{-\nu N}}{N_1! \ldots N_M!} \int_{(\omega_1')^{N_1}} \cdots \int_{(\omega_M')^{N_M}} d\underset{\sim}{x}_1 \ldots d\underset{\sim}{x}_N \, e^{-\beta V_N} \tag{4.1}$$

where $N_1 \ldots N_M$ is any set of integers whose sum is N. and which satisfy

$$0 \leq N_i \leq N_c(\omega') \tag{4.2}$$

where $N_c(\omega')$ is the maximum number of spheres of diameter r_o whose centres can be contained by one cube ω_i'. The notation in (4.1) indicates that the first N_1 volume integrations are over ω_1', the next N_2 over ω_2', and so on. It follows that

$$Z(N,\Omega,\gamma) > \left[\prod_{i=1}^{M} Z^o(N_i, \omega')\right] \exp(-\beta Q_{max}'' - \beta W_{max}) \tag{4.3}$$

where Z^o is the partition funcion of the reference system : Q_{max}'' is an upper bound, for all $\underset{\sim}{x}_1 \ldots \underset{\sim}{x}_N$ and all N, on the total energy of interaction due to $q(\underset{\sim}{r})$ resulting from pairs of particles that are in different cells ω_i' : and $W_{max}(N_1 \ldots N_M)$ is an upper bound on the total potential energy due to $\gamma^\nu K(\gamma \underset{\sim}{r})$ and $\psi(\gamma \underset{\sim}{x})$ for configurations specified

by the integral in (4.1).

To estimate W_{max} we define

$$\psi_i^+ \equiv \sup_{\underset{\sim}{x} \in \omega_i} \psi(\gamma \underset{\sim}{x}) \geqq \sup_{\underset{\sim}{x} \in \omega_i'} \psi(\gamma \underset{\sim}{x}) \tag{4.4}$$

Then ψ contributes $\sum_i N_i \psi_i^+$ to W_{max}. Next define

$$K_{ij}^+ \equiv \sup_{\underset{\sim}{x} \in \omega_i,\ \underset{\sim}{x}' \in \omega_j} K(\gamma \underset{\sim}{x} - \gamma \underset{\sim}{x}') . \tag{4.5}$$

Then K contributes to W_{max} the term $\frac{1}{2} \gamma^\nu \sum_{i \neq j} N_i N_j K_{ij}^+$ due to particles in different cells ω_i', and the term $\frac{1}{2} \gamma^\nu \sum_i N_i (N_i - 1) K_{ii}^+$ due to particles in the same cell. Consequently we have

$$W_{max} = \frac{1}{2} \gamma^\nu \sum_i^M \sum_j^M N_i N_j K_{ij}^+ + \sum_i^M (N_i \psi_i^+ - \tfrac{1}{2} \gamma^\nu N_i K_{ii}^+) \tag{4.6}$$

The grand partition function, defined by (2.3), has a lower bound given by

$$\Xi(\mu, \Omega, \gamma) > \exp(\beta \mu N) \, Z(N, \Omega, \gamma) \tag{4.7}$$

for any N. It follows from (4.3, 6 and 7) that the pressure P, defined by (2.2), has a lower bound given by

$$P(\mu, \Omega, \gamma) > - Q''_{max}/|\Omega| - \tfrac{1}{2} \gamma^\nu |\Omega|^{-1} \sum_{ij} N_i N_j K_{ij}^+$$

$$+ |\Omega|^{-1} \sum_i [N_i \mu - N_i \psi_i^+ + \beta^{-1} \log Z^0(N_i, \omega') + \tfrac{1}{2} \gamma^\nu N_i K_{ii}^+] \tag{4.8}$$

for any set of integers $0 \leqq N_i \leqq N_c(\omega')$. (Their sum is now arbitrary).

The quantity $Q_{max}/|\Omega| \equiv \varepsilon_1$, say, vanishes in the LP triple limit (2.17) for a suitable choice of ω', as shown by LP[7]. Also the final term in (4.8) satisfies

$$\tfrac{1}{2}\gamma^{\nu} \sum_i N_i K^+_{ii}/|\Omega| \geqq -\tfrac{1}{2}\gamma^{\nu}\overline{K}\, N_c(\omega)/\omega \equiv -\varepsilon_2 \text{, say,} \quad (4.9)$$

from (2.8). Then ε_2 vanishes in the LP triple limit. [It is convenient to replace K^+_{ij} in (4.8) by

$$K^-_{ij} \equiv \inf_{\underset{\sim}{x}\in\omega_i,\ \underset{\sim}{x}'\in\omega_j} K(\gamma\underset{\sim}{x} - \gamma\underset{\sim}{x}') \quad (4.10)$$

We can make this replacement if we also subtract from the right side of (4.8) the correction term

$$\begin{aligned} &\tfrac{1}{2}\gamma^{\nu}|\Omega|^{-1}\sum_{ij} N_i N_j (K^+_{ij} - K^-_{ij}) \\ &\qquad \leqq [N_c(\omega)/\omega]^2 \sum_i{}^{\infty} \gamma^{\nu}\omega(K^+_{ij} - K^-_{ij}) \equiv \varepsilon_3 \text{, say,} \end{aligned} \quad (4.11)$$

where the sum $\sum^{\infty}$ is over an infinite lattice of ω_i's. But from (2.8) and (2.9), $\int d\underset{\sim}{s}\, K(\underset{\sim}{s})$ exists as a Riemann integral

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[7] Since our Q''_{max} is an upper bound for all N_i, we must replace ρ by ρ_c in the estimate of this quantity given by LP.

and is finite. Hence, as shown by LP,

$$\lim_{\gamma\to 0} \sum_{i}^{\infty} \gamma^{\nu} \omega K_{ij}^{\pm} = \int d\underset{\sim}{s}\, K(\underset{\sim}{s}) , \quad \text{for all } j . \tag{4.12}$$

It follows that ε_3 vanishes in the LP triple limit. Similarly we can replace ψ_i^+ in (4.8) by

$$\psi_i^- \equiv \inf_{\underset{\sim}{x}\in\omega_i} \psi(\gamma\underset{\sim}{x}) \tag{4.13}$$

if we subtract the correction term

$$|\Omega|^{-1}\sum_{i}^{M} N_i(\psi_i^+ - \psi_i^-) \leq N_c(\omega)|\Omega|^{-1}\sum_{i}^{M}(\psi_i^+ - \psi_i^-) \equiv \varepsilon_4 , \text{ say.} \tag{4.14}$$

From conditions (2.10, 11 and 12) we deduce that $\psi(\underset{\sim}{y})$ is Riemann integrable over [redacted] its unit cell J, and hence

$$\lim_{\gamma\to 0}\ \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|}\sum_{i}^{M} \psi_i^{\pm}\omega = \frac{1}{|J|}\int_J d\underset{\sim}{y}\, \psi(\underset{\sim}{y}) \tag{4.15}$$

It follows that ε_4 vanishes in the LP triple limit. The inequality (4.8) now reduces to

$$P(\mu,\Omega,\gamma) > |\Omega|^{-1}\sum_{i}[N_i\mu - N_i\psi_i^- - A^0(N_i,\omega')]$$

$$- \tfrac{1}{2}\gamma^{\nu}|\Omega|^{-1}\sum_{ij} N_iN_jK_{ij}^- - \varepsilon_1 \ldots - \varepsilon_4 \tag{4.16}$$

where A^0, the free energy of the reference system, is defined by $A^0(N,\Omega) \equiv -\beta^{-1}\log Z^0(N,\Omega)$.

The next step is to replace $A^0(N_i,\omega')$ by $\omega\, a^0(N_i/\omega)$ plus a correction, where $a^0(\rho) \equiv \lim_{|\Omega|\to\infty} A^0(\rho|\Omega|,\Omega)/|\Omega|$. [redacted]. To do this, we note that (4.16) holds if we impose any additional restriction on the N_i's. In particular, it holds if we specify that $N_i \leq \rho'\omega$ where ρ' is chosen to satisfy $0 < \rho' < \rho_c$. But, if ρ lies in the closed interval $[0,\rho']$ and $A^0(N,\Omega)$ is defined for non-integral N by linear interpolation [10], then the sequence of functions $A^0(\rho\omega,\omega')/\omega$ converges uniformly in ρ to $a^0(\rho)$ as $\omega\to\infty$ and $\omega/\omega'\to 1$, [10]. Hence, we can find a positive function $\varepsilon_5(\omega,\omega')$, independent of N_i (but depending on ρ') such that

$$A^0(N_i,\omega')/\omega \quad < \quad a^0(N_i/\omega) \quad + \quad \varepsilon_5(\omega,\omega') \qquad (4.17)$$

for all $N_i \leq \rho'\omega$, where $\varepsilon_5(\omega,\omega') \to 0$ as $\omega\to\infty$ and $\omega/\omega'\to 1$. It follows that ε_5 vanishes in the LP triple limit. We can now replace $A^0(N_i,\omega')$ in (4.16) by $a^0(N_i/\omega)\omega$, if we subtract the correction ε_5 from the right hand side.

The next step is to replace the N_i's in (4.16) by the step function

$$n_{step}(\underset{\sim}{y}) \quad \equiv \quad N_i/\omega \quad \text{for} \quad \underset{\sim}{y} \in \bar{\omega}_i \ , \qquad (4.18)$$

where $\bar{\omega}_i$ is defined as the set of points $\underset{\sim}{y}$ such that $\underset{\sim}{y}/\gamma \in \omega_i$. Thus $\bar{\omega}_i$ is a cube of volume $\bar{\omega} \equiv \gamma^\nu\omega$. It follows from (4.10) and (4.13) that

$$\bar{\psi}_i = \inf_{\underset{\sim}{y} \in \bar{\omega}_i} \psi(\underset{\sim}{y}) \tag{4.19}$$

and

$$\bar{K}_{ij} = \inf_{\underset{\sim}{y} \in \bar{\omega}_i,\ \underset{\sim}{y}' \in \bar{\omega}_j} K(\underset{\sim}{y}-\underset{\sim}{y}') \tag{4.20}$$

Let us also define $\bar{\Omega}$ as the set of points $\underset{\sim}{y}$ such that $\underset{\sim}{y}/\gamma \in \Omega$. The set $\bar{\Omega}$ is a cube of volume $\gamma^\nu|\Omega|$ and is filled by the cells $\bar{\omega}_1 \ldots \bar{\omega}_M$. Now substituting (4.17-20) in (4.16) we obtain, for any n_{step},

$$P(\mu,\Omega,\gamma) > F(n_{step},\bar{\Omega}) - \varepsilon_1 \ldots - \varepsilon_5 \tag{4.21}$$

where F is defined by (2.15).

The next step is to use lemma 2 and replace n_{step} by a function $n' \in \mathcal{R}(\rho')$, where $\mathcal{R}(\rho')$ was defined just before lemma 2. Firstly, for such an n', let us define the step function

$$n'_\gamma(\underset{\sim}{y}) \equiv \frac{1}{\bar{\omega}} \int_{\bar{\omega}_i} d\underset{\sim}{y}\, n'(\underset{\sim}{y}) \quad \text{for } \underset{\sim}{y} \in \bar{\omega}_i \text{ and all } i. \tag{4.22}$$

We can find an n_{step} such that

$$\left| n'_\gamma(\underset{\sim}{y}) - n_{step}(\underset{\sim}{y}) \right| < 1/\omega \quad \text{for all } \underset{\sim}{y}. \tag{4.23}$$

Secondly, if Γ is a unit cell of the periodic function n', we dissect the space of vectors $\underset{\sim}{y}$ into an infinite lattice of cells Γ_λ congruent to Γ. Then we have

$$\frac{1}{|\bar{\Omega}|}\int_{\bar{\Omega}} dy\,|n'(y) - n'_\gamma(y)| = \frac{1}{k}\sum_{\lambda=1}^{k}\frac{1}{|\Gamma|}\int_{\Gamma_\lambda} dy\,|n'(y) - n'_\gamma(y)| + O(|\Omega|^{-1/4}) \tag{4.24}$$

where $\Gamma_1 \ldots \Gamma_k$ is the set of Γ_λ's which lie entirely inside $\bar{\Omega}$. Although n' is periodic over the Γ_λ's, n'_γ is not since each Γ_λ is subdivided differently by the $\bar{\omega}_i$'s. However, by the theorem of Darboux [12] shows that

$$\int_{\Gamma_\lambda} dy\,|n' - n'_\gamma| < \delta(\bar{\omega}) \quad \text{for all } \lambda, \tag{4.25}$$

where $\delta(\bar{\omega})$ is independent of λ and tends to zero as $\bar{\omega} \to 0$ and hence as $\gamma \to 0$. It follows from (4.24) that

$$\lim_{\gamma\to 0} \limsup_{|\Omega|\to\infty} \frac{1}{|\bar{\Omega}|}\int_{\bar{\Omega}} dy\,|n' - n'_\gamma| = 0 \tag{4.26}$$

Combining this with (4.23), we deduce that for any $n' \in \mathcal{R}(\rho')$, we can find an $n_{step}(y)$ (which depends also on γ and ω) such that $|\bar{\Omega}|^{-1}\int_{\bar{\Omega}} dy\,|n' - n_{step}|$ vanishes in the LP triple limit. Since n_{step} belongs to $\mathcal{R}(\rho')$, we deduce from lemma 2 that

$$|F(n',\bar{\Omega}) - F(n_{step},\bar{\Omega})| < \varepsilon_6 \tag{4.27}$$

where ε_6 vanishes in the LP triple limit. From (4.21) and (4.25) we conclude that for all $n' \in \mathcal{R}(\rho')$

$$P(\mu,\Omega,\gamma) > F(n',\bar{\Omega}) - \varepsilon_1 \ldots - \varepsilon_6 . \tag{4.28}$$

The next step is to show that n' may be replaced by

any function $n \in \mathcal{R}$. For such an n , let us choose

$$n'(\underset{\sim}{y}) \equiv \begin{cases} n(\underset{\sim}{y}) & \text{where } 0 \leqq n(\underset{\sim}{y}) \leqq \rho' \\ \rho' & \text{elsewhere ,} \end{cases} \tag{4.29}$$

which clearly belongs to $\mathcal{R}(\rho')$. Hence (4.28) holds for this n' . Equation (4.29) implies that $|n(\underset{\sim}{y}) - n'(\underset{\sim}{y})| \leqq \rho_c - \rho'$ for all $\underset{\sim}{y}$, and also, since $a^o(\rho)$ is convex that $a^o[n'(\underset{\sim}{y})] \leqq a^o[n(\underset{\sim}{y})]$ for $\rho' \geqq \rho_o$, where ρ_o is a value of ρ where $a^o(\rho)$ is minimum. Therefore, by an argument like that of lemma 2 with δ replaced by $\rho_c - \rho'$, we find that, provided $\rho' \geqslant \rho_o$,

$$F(n', \bar{\Omega}) \geqq F(n, \bar{\Omega}) - \Delta \quad \text{for all } \bar{\Omega} , \tag{4.30}$$

where

$$\Delta \equiv [|\mu| + \bar{\psi} + \rho_c \int d\underset{\sim}{s} |K(\underset{\sim}{s})|\,](\rho_c - \rho') . \tag{4.31}$$

Substituting (4.30) in (4.28) gives

$$P(\mu, \Omega, \gamma) \geqq F(n, \bar{\Omega}) - \varepsilon_1 \ldots - \varepsilon_6 - \Delta \tag{4.32}$$

Since this holds for all $n \in \mathcal{R}$, it follows that

$$P(\mu, \Omega, \gamma) \geqq \sup_{n \in \mathcal{R}} F(n, \bar{\Omega}) - \varepsilon_1 \ldots - \varepsilon_6 - \Delta \tag{4.33}$$

Finally , taking the LP triple limit followed by the limit $\rho' \to \rho_c$ gives

$$\liminf_{\gamma \to 0} p(\mu, \gamma) \geqq \lim_{|D| \to \infty} \sup_{n \in \mathcal{R}} F(n, \mu, D) \tag{4.34}$$

where the right side was proved to exist in section III. This takes us half way in our proof of the statement (2.13) of theorem 1.

V. Upper Bound on the Pressure.

To find an upper bound on the pressure, we need an upper bound on Z. We use the same construction of cells ω_i as before and a similar method. Then, with the notation of (4.1), we have

$$Z(N,\Omega,\gamma) = \sum_{N_1 \dots N_M}^{N} \frac{\Lambda^{-\nu N}}{N_1! \dots N_M!} \int_{(\omega_1)^{N_1}} \cdots \int_{(\omega_M)^{N_M}} d\underset{\sim}{x}_1 \dots d\underset{\sim}{x}_N \, e^{-\beta V_N} \tag{5.1}$$

where the sum $\sum^{N}$ is over all integers N_i whose sum is N and which satisfy $0 \leq N_i \leq N_c(\omega)$. It follows that

$$Z(N,\Omega,\gamma) < \exp(-\beta \tilde{Q}_{min}) \sum_{N_1 \dots N_M}^{N} \left[\prod_{i=1}^{M} Z^0(N_i,\omega) \right] \exp\left[-\beta W_{min}(N_1 \dots N_M \right. \tag{5.2}$$

where $\tilde{Q}_{min}$ is a lower bound, for all $\underset{\sim}{x}_1 \cdots \underset{\sim}{x}_N$ and all N, on the total interaction energy due to $q(\underset{\sim}{x})$ resulting from pairs of particles in different cells ω_i. Also W_{min} is

a lower bound on the potential energy due to $\gamma^{\nu}K(\gamma\underset{\sim}{r})$ and $\psi(\gamma\underset{\sim}{X})$ for configurations specified by $N_1 \ldots N_M$. As in the derivation of (4·6) we deduce that

$$W_{min} = \frac{1}{2}\gamma^{\nu}\sum_{ij} N_i N_j K^{-}_{ij} + \sum_i (N_i \psi^{-}_i - \frac{1}{2}\gamma^{\nu} N_i K^{-}_{ii}) \tag{5.3}$$

where K^{-}_{ij} and ψ^{-}_i are defined by (4.10) and (4.13).

It follows from (2.3) that

$$\Xi(\mu,\Omega,\gamma) < e^{-\beta\tilde{Q}_{min}} \sum_{N_1..N_M} \Big[\prod_i Z^{o}(N_i,\omega) e^{\beta\mu N_i}\Big] e^{-\beta W_{min}(N_1..N_M)} \tag{5.4}$$

where the restriction that the N_i's sum to N no longer applies. Since $N_i \leq N_c(\omega)$, there are at most $N_c(\omega)^M$ terms in the summation in (5.4), so that

$$\Xi(\mu,\Omega,\gamma) < e^{-\beta\tilde{Q}_{min}} N_c(\omega)^M \max_{N_1..N_M} \Big\{ e^{-\beta W_{min}} \prod_i e^{\beta\mu N_i} Z^{o}(N_i,\omega) \Big\} \tag{5.5}$$

Then (2.2) gives

$$P(\mu,\Omega,\gamma) < \frac{1}{|\Omega|} \max_{N_1..N_M} \Big\{ \sum_i [N_i\mu - A^{o}(N_i,\omega)] - W_{min} \Big\} - \tilde{Q}_{min}/|\Omega| - (\beta\omega)^{-1} \log N_c(\omega) \tag{5.6}$$

This inequality still holds if we allow the maximum to range over non-integral values of the N_i, where $A^{o}(N_i,\omega)$ is defined by linear interpolation [10] for such N_i.

The term $\tilde{Q}_{min}/|\Omega| \equiv \varepsilon_1'$ say, vanishes in the [redacted] triple limit as shown by LP. The term $(\beta\omega)^{-1} \log N_c(\omega) \equiv \varepsilon_2'$ say, also vanishes in this [redacted] limit because, from LP, $1 \leqq N_c(\omega) < \rho_c(\omega^{1/\nu} + 2r_o)^\nu$. Put $\varepsilon_3' \equiv \varepsilon_2$, $\varepsilon_4' \equiv \varepsilon_3$ and $\varepsilon_5' \equiv \varepsilon_4$, where ε_2, ε_3 and ε_4 were defined in the previous section and shown to vanish in the LP triple limit. Then (5.6) becomes

$$P(\mu,\Omega,\gamma) < \frac{1}{|\Omega|} \max_{N_1..N_M} \Big\{ \sum_i [N_i\mu - N_i\psi_i^+ - A^o(N_i,\omega)] - \frac{1}{2}\gamma^\nu \sum_{ij} N_i N_j K^+_{ij} \Big\} + \varepsilon_1' \ldots + \varepsilon_5' \qquad (5.7)$$

where we have replaced ψ_i^- and K_{ij}^- by ψ_i^+ and K_{ij}^+, and added the appropriate correction terms.

The next step is to replace A^o by a^o. To do this we first define

$$f(N) \equiv \begin{cases} N & \text{if } N \leqq \rho'\omega, \\ \rho'\omega & \text{if } N \geqq \rho'\omega, \end{cases} \qquad (5.8)$$

where $0 < \rho' < \rho_c$. Using the inequality of PENROSE [13],

$$Z^o(N+1,\omega) \leqq Z^o(N,\omega)\Lambda^{-\nu} e^{2\beta\Phi'}\left[(\omega^{1/\nu}+r_o)^\nu/N - 1/\rho_c\right], \qquad (5.9)$$

where Φ' is a certain positive constant, we deduce that $A^o(N,\omega) > A^o(N',\omega)$ for all ω, N and N' such that $N > N' > \rho_1(\omega^{1/\nu}+r_o)^\nu$, where

$$\rho_I \equiv [1/\rho_c + \Lambda^\nu e^{-2\beta\Phi'}]^{-1} < \rho_c . \qquad (5.10)$$

Since $N_i \geqq f(N_i)$, it follows that $A^0(N_i,\omega) \geqq A^0[f(N_i),\omega]$ for $\rho' \geqq \rho_I(1+r_0\omega^{-1/\nu})^\nu$. Also, since $N_i - f(N_i) \leqq \omega(\rho_c - \rho')$, we deduce by an argument like that leading to (4.32) that

$$P(\mu,\Omega,\gamma) < \frac{1}{|\Omega|} \max_{N_1..N_M} \Big\{ \sum_i [f(N_i)\mu - f(N_i)\psi_i^+ - A^0(f(N_i),\omega)] - \frac{1}{2}\gamma^\nu \sum_{ij} f(N_i)f(N_j)K_{ij}^+ \Big\} + \varepsilon_1' \ldots + \varepsilon_5' + \Delta \qquad (5.11)$$

where Δ is defined by (4.31). Let us put $N_i' \equiv f(N_i)$. Then (5.11) is unchanged if we replace the $f(N_i)$ by the N_i', and maximise with respect to the N_i'. Since $N_i' \leqq \rho'\omega$ we have, by an argument like that leading to (4.17), that

$$A^0(N_i',\omega)/\omega < a^0(N_i'/\omega) + \varepsilon_6'(\omega) \qquad (5.12)$$

where $\varepsilon_6'(\omega)$ is a positive function which vanishes when $\omega \to \infty$. Thus ε_6' vanishes in the LP triple limit. Now (5.11) reduces to

$$P(\mu,\Omega,\gamma) < \frac{1}{|\Omega|} \max_{N_1'..N_M'} \Big\{ \sum_i [N_i'\mu - N_i'\psi_i^+ - a^0(N_i'/\omega)\omega] - \frac{1}{2}\gamma^\nu \sum_{ij} N_i'N_j'K_{ij}^+ \Big\} + \varepsilon_1' \ldots + \varepsilon_6' + \Delta \qquad (5.13)$$

Let $\mathcal{S}_M$ be the class of step functions which are of

the form (4.18) in $\bar{\Omega}$, and are periodic with unit cell $\bar{\Omega}$. Then from (5.13) we have

$$P(\mu,\Omega,\gamma) < \sup_{n\in\mathcal{S}_M} F(n,\bar{\Omega}) + \varepsilon_1' \ldots + \varepsilon_6' + \Delta$$

$$\leqq \sup_{n\in\mathcal{R}} F(n,\bar{\Omega}) + \varepsilon_1' \ldots + \varepsilon_6' + \Delta \qquad (5.14)$$

since $\mathcal{S}_M \subset \mathcal{R}$. Finally, taking the LP triple limit, followed by the limit $\rho' \to \rho_c$, we have

$$\limsup_{\gamma\to 0} p(\mu,\gamma) \leqq \lim_{|D|\to\infty} \sup_{n\in\mathcal{R}} F(n,D) \qquad (5.15)$$

Combining this with (4.34) we deduce that $p(\mu,0+)$ exists and is given by the statement (2.13) of theorem 1. The alternative statement (2.14) follows from lemma 1, as shown in section III.

To prove that $p(\mu,\gamma)$ tends to $p(\mu,0+)$ uniformly on any interval, we note that for $|\mu| \leq m$, our correction terms can be made to depend on m and not on μ. This completes the proof of theorem 1.

VI. The Free Energy.

In this section we derive [redacted] results for the free energy, corresponding to those given in theorem 1 for the pressure. The free energy of a system of N particles in a cube Ω is defined by

$$A(N,\Omega,\gamma) \equiv -\beta^{-1} \log Z(N,\Omega,\gamma) \tag{6.1}$$

for integral N and by linear interpolation [10] for non-integral N. The free energy density is defined by

$$a(\rho,\gamma) \equiv \lim_{|\Omega|\to\infty} A(\rho|\Omega|,\Omega,\gamma)/|\Omega| \tag{6.2}$$

which exists [9] because of conditions (2.6 - 12). (See the discussion just before theorem 1.) The van der Waals limit of the free energy density is defined by

$$a(\rho,0+) \equiv \lim_{\gamma\to 0} a(\rho,\gamma) \tag{6.3}$$

The second main result of this paper is

Theorem 2. Under conditions (2.6 -12), the van der Waals limit $a(\rho,0+)$ of the free energy density exists and is given by

$$a(\rho,0+) = \lim_{|D|\to\infty} \inf_{n\in\mathscr{C}_D(\rho)} G(n,D) \tag{6.4}$$

or equivalently

$$a(\rho,0+) = \inf_{n\in\mathscr{C}(\rho)} G(n,\infty) \tag{6.5}$$

where $\mathscr{C}(\rho)$ is the subclass of $\mathscr{R}$ consisting of functions n which also satisfy

$$\lim_{|D|\to\infty} \frac{1}{|D|}\int_D d\underset{\sim}{y}\; n(\underset{\sim}{y}) \;=\; \rho\,, \tag{6.6}$$

$\mathscr{C}_D(\rho)$ is the subclass of $\mathscr{C}(\rho)$ comprising functions with unit cell D and $G(n,D)$, is defined as the functional

$$\frac{1}{|D|}\int_D d\underset{\sim}{y}\left\{a^o[n(\underset{\sim}{y})] + \psi(\underset{\sim}{y})n(\underset{\sim}{y})\right\} \;+\; \frac{1}{2|D|}\int_D d\underset{\sim}{y}\int_D d\underset{\sim}{y}'\, n(\underset{\sim}{y})n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}') \tag{6.7}$$

and

$$G(n,\infty) \;\equiv\; \lim_{|D|\to\infty} G(n,D) \tag{6.8}$$

Further, the convergence of $a(\rho,\gamma)$ to $a(\rho,0+)$ is uniform in ρ for $0 \leqq \rho \leqq \rho'$ if $\rho' < \rho_c$.

The limits (6.4, 6 and 8) are taken over an ascending sequence of similarly oriented cubes D, as in theorem 1. The existence of all the limits involving $|D|\to\infty$ and the infima follows from arguments like those of section III.

Before proving theorem 2, we note that if $\psi = 0$ and the minimal function in (6.5) happens to be $n = \rho$, then $a(\rho,0+) = a^o(\rho) + \frac{1}{2}\alpha\rho^2$, where $\alpha \equiv \int d\underset{\sim}{s}\; K(\underset{\sim}{s})$. This formula was shown by LP to hold for all ρ and all temperatures if K has a non-negative Fourier transform, and for restricted ranges of ρ and of temperature if K is a more general function.

Theorem 2 can be proved from first principles by a

method similar to that used for theorem 1. Instead, we give a simpler proof covering only the case $\psi = 0$. We use theorem 1 together with the standard formula [15]

$$a(\rho,\gamma) = \max_{\mu} [\mu\rho - p(\mu,\gamma)] \tag{6.9}$$

Taking the limit $\gamma \to 0$ of this gives

$$a(\rho,0+) = \max_{\mu} [\mu\rho - p(\mu,0+)] \tag{6.10}$$

where the interchange[2] of the limit and the maximum is justified because, by theorem 1, $p(\mu,\gamma)$ tends to $p(\mu,0+)$ uniformly in μ. From the equation (2.14) for $p(\mu,0+)$ we deduce that

$$\begin{aligned} p(\mu,0+) &= \sup_{\rho} \sup_{n \in \mathcal{C}(\rho)} F(n,\mu,\infty) \\ &= \sup_{\rho} \sup_{n \in \mathcal{C}(\rho)} \lim_{|D|\to\infty} \left[\mu \frac{1}{|D|} \int_D d\underset{\sim}{y}\, n(\underset{\sim}{y}) - G(n,D)\right] \\ &= \sup_{\rho} \left[\mu\rho - \inf_{n \in \mathcal{C}(\rho)} G(n,\infty)\right] \end{aligned} \tag{6.11}$$

Substituting (6.11) in (6.10) gives

$$a(\rho,0+) = \max_{\mu} \inf_{\rho'} \left[(\rho - \rho')\mu + \inf_{n \in \mathcal{C}(\rho')} G(n,\infty)\right] \tag{6.12}$$

To proceed further we need two lemmas.

Lemma 3. The function[8]

$$f(\rho) \equiv \inf_{n \in \mathcal{C}(\rho)} G(n,\infty) \tag{6.13}$$

is a convex function of ρ, (for $\mathcal{V} = 0$).

Lemma 4. If $g(\rho)$ is convex then

$$\max_{\mu} \min_{\rho'} [(\rho-\rho')\mu + g(\rho)] = g(\rho) \tag{6.14}$$

Lemma 3 is equivalent [14] to the statement $f(\frac{1}{2}\rho_1 + \frac{1}{2}\rho_2) \leq \frac{1}{2}f(\rho_1) + \frac{1}{2}f(\rho_2)$ (6.15) for any ρ_1 and ρ_2 in $[0,\rho_c)$. To prove this statement, consider an infinite lattice of identical parallelepipeds Γ_λ filling ν-dimensional space. ~~(the cells must of course be parallelopipeds).~~ Consider also an infinite fixed plane (ν-1 dimensional) coinciding with faces of these Γ_λ (Fig. 2). Now introduce an ascending sequence of bounded regions R, similar to the Γ_λ in shape and orientation, and chosen so that each R is bisected by the fixed plane, while the faces of each R coincide with faces of the Γ_λ. Let R_1 and R_2 be the halves of R on opposite sides of the fixed plane. Then the definition (6-7) implies

$$G(n,R) \leq \frac{1}{2} G(n,R_1) + \frac{1}{2} G(n,R_2) + \Delta(R) \tag{6.16}$$

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[8] Note that $\inf_{n \in \mathcal{C}(\rho)} G(n,D)$ is not necessarily convex.

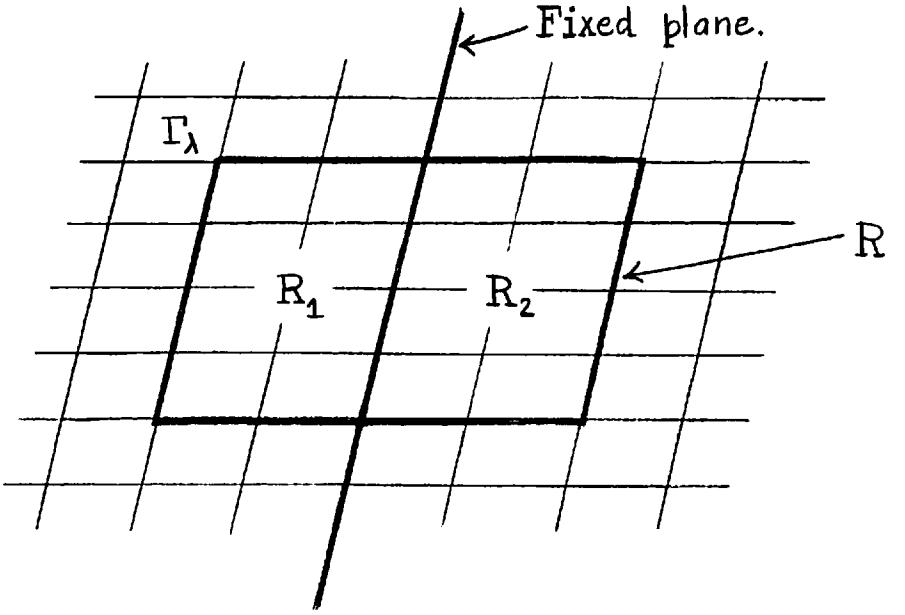

Fig 2. Construction used in the proof of lemma 3.

where (see (3.6))

$$\Delta(R) \equiv \frac{\rho_c^2}{|R|}\int_{R_1} d\underset{\sim}{y}\int_{R_2} d\underset{\sim}{y}'\,|K(\underset{\sim}{y}-\underset{\sim}{y}')| \qquad (6.17)$$

$$\longrightarrow 0 \quad \text{as} \quad |R|\longrightarrow\infty\ .$$

For any ρ, let $\mathscr{C}_R(\rho)$ and $\mathscr{C}_\Gamma(\rho)$ be the subclasses of $\mathscr{C}(\rho)$ consisting of functions n with unit cells R and Γ_λ respectively, and let $\mathscr{C}_R(\rho_1,\rho_2)$ be the class of periodic functions n with unit cell R and satisfying the conditions

$$\frac{1}{|\Gamma_\lambda|}\int_{\Gamma_\lambda} d\underset{\sim}{y}\ n(\underset{\sim}{y}) = \begin{cases}\rho_1 & \text{if} \quad \Gamma_\lambda\subset R_1\\ \rho_2 & \text{if} \quad \Gamma_\lambda\subset R_2\ .\end{cases} \qquad (6.18)$$

Since $|R_1| = |R_2|$, these conditions imply

$$\frac{1}{|R|}\int_R d\underset{\sim}{y}\ n(\underset{\sim}{y}) = \tfrac{1}{2}(\rho_1+\rho_2)\ , \qquad (6.19)$$

so that $\mathscr{C}_R(\rho_1,\rho_2)$ is a subclass of $\mathscr{C}_R(\tfrac{1}{2}\rho_1+\tfrac{1}{2}\rho_2)$. With (6.16) this gives

$$\inf_{n\in\mathscr{C}_R(\frac{1}{2}\rho_1+\frac{1}{2}\rho_2)} G(n,R) \leqq \inf_{n\in\mathscr{C}_R(\rho_1,\rho_2)} G(n,R)$$

$$\leqq \frac{1}{2}\sum_{i=1,2}\ \inf_{n\in\mathscr{C}_\Gamma(\rho_i)} G(n,R_i) + \Delta(R)\ . \qquad (6.20)$$

As in lemma 1, we can replace $G(n,R)$ and $G(n,R_{ii})$ by $G(n,\infty)$ if we add to the right side of (6.20) a correction which

vanishes in the limit $|R|\to\infty$. Then, since $\mathcal{C}_R(\rho)\subset\mathcal{C}(\rho)$, we obtain on taking this limit

$$\inf_{n\in\mathcal{C}(\frac{1}{2}\rho_1+\frac{1}{2}\rho_2)} G(n,\infty) \leqq \frac{1}{2}\sum_i \inf_{n\in\mathcal{C}_\Gamma(\rho_i)} G(n,\infty). \quad (6.21)$$

Since this holds for parallelepipeds Γ_λ of all shapes and sizes, it also holds if we take the infimum in Γ of the right side, which gives the desired inequality (6.15).

To prove lemma 4, we write $M(\rho)$ for the left side of (6.14). Since

$$\min_{\rho'} [(\rho-\rho')\mu + g(\rho')] \leqq g(\rho) \quad (6.22)$$

for all μ, we see that $M(\rho)\leqq g(\rho)$. Also, since g is convex, its tangent at any point ρ never lies above the curve [14]. Taking μ to be the slope of this tangent, we have $g(\rho')+(\rho-\rho')\mu \geqq g(\rho)$ for all ρ', so that

$$\min_{\rho'} [(\rho-\rho')\mu + g(\rho')] \geqq g(\rho). \quad (6.23)$$

It follows that $M(\rho)\geqq g(\rho)$, and the proof of lemma 4 is complete[9].

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[9] The same argument proves that $\sup_\mu \inf_{\rho'} [(\rho-\rho')\mu + f(\rho')] = CE\, f(\rho)$ for any f, where CE f was defined in section I.

Using lemmas 3 and 4 in (6.12) we obtain (6.5). We can deduce (6.4) from (6.5) by using the analogue of lemma 1. That the convergence of $a(\rho,\gamma)$ is uniform in ρ can be deduced from (6.9) and the fact that the convergence of $p(\mu,\gamma)$ is uniform in μ. This completes the proof of theorem 2.

As a corallary, we note that $a(\rho,0+)$ is convex in ρ. This follows from (6.5) and lemma 3, or alternatively from the fact that $a(\rho,0+)$ is the limit of a sequence of functions $a(\rho,\gamma)$ which are known [10] to be convex.

VII. Discussion.

Our main results are theorems 1 and 2 which prove the existence of and give expressions for the van der Waals limits $p(\mu,0+)$ and $a(\rho,0+)$ of the pressure and free energy density.

These results are fairly general, being easily extended to classical lattice gases and other lattice systems that are isomorphic to these gases. [redacted]

A more difficult generalization would be the replacement of the hard core condition (2.7) by the condition $q(\underset{\sim}{r}) > \text{constant}.\ |\underset{\sim}{r}|^{-\nu-\varepsilon}$ for small $|\underset{\sim}{r}|$. It may be possible to do this by using a result of DOBRUSHIN and MINLOS [16]. It may also be possible, in a more sophisticated treatment, to replace the conditions on n, K and ψ, by the condition of Lebesgue measurability. The only place where we require Riemann integrability of n is in equation (4.25).

The result (2.13) raises the question of the significance

of the function

$$\mathcal{P}(\mu,D) \equiv \sup_{n\in\mathcal{R}} F(n,D) \tag{7.1}$$

One can show by our methods that

$$\mathcal{P}(\mu,D) = \lim_{\gamma\to 0} P(\mu,D_\gamma,\gamma) \tag{7.2}$$

where D_γ is a cube of volume $\gamma^{-\nu}|D|$, defined as the set of points $\underset{\sim}{x}$ such that $\gamma\underset{\sim}{x} \in D$. The limit (7.2) is thus a combined van der Waals and thermodynamic limit in which the sides of the container grow at the same rate as the range γ^{-1} of the Kac potential. One can also define a free energy density $\mathcal{A}(\rho,D)$ like (7.1) and prove the analogue of (7.2). One finds that $\mathcal{A}$ is not necessarily convex in ρ (but is probably differentiable), and is not related to $\mathcal{P}$ by an equation like (6.10); i.e. the canonical and grand canonical ensembles are not equivalent in this limit. Possibly, $\mathcal{A}$ represents a finite system of volume $|D|$, which is, roughly speaking, small enough to be thermodynamically unstable but large enough to behave like a continuum. This may have practical application.

It is possible to rederive the results of LP [4] using our theorems 1 and 2, and also prove that there some functions K for which (1.2,3 and 4) do not hold. Theorems 1 and 2 can also be used to evaluate certain correlation functions in the van der Waals limit. We hope to present this in a future paper.

Finally, an outstanding unsolved problem is to prove that $a(\rho,0+)$ is, as seems likely, differentiable [16] with respect to ρ. We can prove this only in the cases where (1.2) holds.

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Part II

EXISTENCE AND CONTINUITY OF THE CANONICAL PRESSURE

Abstract.

For a ν-dimensional system of particles with the two-body potential $q(\underset{\sim}{r}) + \gamma^{\nu} K(\gamma \underset{\sim}{r})$ and density ρ, it is proved under fairly weak conditions on q and K that the canonical pressure $\pi(\rho,\gamma)$ and chemical potential $\mu(\rho,\gamma)$ tend to definite limits when $\gamma \to 0$. The limiting functions are absolutely continuous and are given in terms of the derivative of the limiting free energy density $a(\rho,0+) = \lim_{\gamma \to 0} a(\rho,\gamma)$ which was found in part I.

I. Introduction.

In part I of these papers [1] we considered the free energy density $a(\rho,\gamma)$ of a ν-dimensional system of particles with the two-body potential

$$q(\underset{\sim}{x}) + \gamma^{\nu}K(\gamma\underset{\sim}{x}) \tag{1.1}$$

and density ρ. (We assume there is no external field in the present paper). Under fairly weak conditions on q and K we proved that the van der Waals limit $a(\rho,0+) \equiv \lim_{\gamma\to 0} a(\rho,\gamma)$ exists and is given by a variational formula.

In the present paper we consider the canonical chemical potential

$$\mu(\rho,\gamma) \equiv \frac{\partial}{\partial\rho}\, a(\rho,\gamma) \tag{1.2}$$

and the canonical pressure

$$\pi(\rho,\gamma) \equiv (\rho\frac{\partial}{\partial\rho} - 1)\, a(\rho,\gamma) \tag{1.3}$$

for the same system. The existence of these functions was proved by DOBRUSHIN and MINLOS [2] (see also [3]). We prove that their van der Waals limits

$$\mu(\rho,0+) \equiv \lim_{\gamma\to 0} \mu(\rho,\gamma) \tag{1.4}$$

$$\pi(\rho,0+) \equiv \lim_{\gamma\to 0} \pi(\rho,\gamma) \tag{1.5}$$

exist, are absolutely continuous functions of ρ (i.e.

differentiable almost everywhere [4], and are given by

$$\mu(\rho,0+) = \frac{\partial}{\partial\rho}\, a(\rho,0+) \tag{1.6}$$

$$\pi(\rho,0+) = (\rho\frac{\partial}{\partial\rho} - 1)\, a(\rho,0+) \tag{1.7}$$

The results (1.6) and (1.7) state that the limit $\gamma\to 0$ and the derivative $\partial/\partial\rho$ of $a(\rho,\gamma)$ can be interchanged, and that $\mu(\rho,0+)$ and $\pi(\rho,0+)$ can be calculated in principle from the variational formula for $a(\rho,0+)$ given in part I.

Our method consists of proving firstly that $a(\rho,0+)$ is differentiable. Since $a(\rho,0+)$ is convex, as shown in part I, its left and right hand derivatives, denoted by $\partial_- a(\rho,0+)$ and $\partial_+ a(\rho,0+)$ respectively, exist and satisfy [4]

$$\partial_- a(\rho,0+) \leqq \partial_+ a(\rho,0+) \tag{1.8}$$

We prove the reverse of this in section III using an inequality obtained in section II, and deduce the consequences in section IV.

The conditions to be satisfied by q and K are, as in part I,

$$q(\underset{\sim}{r}) = q(-\underset{\sim}{r}) \ , \quad K(\underset{\sim}{s}) = K(-\underset{\sim}{s}) \ , \tag{1.9}$$

$$\left.\begin{aligned} &q(\underset{\sim}{r}) = \infty \quad \text{for } |\underset{\sim}{r}| < r_0 \quad \text{(hard core contition)},\\ &|q(\underset{\sim}{r})| < A\,|\underset{\sim}{r}|^{-\nu-\varepsilon} \quad \text{for } |\underset{\sim}{r}| \geqq r_0 \ ,\\ &q \text{ is measurable,} \end{aligned}\right\} \tag{1.10}$$

$|K(\underset{\sim}{s})| < k(|\underset{\sim}{s}|) < \overline{K}$ for all $\underset{\sim}{s}$, where $k(t)$ is a positive non-increasing function such that $\int d\underset{\sim}{s}\, k(|\underset{\sim}{s}|) < \infty$, K is Riemann integrable on any bounded region of ν-dimensional space, (1.11)

where A, $\overline{K}$, r_o and ε are positive constants.

II. Inequality for $a(\rho,\gamma)$.

To obtain a suitable inequality for $a(\rho,\gamma)$ we use the result (3.23) of DOBRUSHIN and MINLOS [2]. Let $Z(N,\Omega,\gamma)$ be the partition function [1] for N particles in a cube Ω with the two-body potential (1.1), and let N_1 and N_2 be positive integers that do not exceed the maximum value of N for which $Z(N,\Omega,\gamma)$ is defined. The result then states that for $N_1 < N_2$

$$N_1\left(\frac{Z(N_1)}{Z(N_1-1)} + C'\right) \leq N_2\left(\frac{Z(N_2)}{Z(N_2-1)} + C'\right) \tag{2.1}$$

where

$$C'(\gamma) \equiv \Lambda^{-\nu}\exp[2\beta\Phi' + 2\beta\Psi'(\gamma)]\int d\underset{\sim}{r}\left(1 - \exp[-\beta q_+(\underset{\sim}{r}) - \beta\gamma^{\nu}K_+(\gamma\underset{\sim}{r})]\right) \tag{2.2}$$

where $q_+(\underset{\sim}{r}) \equiv \max(q(\underset{\sim}{r}),0)$ and $K_+(\underset{\sim}{s}) \equiv \max(K(\underset{\sim}{s}),0)$, (see also [3]). Here Λ is the thermal wavelength [1], while $-2\Phi'$ and $-2\Psi'$ are lower bounds on the potential energy,

due to $q(\underset{\sim}{x})$ and $\gamma^{\nu}K(\gamma\underset{\sim}{x})$ respectively, of a single particle interacting with any number of other particles. The existence of these lower bounds is a consequence [5] of the conditions (1.9 to 11).

From (2.1) we shall deduce the new inequality

$$N_1\left[\left(\frac{Z(N)}{Z(N_1)}\right)^{1/(N-N_1)} + C'\right] \leqq N_2\left[\left(\frac{Z(N_2)}{Z(N)}\right)^{1/(N_2-N)} + C'\right] \qquad (2.3)$$

for $N_1 < N < N_2$. To prove this we firstly use (2.1) to obtain

$$\begin{aligned} 0 < \frac{Z(N)}{Z(N_1)} &= \prod_{N'=N_1+1}^{N} \frac{Z(N')}{Z(N'-1)} \\ &\leqq \prod_{N'=N_1+1}^{N} \left[\frac{N}{N'}\left(\frac{Z(N)}{Z(N-1)} + C'\right) - C'\right] \\ &\leqq \left[\frac{N}{N_1}\left(\frac{Z(N)}{Z(N-1)} + C'\right) - C'\right]^{N-N_1} \end{aligned} \qquad (2.4)$$

This gives

$$N_1\left[\left(\frac{Z(N)}{Z(N_1)}\right)^{1/(N-N_1)} + C'\right] < N\left(\frac{Z(N)}{Z(N-1)} + C'\right) \qquad (2.5)$$

Secondly, we use (2.1) to obtain for $N < N' \leqq N_2$

$$\frac{Z(N')}{Z(N'-1)} > \frac{N}{N_2}\left(\frac{Z(N)}{Z(N-1)} + C'\right) - C' \qquad (2.6)$$

Suppose, for a given N, that N_2 is so small that the right side of (2.6) is non-negative. We then have, as in (2.4),

$$\frac{Z(N_2)}{Z(N)} = \prod_{N'=N+1}^{N_2} \frac{Z(N')}{Z(N'-1)}$$

$$\geq \left[\frac{N}{N_2}\left(\frac{Z(N)}{Z(N-1)} + C'\right) - C'\right]^{N_2-N} \qquad (2.7)$$

which gives

$$N\left(\frac{Z(N)}{Z(N-1)} + C'\right) \leq N_2\left[\left(\frac{Z(N_2)}{Z(N)}\right)^{1/(N_2-N)} + C'\right] \qquad (2.8)$$

On the other hand, if N_2 is such that the right side of (2.6) is negative then (2.8) still holds because $[Z(N_2)/Z(N)]^{1/(N_2-N)}$ is positive. Combining (2.5) and (2.8) gives the desired inequality (2.3).

To obtain an inequality for the free energy density

$$a(\rho,\gamma) \equiv -\lim_{|\Omega|\to\infty} \frac{1}{\beta|\Omega|} \log Z(\rho|\Omega|,\Omega,\gamma) \qquad (2.9)$$

where $|\Omega|$ is the volume of Ω, we take the thermodynamic limits $|\Omega|\to\infty$, $N/|\Omega|\to\rho$ and $N_i/|\Omega|\to\rho_i$ of (2.3). This immediately gives

$$\rho_1\left[C'(\gamma) + \exp\left(\frac{\beta a(\rho_1,\gamma) - \beta a(\rho,\gamma)}{\rho - \rho_1}\right)\right]$$

$$\leq \rho_2\left[C'(\gamma) + \exp\left(\frac{\beta a(\rho,\gamma) - \beta a(\rho_2,\gamma)}{\rho_2 - \rho}\right)\right] \qquad (2.10)$$

for all γ and all ρ, ρ_1 and ρ_2 that satisfy $0 \leq \rho_1 < \rho < \rho_2 < \rho_c$, where ρ_c is the maximum density

permitted by q .

Before proceeding with the main part of the proof, we note that since $a(\rho,\gamma)$ is convex [3] in ρ , it satisfies an inequality like (1.8). Also, taking the limits $\rho_1 \to \rho$ and $\rho_2 \to \rho$ of (2.10) gives $a_- a(\rho,\gamma) \geqq a_+ a(\rho,\gamma)$, which proves that $a(\rho,\gamma)$ is differentiable. The same result was obtained in [2] by a slightly different method.

III. Differentiability of $a(\rho,0+)$.

In this section we prove that $a(\rho,0+)$ is differentiable by considering the limit $\gamma \to 0$ of (2.10). Firstly we note that (2.10) still holds if C' is replaced by an upper bound, C say, on C'. To find a suitable upper bound we note that $q_+ \geqq 0$, $K_+ \geqq 0$ and $1 - e^{-x} \leqq x$ for all x , which gives

$$1 - e^{-\beta(q_+ + \gamma^\nu K_+)} = (1 - e^{-\beta q_+}) + e^{-\beta q_+}(1 - e^{-\beta\gamma^\nu K_+}) \leqq (1 - e^{-\beta q_+}) + \beta\gamma^\nu K_+ \qquad (3.1)$$

It follows that

$$\int d\underset{\sim}{r}\left(1 - \exp[-\beta q_+(\underset{\sim}{r}) - \beta\gamma^\nu K_+(\gamma\underset{\sim}{r})]\right) \leqq B + \beta\alpha_+ \qquad (3.2)$$

where

$$B \equiv \int d\underset{\sim}{r}\left(1 - \exp[-\beta q_+(\underset{\sim}{r})]\right) \qquad (3.3)$$

and $$\alpha_+ \equiv \int d\underset{\sim}{s}\, K_+(\underset{\sim}{s}) \tag{3.4}$$

Also, let us choose

$$\Psi'(\gamma) \equiv -\frac{1}{2} \inf_{\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots} \sum_{a=1}^{\infty} \gamma^\nu K(\gamma \underset{\sim}{r}_a) \tag{3.5}$$

the infimum being over $\underset{\sim}{r}_a$'s that are subject to $|\underset{\sim}{r}_a - \underset{\sim}{r}_b| \geq r_o$ for all $a \neq b$, where r_o is the hard core diameter of q. to obtain an upper bound on Ψ' we consider, as in part I, an infinite lattice of identical cubes $\omega_1, \omega_2, \ldots$ of volume ω filling ν-dimensional space. Putting

$$K_i \equiv \inf_{\underset{\sim}{r} \in \omega_i} K_-(\gamma \underset{\sim}{r}) \tag{3.6}$$

where $K_-(\underset{\sim}{s}) \equiv \min(K(\underset{\sim}{s}), 0)$, we obtain

$$\sum_{a=1}^{\infty} K(\gamma \underset{\sim}{r}_a) \geq \sum_{i=1}^{\infty} N_i K_i \tag{3.7}$$

where N_i is the number of particles whose centres are contained in ω_i for a given $(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots)$. As shown in [6], $N_i \leq \rho_c(\omega^{1/\nu} + 2r_o)^\nu$. Hence, from (3.5) and (3.7), we have for all γ and ω

$$\Psi'(\gamma) \leq \Psi(\gamma, \omega) \equiv -\tfrac{1}{2}\rho_c(1 + 2r_o\omega^{-1/\nu})^\nu \sum_{i=1}^{\infty} (\gamma^\nu \omega) K_i \tag{3.8}$$

Together with (3.2) and (2.2) this gives for all γ and ω

$$C'(\gamma) \leq C(\gamma, \omega) \equiv \Lambda^{-\nu}(B + \beta\alpha_+) e^{2\beta[\Phi' + \Psi(\gamma, \omega)]} \tag{3.9}$$

Now consider the limits $\gamma \to 0$ followed by $\omega \to \infty$ of $C(\gamma,\omega)$. The conditions (1.11) imply [7] that

$$\lim_{\omega\to\infty} \lim_{\gamma\to 0} \Psi(\gamma,\omega) = -\frac{1}{2}\rho_c\alpha_- \tag{3.10}$$

where $$\alpha_- \equiv \int d\underset{\sim}{s}\, K_-(\underset{\sim}{s}) \,. \tag{3.11}$$

This, together with (3.9) implies that

$$C(0+) \equiv \lim_{\omega\to\infty} \lim_{\gamma\to 0} C(\gamma,\omega) = \Lambda^{-\nu}(B + \beta\alpha_+)e^{\beta(2\Phi' - \rho_c\alpha_-)} \tag{3.12}$$

The expression on the right side simplifies in an obvious way if K is either non-positive of non-negative.

Since the limit (3.12) exists, we can replace $C'(\gamma)$ by $C(\gamma,\omega)$ in (2.10), and take the limits $\gamma\to 0$ followed by $\omega\to\infty$ of the resulting inequality. This yields[1]

$$\rho_1\left[C(0+) + \exp\left(\frac{\beta a(\rho_1,0+) - \beta a(\rho,0+)}{\rho - \rho_1}\right)\right]$$

$$\leq \rho_2\left[C(0+) + \exp\left(\frac{\beta a(\rho,0+) - \beta a(\rho_2,0+)}{\rho_2 - \rho}\right)\right] \tag{3.13}$$

for all ρ, ρ_1 and ρ_2 that satisfy $0 \leq \rho_1 < \rho < \rho_2 < \rho_c$.

Finally, taking the limits $\rho_1 \to \rho$ and $\rho_2 \to \rho$ gives

$$\partial_- a(\rho,0+) \geq \partial_+ a(\rho,0+) \tag{3.14}$$

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[1] We have tried, without success, to deduce (3.13) directly from the variational formula for $a(\rho,0+)$ given in part I.

which together with (1.8) implies that $a(\rho,0+)$ is differentiable.

IV. Existence and Continuity of $\mu(\rho,0+)$ and $\pi(\rho,0+)$.

The existence of $\mu(\rho,0+)$ and the statement (1.6) follow from the differentiability of $a(\rho,0+)$ and the inequality

$$\partial_- a(\rho,0+) \leqq \liminf_{\gamma\to 0} \mu(\rho,\gamma) \leqq \limsup_{\gamma\to 0} \mu(\rho,\gamma) \leqq \partial_+ a(\rho,0+) \tag{4.1}$$

which in turn follows from the convexity of $a(\rho,\gamma)$, (see equation (6.5) of reference [7]). The existence of $\pi(\rho,0+)$ and the statement (1.7) follow from (1.3), (1.5) and (1.6).

The prove the absolute continuity of $\mu(\rho,0+)$ and $\pi(\rho,0+)$ we use the Lipschitz condition

$$0 \leqq \pi(\rho_2,\gamma) - \pi(\rho_1,\gamma) \leqq (\rho_2 - \rho_1)\beta^{-1}[1 + C'(\gamma)e^{\beta\mu(\rho,\gamma)}] \tag{4.2}$$

for all γ and all ρ_1, ρ_2 and ρ that satisfy $0 \leqq \rho_1 < \rho < \rho_2 < \rho_c$. The first inequality in (4.2) states that $\pi(\rho,\gamma)$ is non-decreasing [3] in ρ, while the second inequality is due to PENROSE [3] and can be deduced from (2.1). Again we can replace $C'(\gamma)$ by $C(\gamma,\omega)$ in (4.2) and take the limits $\gamma\to 0$ and $\omega\to\infty$. This gives a Lipschitz condition

on $\pi(\rho,0+)$ which proves [4] that it, and hence $\mu(\rho,0+)$, are absolutely continuous.

As a corollary, we note that when $\partial\pi(\rho,0+)/\partial\rho$ exists it satisfies

$$0 \leqq \frac{\partial}{\partial\rho}\pi(\rho,0+) \leqq \beta^{-1}[1 + C(0+)e^{\beta\mu(\rho,0+)}] \qquad (4.3)$$

where $C(0+)$ is given by (3.12). This derivative does not always exist: for example, it has discontinuities in the special case $K \leqq 0$ considered by LEBOWITZ and PENROSE [7],[1].

Using the methods of DOBRUSHIN and MINLOS [2], it may be possible to extend our results to cover the case where q does not have a hard core, provided that the existence of $a(\rho,0+$ can also be proved in this case

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Part III.

DEVIATION FROM THE VAN DER WAALS - MAXWELL THEORY

PART III

Abstract. We examine the limiting free energy density $a(\rho,0+) \equiv \lim_{\gamma\to 0} a(\rho,\gamma)$ of a classical system of particles with the two-body potential $q(\underset{\sim}{r}) + \gamma^{\nu}K(\gamma\underset{\sim}{r})$, at density ρ in ν dimensions. Starting from a variational formula for $a(\rho,0+)$, obtained in Part I of these papers, we obtain a new upper bound on $a(\rho,0+)$ given by

$$a(\rho,0+) \leq \mathrm{CE}\left\{\mathrm{ME}[a^{0}(\rho) + \frac{1}{4\nu}\tilde{K}_{\min}\rho^{2}] + (\tfrac{1}{2}\alpha - \tfrac{1}{4\nu}\tilde{K}_{\min})\rho^{2}\right\}$$

Here ME f, called the mid-point envelope of f, is defined for any function f by

$$\mathrm{ME}\ f(\rho) \equiv \inf_{h} \tfrac{1}{2}[f(\rho+h) + f(\rho-h)],$$

CE f, called the convex envelope of f, is defined for any f as the maximal convex function not exceeding f: also $\alpha \equiv \int d\underset{\sim}{s}\ \mathbf{K}(\underset{\sim}{s})$ and $\tilde{K}_{\min}$ is the minimum of the Fourier transform of K, while $a^{0}(\rho)$ is the free energy density for K=0.

For the class of functions K such that $\tilde{K}_{\min} < 0$ and $\tilde{K}_{\min} < 2\nu\alpha$, we deduce from this upper bound that $a(\rho,0+) < \mathrm{CE}[a^{0}(\rho) + \frac{1}{2}\alpha\rho^{2}]$ for all values of ρ where $a^{0}(\rho) + \frac{1}{4\nu}\tilde{K}_{\min}\rho^{2}$ differs from its mid-point envelope. Consequently, the generalized van der Waals equation $a(\rho,0+) = \mathrm{CE}[a^{0}(\rho) + \frac{1}{2}\alpha\rho^{2}]$ does not apply in this case. We prove that in a certain sense the local density in non-uniform over distances of order γ^{-1} in this case, and infer that this density is periodic.

We also give a simpler derivation of other bounds on $a(\rho,0$ obtained by Lebowitz and Penrose.

I. Introduction

Following the work of Kac, Uhlenbeck and Hemmer [1] and van Kampen [2] on the van der Waals equation, Lebowitz and Penrose [3] (henceforth referred to as LP) considered the pressure of a ν-dimensional system of particles with the two-body potential

$$q(\underset{\sim}{r}) + \gamma^{\nu}K(\gamma\underset{\sim}{r}) \tag{1.1}$$

and showed that in the limit $\gamma \to 0$ this pressure was given, for a certain class of functions K, by a generalization of the van der Waals equation together with the Maxwell construction. In the present paper we prove that, for a different class of functions K, this equation does not hold.

Our method is based on the results of part I of this series of papers [4]. We there proved that the free energy density $a(\rho,T,\gamma)$ of a classical system of particles, with the two-body potential (1.1) at temperature T and density ρ, tends to a definite limit when $\gamma \to 0$ (the van der Waals limit), provided that both q and K satisfy fairly weak tempering conditions and that q has a hard core. Here $q(\underset{\sim}{r})$ is called the reference potential and $\gamma^{\nu}K(\gamma\underset{\sim}{r})$ the Kac potential. We proved further that

$$a(\rho,T,0+) \equiv \lim_{\gamma\to 0} a(\rho,T,\gamma) = \inf_{n\in\mathcal{C}(\rho)} G(n,T) \tag{1.2}$$

where the functional G is given by

$$G(n,T) = \frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\left\{a^{0}[n(\underset{\sim}{y}),T] + \tfrac{1}{2}n(\underset{\sim}{y})\int d\underset{\sim}{y}'\, n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}')\right\} \tag{1.3}$$

the integral with respect to $\underset{\sim}{y}'$ being over all of ν-dimensional space. Here $\mathcal{C}(\rho)$ is the class of functions n that are (i) bounded by 0 and ρ_c (the maximum density permitted by q), are (ii) Riemann integrable over any bounded region, are (iii) periodic, and (iv) have space average ρ, i.e.

$$\frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\; n(\underset{\sim}{y}) = \rho \qquad (1.4)$$

The region Γ (which depends on n) is the unit cell of n and has volume $|\Gamma|$. The function $a^0(\rho,T)$ is the free energy density corresponding to a system with the two-body potential $q(\underset{\sim}{r})$, called the reference system.

We shall use (1.2 and 3) to obtain an upper bound on $a(\rho,T,0+)$, but first let us consider the bounds already obtained by LP. They showed that

$$CE[a^0(\rho,T) + \tfrac{1}{2}\tilde{K}_{min}\rho^2] + \tfrac{1}{2}(\alpha - \tilde{K}_{min})\rho^2 \leq a(\rho,T,0+) \leq CE[a^0(\rho,T) + \tfrac{1}{2}\alpha\rho^2] \qquad (1.5)$$

where $\tilde{K}_{min}$ is the minimum of the Fourier transform

$$\tilde{K}(\underset{\sim}{p}) \equiv \int d\underset{\sim}{s}\; e^{2\pi i \underset{\sim}{p}\cdot\underset{\sim}{s}}\, K(\underset{\sim}{s}) \;, \qquad (1.6)$$

$\alpha \equiv \int d\underset{\sim}{s}\; K(\underset{\sim}{s}) = \tilde{K}(0)$, and CE f, called the convex envelope of f, is defined for arbitrary f as the maximal convex function not exceeding f. These bounds coincide in the following cases:

(a). If $\tilde{K}(\underset{\sim}{p}) \geqq 0$ for all $\underset{\sim}{p}$ (so that $\alpha \geqq 0$) then

$$a(\rho,T,0+) = a^{o}(\rho,T) + \frac{1}{2}\alpha\rho^{2} \quad \text{for all } \rho \text{ and } T. \qquad (1.7)$$

(b). If[1] $\tilde{K}(\underset{\sim}{p}) \geqq \tilde{K}(0)$ for all $\underset{\sim}{p}$ (of which a special case is $K(\underset{\sim}{s}) \leqq 0$ for all $\underset{\sim}{s}$) then

$$a(\rho,T,0+) = CE[a^{o}(\rho,T) + \frac{1}{2}\alpha\rho^{2}] \quad \text{for all } \rho \text{ and } T. \qquad (1.8)$$

The canonical pressure corresponding to (1.8) is given by a generalization of the van der Waals - Maxwell equation of state.

(c). For a general K, (1.7) holds for values of ρ and T where $a^{o} + \frac{1}{2}\tilde{K}_{min}\rho^{2}$ coincides with its convex envelope. One expects for any a^{o}, and can show for certain cases of a^{o}, that this happens at least when $\rho \approx 0$ and $\rho \approx \rho_{c}$.

(d). If a^{o} shows no first order phase transition and $T^{-1}\partial^{2}a^{o}(\rho,T)/\partial\rho^{2} \geqq C$ for all ρ and T, where C is a positive constant, then (1.7) holds for all ρ provided that

$$T \geqq |\tilde{K}_{min}|/C \qquad (1.9)$$

To prove this, we merely note that $a^{o} + \frac{1}{2}\tilde{K}_{min}\rho^{2}$ is convex when (1.9) holds. As an example, when q corresponds to a one-dimensional system of hard rods of length r_{o} we find that $C = 27k/4r_{o}$ where k is Boltzmann's constant.

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[1] This implies $\alpha \leqq 0$ since $\tilde{K}(\underset{\sim}{p}) \to 0$ as $|\underset{\sim}{p}| \to \infty$.

The bounds on $a(\rho,T,0+)$ given by (1.5) do not exclude the possibility that (1.8) might hold for all functions K and for all ρ and T. To show that this is not so, we obtain a stronger upper bound on $a(\rho,T,0+)$ which enables us to find some conditions under which $a(\rho,T,0+) < CE[a^o(\rho,T) + \frac{1}{2}\alpha\rho^2]$.

II. Stronger Upper Bound on the Free Energy

This section is devoted to obtaining the above mentioned upper bound on $a(\rho,0+)$ (dependence on T is henceforth omitted from the notation). Our method consists of choosing judiciously a function $n \in \mathscr{C}(\rho)$, noting that $a(\rho,0+) \leqq G(n)$, and finding an upper bound on $G(n)$ for this function n.

As a first choice one might try $n = \rho$, which clearly belongs to $\mathscr{C}(\rho)$, and which gives $a(\rho,0+) \leqq a^o(\rho) + \frac{1}{2}\alpha\rho^2$. Since $a(\rho,0+)$ is convex [4], it follows that $a(\rho,0+) \leqq CE[a^o(\rho) + \frac{1}{2}\alpha\rho^2]$. This is just the result (1.5) of LP, but here it is an almost trivial consequence of the variational formula.

To obtain a stronger upper bound, let $\underset{\sim}{p}_o$ be a value of $\underset{\sim}{p}$ where $\tilde{K}(\underset{\sim}{p})$ attains[2] its minimum, i.e. $\tilde{K}(\underset{\sim}{p}_o) = \tilde{K}_{min}$. We

---

[2] The minimum is attained because $\tilde{K}(\underset{\sim}{p})$ is continuous [3].

assume that K, and hence $\tilde{K}$, has at least cubic rotational symmetry. Examples are the continuum system where K has spherical symmetry, and a lattice gas with a cubic lattice. In this case there are ν orthogonal vectors, $\underset{\sim}{p}_o^1, \underset{\sim}{p}_o^2, \ldots \underset{\sim}{p}_o^\nu$ ($\underset{\sim}{p}_o^1 \equiv \underset{\sim}{p}_c$) say, of equal length and such that $\tilde{K}(\pm\underset{\sim}{p}_o^i) = \tilde{K}_{min}$ for $i = 1,2,\ldots\nu$. Now let us choose

$$n(\underset{\sim}{y}) = \rho + \frac{h}{\nu}\sum_{i=1}^{\nu} \sin(2\pi \underset{\sim}{p}_o^i \cdot \underset{\sim}{y}) \tag{2.1}$$

where h is a positive constant such that $0 \leq \rho - h$ and $\rho + h \leq \rho_c$. Hence we have $n \in \mathcal{C}(\rho)$. The unit cell Γ of n is in this case a cube of side $|\underset{\sim}{p}_o|^{-1}$. Our choice of n is motivated by the conjecture of LP that spatial ordering may occur; the sine function is chosen so that the calculations are simple; and the period is chosen so as to give the best possible upper bound for functions of this form.

To obtain an upper bound on $G(n)$, defined by (1.3), we first find an upper bound on its quadratic term

$$I(n) \equiv \frac{1}{|\Gamma|}\int_\Gamma d\underset{\sim}{y} \int d\underset{\sim}{y}' \; K(\underset{\sim}{y}-\underset{\sim}{y}')n(\underset{\sim}{y})n(\underset{\sim}{y}') \tag{2.2}$$

This can be written as

$$I(n) = \sum_{\underset{\sim}{p} \in V_\Gamma} \tilde{K}(\underset{\sim}{p}) \, |\tilde{n}(\underset{\sim}{p})|^2 \tag{2.3}$$

where V_Γ is the set of all vectors that connect lattice points

in the reciprocal lattice corresponding to the lattice with unit cell Γ. Also $\tilde{K}$ is defined by (1.6) and $\tilde{n}$ by

$$\tilde{n}(\underset{\sim}{p}) \equiv \frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\; n(\underset{\sim}{y})\; e^{2\pi i \underset{\sim}{p}\cdot\underset{\sim}{y}} . \tag{2.4}$$

For the choice (2.1) of n we obtain

$$|\tilde{n}(\underset{\sim}{p})| = \begin{cases} \rho & \text{for } \underset{\sim}{p} = 0 , \\ h/2\nu & \text{for } \underset{\sim}{p} = \pm\underset{\sim}{p}_o^1, \ldots \pm\underset{\sim}{p}_o^\nu , \\ 0 & \text{otherwise.} \end{cases} \tag{2.5}$$

Hence from (2.3) we have

$$\begin{aligned} I(n) &= \tilde{K}(0)\rho^2 + 2\nu\tilde{K}(\underset{\sim}{p}_o)(h/2\nu)^2 \\ &= \alpha\rho^2 + \frac{1}{2\nu}\tilde{K}_{\min} h^2 . \end{aligned} \tag{2.6}$$

Next we find an upper bound on the integral involving a^o in the functional $G(n)$. Since $a^o(\rho)$ is convex we have, for all ρ' in the interval $[\rho-h, \rho+h]$,

$$a^o(\rho') \leq \frac{\rho'-\rho+h}{2h}\, a^o(\rho+h) + \frac{\rho+h-\rho'}{2h}\, a^o(\rho-h) \tag{2.7}$$

But (3.1) implies that $\rho-h \leq n(\underset{\sim}{y}) \leq \rho+h$ for all $\underset{\sim}{y}$, and hence

$$\begin{aligned} \frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\; a^o[n(\underset{\sim}{y})] &\leq \frac{a^o(\rho+h)}{2h|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}[n(\underset{\sim}{y}) - \rho + h] \\ &\quad + \frac{a^o(\rho-h)}{2h|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}[\rho + h - n(\underset{\sim}{y})] \\ &= \frac{1}{2}\, a^o(\rho+h) + \frac{1}{2}\, a^o(\rho-h) \end{aligned} \tag{2.8}$$

Combining (2.6) with (2.8) gives an upper bound on $a(\rho,0+)$ which is conveniently expressed in the form

$$a(\rho,0+) \leq \frac{1}{2}\left\{a^0(\rho+h) + a^0(\rho-h) + \frac{1}{4\nu}\tilde{K}_{min}[(\rho+h)^2 + (\rho-h)^2]\right\}$$
$$(\tfrac{1}{2}\alpha - \frac{1}{4\nu}\tilde{K}_{min})\rho^2. \qquad (2.9)$$

Since this holds for all h, we can minimize the right side with respect to h which gives

$$a(\rho,0+) \leq ME[a^0(\rho) + \frac{1}{4\nu}\tilde{K}_{min}\rho^2] + (\tfrac{1}{2}\alpha - \frac{1}{4\nu}\tilde{K}_{min})\rho^2, \qquad (2.10)$$

where $ME\ f(\rho)$, called the mid-point envelope of f, is defined for any f by

$$ME\ f(\rho) \equiv \inf_h \tfrac{1}{2}[f(\rho+h) + f(\rho-h)] \qquad (2.11)$$

and is discussed in the Appendix. Since $a(\rho,0+)$ is convex, we obtain from (2.10) our first main result :

Theorem. If q and K satisfy the conditions [4] of Part I, and K has at least cubic symmetry, then

$$a(\rho,0+) \leq CE\left\{ME[a^0(\rho) + \frac{1}{4\nu}\tilde{K}_{min}\rho^2] + (\tfrac{1}{2}\alpha - \frac{1}{4\nu}\tilde{K}_{min})\rho^2\right\} \qquad (2.12)$$

We note that this upper bound is at least as strong as the LP upper bound $CE[a^\alpha + \frac{1}{2}\alpha\rho^2]$ because, from (2.11), $ME\ f \leq f$ for any function f.

III. Deviation from the van der Waals - Maxwell Theory

In this section we consider the consequences of our theorem. We shall prove the following

Corollary. If $\tilde{K}_{min} < 0$ and $\tilde{K}_{min} < 2\nu\alpha$, then

$$a(\rho,T,0+) < CE[a^o(\rho,T) + \tfrac{1}{2}\alpha\rho^2]$$

for all values of ρ and T where $a^o(\rho,T) + \frac{1}{4\nu}\tilde{K}_{min}\rho^2$ differs from its mid-point envelope.

Before giving the general proof, we consider the special case where $a^o + \frac{1}{2}\alpha\rho^2$ is $\overset{a}{\wedge}$convex function of ρ for a given T (this is true for all T if $\alpha \geq 0$). The conditions of the corollary imply that $ME[a^c + \frac{1}{4\nu}\tilde{K}_{min}\rho^2] + (\frac{1}{2}\alpha - \frac{1}{4\nu}\tilde{K}_{min})\rho^2 < a^o + \frac{1}{2}\alpha\rho^2$, whence the result follows by the theorem.

For the general proof we need

Lemma 1. For any function f

$$CE\, f(\rho) + \rho^2 < CE[f(\rho) + \rho^2] \qquad (3.1)$$

in any interval[3] of values of ρ where $CE\, f(\rho) < f(\rho)$.

---

[3] Eq.(3.1) does not hold if ρ is an isolated pointed at which $CEf < f$. No such isolated points occur if, for example, f is continuous. The same applies to (3.2).

Lemma 2. For any function f,

$$CE[ME\ f(\rho) + \rho^2] \leq CE[f(\rho) + \rho^2] \tag{3.2}$$

in any interval[3] of values of ρ where $ME\ f(\rho) < f(\rho)$.

To prove Lemma 1 put

$$F(\rho) \equiv CEf(\rho) + \rho^2 \tag{3.3}$$

In any interval (ρ_1, ρ_2), the graph (see Fig 1) of $F(\rho)$ always lies on or below a parabola, of curvature 2, cutting F at ρ_1 and ρ_2, i.e.

$$F(\rho) \leq \frac{\rho_2-\rho}{\rho_2-\rho_1} F(\rho_1) + \frac{\rho-\rho_1}{\rho_2-\rho_1} F(\rho_2) + (\rho-\rho_1)(\rho-\rho_2) \tag{3.4}$$

for $\rho_1 \leq \rho \leq \rho_2$. We also have

$$F(\rho) \leq f_+(\rho) \equiv f(\rho) + \rho^2 \quad \text{for all } \rho, \tag{3.5}$$

so that

$$F(\rho) \leq \frac{\rho_2-\rho}{\rho_2-\rho_1} f_+(\rho_1) + \frac{\rho-\rho_1}{\rho_2-\rho_1} f_+(\rho_2) + (\rho-\rho_1)(\rho-\rho_2) \tag{3.6}$$

for $\rho_1 \leq \rho \leq \rho_2$. Suppose that $C(\rho) \equiv CEf_+(\rho) < f_+(\rho)$ throughout, but not at the end points of an interval (ρ_a, ρ_b), so that $C(\rho_a) = f_+(\rho_a)$ and $C(\rho_b) = f_+(\rho_b)$. Now, setting $\rho_1 = \rho_a$ and $\rho_2 = \rho_b$ in (3.6), we obtain for $\rho_a \leq \rho \leq \rho_b$

$$F(\rho) \leq \frac{\rho_b-\rho}{\rho_b-\rho_a} C_+(\rho_a) + \frac{\rho-\rho_a}{\rho_b-\rho_a} C_+(\rho_b) + (\rho-\rho_a)(\rho-\rho_b) .$$

$$= C(\rho) + (\rho-\rho_a)(\rho-\rho_b) . \tag{3.7}$$

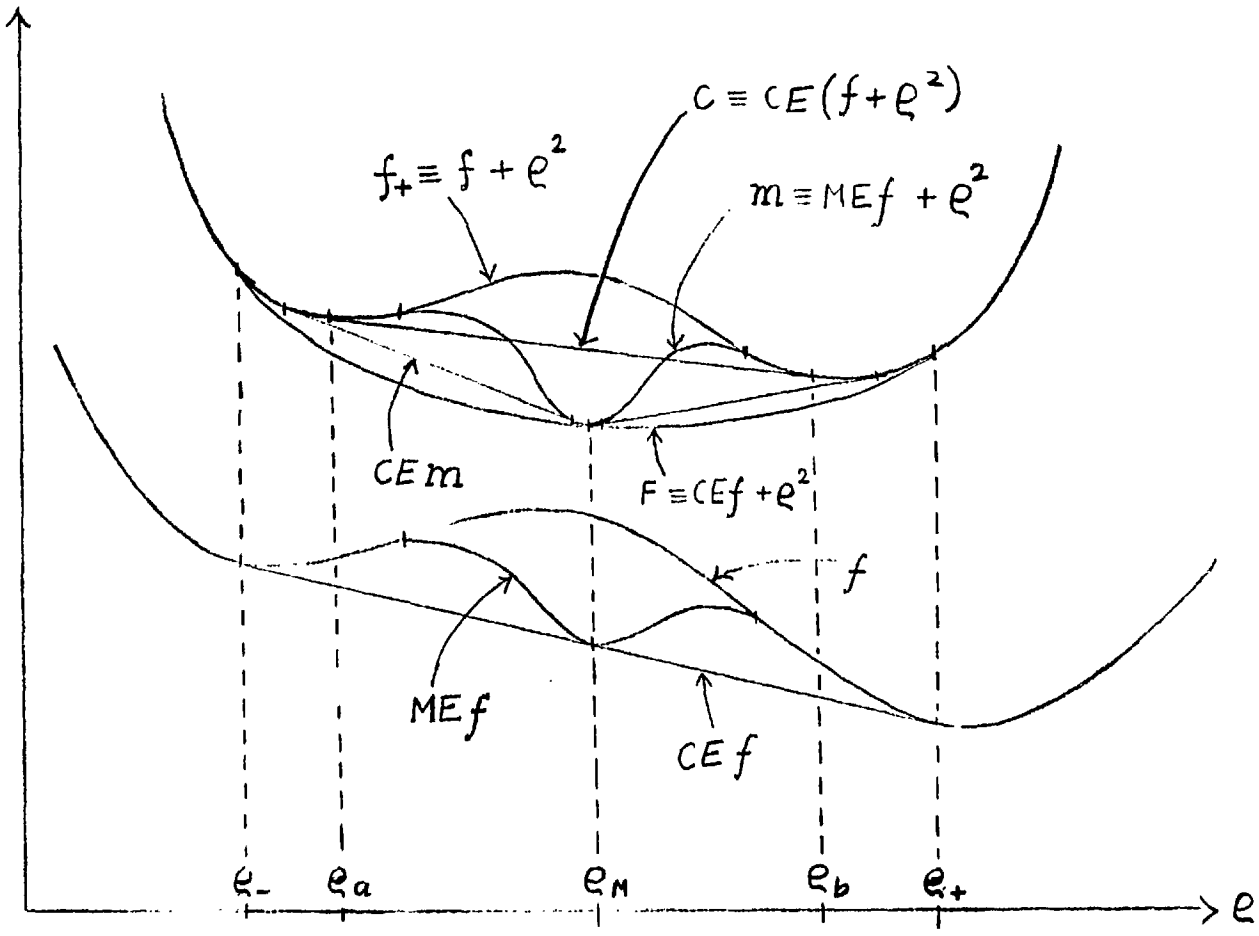

Fig.1. Illustration of the functions used in the proof of Lemmas 1 and 2. In the example shown, $MEf < f$ only where $CE(f+\rho^2) < f+\rho^2$, but this does not hold for all functions f.

Hence we have

$$F(\rho) < C(\rho) \quad \text{for} \quad \rho_a < \rho < \rho_b \,. \tag{3.8}$$

The same applies to any interval defined like (ρ_a, ρ_b). In the remaining intervals where $C(\rho) = f_+(\rho)$, we have, whenever $CEf(\rho) < f(\rho)$,

$$CEf(\rho) + \rho^2 < f(\rho) + \rho^2 = C(\rho) \,, \tag{3.9}$$

which completes the proof of Lemma 1. (This lemma shows, by the way, that if $\tilde{K}_{min} < 0$ and $\tilde{K}_{min} < \alpha$ then the LP bounds given by (1.5) do not coincide when $a^o + \frac{1}{2}\tilde{K}_{min}\rho^2$ differs from its convex envelope.)

To prove Lemma 2, suppose that $CEf(\rho) < f(\rho)$ throughout, but not at the end points of the interval (ρ_-, ρ_+) (see Fig.1). Then, from Lemma 5 of the Appendix,

$$MEf(\rho_M) = CEf(\rho_M) \tag{3.10}$$

where $\rho_M \equiv \frac{1}{2}(\rho_- + \rho_+)$. It follows from this and Lemma 1 that

$$m(\rho_M) < C(\rho_M) \tag{3.11}$$

where

$$m(\rho) = MEf(\rho) + \rho^2 \tag{3.12}$$

Since $CEm(\rho)$ is convex, we have† for $\rho_a \leq \rho \leq \rho_M$

$$CEm(\rho) \leq \frac{\rho_M - \rho}{\rho_M - \rho_a} CEm(\rho_a) + \frac{\rho - \rho_a}{\rho_M - \rho_a} CEm(\rho_M) \tag{3.13}$$

where ρ_a and ρ_b were defined above. But we also have

$$CEm(\rho_a) \leq m(\rho_a) \leq f(\rho_a) + \rho_a^2 = C(\rho_a) \tag{3.14}$$

† Note added after binding: If $\rho_M < \rho_a$ or $\rho_M > \rho_b$, the result (3.16 still holds, but a slightly different proof must be used.

which, together with (3.11) and (3.13), gives for $\rho_a < \rho \leqq \rho_M$

$$CEm(\rho) < \frac{\rho_M - \rho}{\rho_M - \rho_a} C(\rho_a) + \frac{\rho - \rho_a}{\rho_M - \rho_a} C(\rho_M)$$

$$= C(\rho) \tag{3.15}$$

The same holds for $\rho_M \leqq \rho < \rho_b$ so that

$$CEm(\rho) < C(\rho) \quad \text{for} \quad \rho_a < \rho < \rho_b \,. \tag{3.16}$$

If $MEf(\rho) < f(\rho)$ only in the interval $\rho_a < \rho < \rho_b$, or any other interval where $CE(f+\rho^2) < f+\rho^2$, then Lemma 2 is is proved. If $MEf(\rho) < f(\rho)$ in some other interval, then in this interval

$$CE[MEf(\rho) + \rho^2] \leqq MEf(\rho) + \rho^2 < f(\rho) + \rho^2 = CE[f(\rho) + \rho^2] \tag{3.17}$$

which completes the proof of Lemma 2.

The corollary now follows from Lemma 2, the theorem, and the observation that, if λ is a non-negative constant, then for any function f

$$\text{and} \qquad \begin{aligned} ME(\lambda f) &= \lambda\, MEf \\ CE(\lambda f) &= \lambda\, CEf \end{aligned} \tag{3.18}$$

It should be noted that for the class of Kac potentials such that $2\gamma\alpha \leqq \tilde{K}_{min.} < 0$ we have proved neither adherence to nor deviation from the generalized van der Waals - Maxwell theory. We cannot prove deviation because our new upper bound coincides with that of LP in this case. To prove this

we note from the definition (2.11) that for any two functions[4] f and g

$$ME(f+g) \geqq MEf + MEg \tag{3.19}$$

and in particular

$$ME(f+\rho^2) \geqq MEf + \rho^2 \tag{3.20}$$

It follows from (3.18) that, for $2\nu\alpha \leqq \tilde{K}_{min}$,

$$ME[a^o + \frac{1}{4\nu}\tilde{K}_{min}\rho^2] + (\frac{1}{2}\alpha - \frac{1}{4\nu}\tilde{K}_{min})\rho^2 \geqq ME[a^o + \frac{1}{2}\alpha\rho^2] \tag{3.21}$$

Taking the convex envelope of both sides and noting, from Lemma 4 of the Appendix, that CE MEf = CEf for any function f gives

$$CE\left\{ME[a^o + \frac{1}{4\nu}\tilde{K}_{min}\rho^2] + (\frac{1}{2}\alpha - \frac{1}{4\nu}\tilde{K}_{min})\rho^2\right\} \geqq CE[a^o + \frac{1}{2}\alpha\rho^2] \tag{3.22}$$

for $2\nu\alpha \leqq \tilde{K}_{min}$. We already pointed out (at the end of the previous section) that the left side of (3.22) does not exceed its right side, so that (3.22) is in fact an equality. QED.

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[4] Eq.(3.19) also holds if ME is replaced by CE.

IV. The Bounds of Lebowitz and Penrose

In Section II we showed that the LP upper bound $CE(a^0 + \frac{1}{2}\alpha\rho^2)$ on $a(\rho,0+)$ follows almost trivially from our variational formula (1.2). We now show that the LP lower bound, given by (1.5), which they obtained by a rather lengthy argument, also follows readily from the variational formula.

To obtain the lower bound we need

Lemma 3. For any function $f(\rho)$ defined on $[0,\rho_c]$,

$$\inf_{n\in\mathcal{C}(\rho)} \frac{1}{|\Gamma|}\int_\Gamma d\underset{\sim}{y}\, f[n(\underset{\sim}{y})] = CEf(\rho) \tag{4.1}$$

Denoting the left side of (2.2) by $g(\rho)$ we have, since $\rho\in\mathcal{C}(\rho)$, that $g(\rho) \leqq f(\rho)$. But, by an argument like the proof of Lemma 3 in reference [4], we deduce that $g(\rho)$ is convex, and hence $g(\rho) \leqq CEf(\rho)$. Now putting $h(\rho) \equiv CEf(\rho)$ we have, since $f(\rho) \geqq h(\rho)$, that

$$\begin{aligned} g(\rho) &\geqq \inf_{n\in\mathcal{C}(\rho)} \frac{1}{|\Gamma|}\int_\Gamma d\underset{\sim}{y}\, h[n(\underset{\sim}{y})] \\ &\geqq \inf_{n\in\mathcal{C}(\rho)} h\left[\frac{1}{|\Gamma|}\int_\Gamma d\underset{\sim}{y}\, n(\underset{\sim}{y})\right] \\ &= h(\rho)\,, \end{aligned} \tag{4.2}$$

where the second inequality follows [5] from the fact that $h(\rho)$ is convex. This completes the proof of Lemma 3.

Now following LP we express K as the sum of two functions K^+ and K^- chosen so that their Fourier transforms $\tilde{K}^+$ and $\tilde{K}^-$ satisfy for all $\underset{\sim}{p}$

$$\tilde{K}^+(\underset{\sim}{p}) \geqq 0 \quad \text{and} \quad \tilde{K}^-(\underset{\sim}{p}) \geqq \tilde{K}^-(0) = \tilde{K}_{\min} . \tag{4.3}$$

From (2.3), we can write $I = I^+ + I^-$, where

$$I^{\pm}(n) \equiv \sum_{\underset{\sim}{p} \in V_\Gamma} \tilde{K}^{\pm}(\underset{\sim}{p}) \left|\tilde{n}(\underset{\sim}{p})\right|^2 . \tag{4.4}$$

Then from (4.3) we have

$$I^+ \geqq \tilde{K}^+(0) \left|\tilde{n}(0)\right|^2 = (\alpha - \tilde{K}_{\min})\rho^2, \tag{4.5}$$

$$I^- \geqq \tilde{K}^-(0) \sum_{\underset{\sim}{p} \in V_\Gamma} \left|\tilde{n}(\underset{\sim}{p})\right|^2 = \tilde{K}_{\min} \frac{1}{|\Gamma|} \int_\Gamma d\underset{\sim}{y}\; n(\underset{\sim}{y})^2 . \tag{4.6}$$

Adding these and substituting in (1.2 and 3) gives

$$a(\rho,0+) \geqq \inf_{n \in \mathcal{C}(\rho)} \frac{1}{|\Gamma|} \int_\Gamma d\underset{\sim}{y} \left\{ a^\circ[n(\underset{\sim}{y})] + \tfrac{1}{2}\tilde{K}_{\min} n(\underset{\sim}{y})^2 \right\} + \tfrac{1}{2}(\alpha - \tilde{K}_{\min})\rho^2 , \tag{4.7}$$

which, on application of Lemma 3, gives the desired lower bound in (1.5). It seems to be difficult to improve on this lower bound for general functions K .

V. Discussion

Our main results are (i) the Theorem which gives an upper bound (2.12) on the free energy of particle systems in the van der Waals limit, and (ii) the Corollary deduced from this Theorem which, for the class of Kac potentials such that $\tilde{K}_{min} < 0$ and $\tilde{K}_{min} < 2\gamma\alpha$, gives conditions under which the free energy differs from its generalized van der Waals - Maxwell form $CE[a^o + \frac{1}{2}\alpha\rho^2]$. For Ising magnets, the same conditions imply deviation from the Weiss theory of ferromagnetism.

We have proved that the non-uniform periodic density (2.1) gives, in some cases, a lower value of the free energy functional $G(n)$ than does a uniform density ρ or a two-phase mixture of uniform phases. This does not stricily prove that the minimal density is periodic since it is possible that a non-periodic function n (an almost periodic function, for example) could give a lower value of $G(n)$ than all periodic functions n. On the other hand, suppose that the infimum in (1.2) is attained for some $n^* \in \mathscr{C}(\rho)$ (which, by the definition of $\mathscr{C}(\rho)$, makes n^* periodic) : then it follows that, in the above cases, $n^*(\underset{\sim}{y})$ is <u>not</u> almost everywhere equal to ρ. The system could then be described as <u>spatially ordered</u>. For Ising magnets, such ordering represents an antiferromagnetic state. It is

therefore important, for this work, to find the values of ρ (if any) for which the infimum is attained.

As pointed out in Section II, functions n of the form (2.1) give the best upper bound when $\tilde{K}(p_o) = \tilde{K}_{min}$. This leads us to the conjecture that, if the system is one-dimensional, and $\tilde{K}(p)$ has a pronounced minimum at $p = p_o$, then the minimal function n^* (if it exists) has a period of approximately $1/p_o$. It would be interesting to determine the truth or falsity of this conjecture, and to examine, in general, the unit cell of n^*.

For the class of Kac potentials satisfying $2\gamma\alpha \leq \tilde{K}_{min} < 0$, we can prove neither adherence to nor deviation from the van der Waals - Maxwell theory. We expect that deviation occurs, but to prove this would demand a stronger upper bound than (2.12). Such a bound could be obtained by a better choice† of n than (1.3).

It would be interesting if, in the one-dimensional case, one could find a function K in the class $\tilde{K}_{min} < 0$, $\tilde{K}_{min} < 2\gamma\alpha$ for which the thermodynamic functions and the density n^* could be calculated explicitly. It may be possible to perform such a calculation using the variational formula (1.2). A possible alternative approach is the method of Kac, Uhlenbeck and Hemmer [1].

We have been able to solve many of these problems for a

† Note added after binding: If a single sine term, rather than a sum, is used in (3.1), the factor ν disappears throughout.

cell model which is closely related to the present model. For this cell model, the free energy can be calculated exactly, and spatial ordering can be shown to occur. We hope to present this in a future publication.

Appendix. The Mid-Point Envelope

In Sections II and IV we used the following lemmas concerning the mid-point envelope of a function, defined by (2.11).

Lemma 4. For any function f,

$$CEf(\rho) \leq MEf(\rho) \leq f(\rho) \quad \text{for all } \rho . \tag{A.1}$$

The equalities apply for all ρ if f is convex.

Lemma 5. If ρ_M is the mid-point of any double tangent $t(\rho)$ to f, lying on or below f, then

$$MEf(\rho_M) = CEf(\rho_M) = t(\rho_M) . \tag{A.2}$$

These lemmas give some guide to the shape of MEf, an example of which is shown in Fig.2.

To prove Lemma 4 we use Lemma 3. Put

$$n_h(\underset{\sim}{y}) \equiv \begin{cases} \rho+h & \text{for } \underset{\sim}{y}\in\Gamma_+ \\ \rho-h & \text{for } \underset{\sim}{y}\in\Gamma_- , \end{cases} \tag{A.3}$$

where $\Gamma = \Gamma_+ + \Gamma_-$ and $\Gamma_+ = \Gamma_-$ and Γ is the unit cell of n_h.

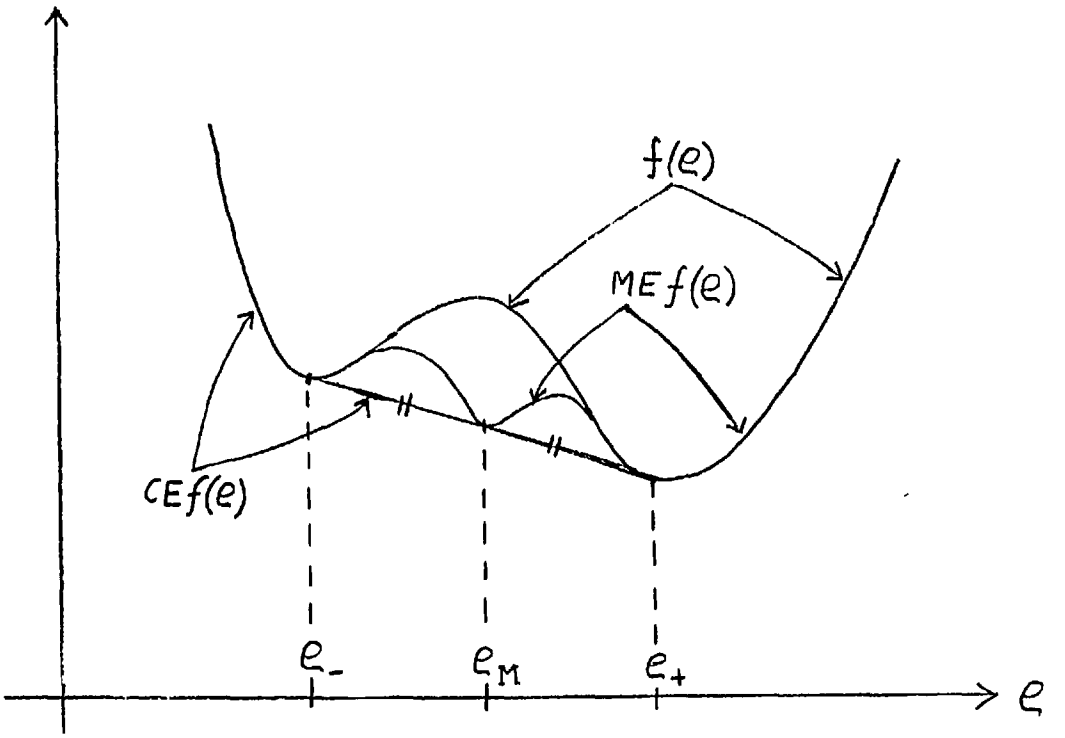

Fig.2. An example of a function f and its envelopes. The lines marked with a double stroke have equal length.

This n_h clearly belongs to $\mathcal{C}(\rho)$, and hence

$$\inf_{n\in\mathcal{C}(\rho)} \frac{1}{|\Gamma|}\int_\Gamma dy\ f[n(y)] \leqq \inf_h \frac{1}{|\Gamma|}\int_\Gamma dy\ f[n_h(y)]$$
$$= \inf_h \tfrac{1}{2}[f(\rho+h) + f(\rho-h)] \qquad (A.4)$$

This, together with Lemma 3 and (2.11), gives the first inequality in (A.1). The second inequality follows directly from (2.11).

To prove Lemma 5, let ρ_+ and ρ_- be the end points of the tangent $t(\rho)$ (see Fig.2). We then have $CEf(\rho_\pm) = f(\rho_\pm)$ so that

$$CEf(\rho_M) = \tfrac{1}{2}[f(\rho_+) + f(\rho_-)]$$
$$\geqq \inf_h \tfrac{1}{2}[f(\rho_M+h) + f(\rho_M-h)]$$
$$= MEf(\rho_M)\ . \qquad (A.5)$$

This together with Lemma 4 gives Lemma 5.

For most functions f, we find that MEf can only be found by numerical methods. The following examples are exceptions which we have found useful :

(i) $$ME(\sin\rho) = -|\sin\rho| \qquad (A.6)$$

(ii) If $f(\rho)$ is a quartic polynomial in ρ, whose fourth derivative f_4 (a constant) is positive, then

$$MEf(\rho) = \begin{cases} f(\rho) & \text{for all } \rho \text{ where } f_2(\rho) \geqq 0\ , \\ f(\rho) - \tfrac{3}{2}[f_2(\rho)]^2/f_4 & \text{where } f_2(\rho) \leqq 0\ , \end{cases}$$

where $f_2(\rho) \equiv \partial^2 f(\rho)/\partial\rho^2$. We leave the proofs of (A.6 and7) to the reader.

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Part IV

VAN KAMPEN'S EQUATION

AND SOME OF ITS CONSEQUENCES

PART IV

Abstract

Starting from a variational formula for the van der Waals limit of the pressure $p(\mu,0+)$ in the Grand formalism, we show that the density function $n^*(y,\mu)$ satisfies an integral equation first obtained by van Kampen. We transform this equation, which is non-linear, Fredholm integral equation of the Hammerstein type. We derive a criterion for the absence of first order phase transitions in terms of the uniqueness of n^*. We apply this criterion, using some standard uniqueness theorems for integral equations of the Hammerstein type, and confirm some previous results about the absence of phase transitions.

We examine second order transitions by a similar method.

Finally we obtain bounds on n^* and $\partial p(\mu,0+)/\partial\mu$.

PART IV

I. Introduction

Because of the difficulty of solving the variational problem derived in Part I, it would be useful if we could determine the general features of the thermodynamic functions without calculating them exactly. In this paper we show how conditions for the absence of phase transitions can be deduced from certain integral equations associated with the variational problem.

We consider the grand canonical pressure $p(\mu,\gamma)$ for the two-body potential $q(\underset{\sim}{r}) + \gamma^{\nu}K(\gamma\underset{\sim}{r})$ and chemical potential μ. It was proved in Part I that

$$p(\mu,0+) \equiv \lim_{\gamma\to 0} p(\mu,\gamma) = \sup_{n\in\mathcal{R}} F(n,\mu) \tag{1.1}$$

where

$$F(n,\mu) \equiv \frac{1}{|\Gamma|}\int_{\Gamma} d\underset{\sim}{y}\Big\{\mu n(\underset{\sim}{y}) - a^{o}[n(\underset{\sim}{y})] - \frac{1}{2}n(\underset{\sim}{y})\int d\underset{\sim}{y}'\, n(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}') \quad , \tag{1.2}$$

where Γ is the unit cell of n, and $\mathcal{R}$ and a^{o} are defined as before.

Let us ignore questions of rigour and assume that the supremum in (1.1) is attained for some function $n^{*}(\underset{\sim}{y},\mu)\in\mathcal{R}$. We can then write

$$p(\mu,0+) = F(n^{*},\mu) \tag{1.3}$$

from which we obtain, denoting the unit cell of n^{*} by Γ^{*},

$$\rho(\mu,0+) \equiv \frac{\partial}{\partial\mu}p(\mu,0+) = \left[\frac{\partial}{\partial\lambda}F(n^* + \lambda\frac{\partial n^*}{\partial\mu}, \mu)\right]_{\lambda=0} + \left(\frac{\partial F}{\partial\mu}\right)_{n^* \text{constant}}$$

$$= \frac{1}{|\Gamma^*|}\int_{\Gamma^*} \underset{\sim}{dy}\; n^*(\underset{\sim}{y},\mu) \qquad (1.4)$$

since F is stationary with respect to any variation of n away from n^*. By definition, a first order phase transition occurs for any value of μ where $\partial p(\mu,0+)/\partial\mu$ is multivalued (or, more precisely, does not exist). We deduce from (1.4) the following :

Criterion 1. A sufficient condition for the absence of a first order phase transition for a given value of μ is that the maximal function $n^*(\underset{\sim}{y},\mu)$ be unique (almost everywhere) apart from other maximal functions which differ from n^* only by a rotation and/or a translation of its argument $\underset{\sim}{y}$.

II. Van Kampen's Equation and Absence of First Order Transitions

To apply Criterion 1, we note that n^* satisfies the condition

$$\left[\frac{\partial}{\partial\lambda}F(n^* + \lambda h, \mu)\right]_{\lambda=0} = 0 \qquad (2.1)$$

for any function $h(\underset{\sim}{y})$ that is bounded, Riemann integrable and periodic. This yields the integral equation (we call it van Kampen's equation [1])

$$\mu = \mu^{o}[n^{*}(\underset{\sim}{y})] + \int d\underset{\sim}{y}' n^{*}(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}') \ , \qquad (2.2)$$

where $\mu^{o}(\rho) \equiv \partial a^{o}(\rho)/\partial\rho$ is the chemical potential of the reference system. Equation (2.2) can be expressed in a standard form by putting $m(\underset{\sim}{y}) \equiv \mu^{o}[n^{*}(\underset{\sim}{y})] - \mu$, and denoting the inverse function of $\mu^{o}(\rho)$ by $\rho^{o}(\mu)$ (the density of the reference system in the grand ensemble). Then (2.2) becomes

$$m(\underset{\sim}{y}) + \int d\underset{\sim}{y}' K(\underset{\sim}{y}-\underset{\sim}{y}')\rho^{o}[m(\underset{\sim}{y})+\mu] = 0 \ , \qquad (2.3)$$

which is a <u>non-linear integral equation of the Hammerstein type</u> [2] for $m(\underset{\sim}{y})$.

Since $\mu^{o}(\rho)$ is non-decreasing, we deduce that $n^{*}(\underset{\sim}{y})$ is unique almost every if $m(\underset{\sim}{y})$ is unique almost everywhere. This reduces the problem to the study of conditions for uniqueness of the solutions of (2.3). Some simple uniqueness theorems are given by Tricomi [2].

Since $\rho^{o}(\mu)$ is a non-decreasing functions, we deduce from Uniqueness Theorem I of [2] that $m(\underset{\sim}{y})$ is unique, and hence there is no first order transition, if K is positive definite (i.e. has a positive Fourier transform). This applies even if the reference system has a phase transition. This is consistent with condition (a), Section I of Part III.

Suppose that $\rho^{o}(\mu)$ is differentiable and that $T\partial\rho^{o}(\mu)/\partial\mu \leq 1/C$ for all μ and T , where C is a positive

constant. Then ρ^0 satisfies the Lipschitz condition

$$\left|\rho^0(\mu_1) - \rho^0(\mu_2)\right| \leq (TC)^{-1}\left|\mu_1-\mu_2\right|.$$

It now follows from Uniqueness Theorem III of [2] that there is no first order transition if $(TC)^{-1}<\left|\tilde{K}_{min}\right|$, where $\tilde{K}_{min}$ is the minimum of the Fourier transform of K. This is consistent with condition (d), Section I of Part III.

We have obtained the above results with very little labour and without any calculation of thermodynamic functions. We therefore expect this method to yield useful new results, but unfortunately we have not as yet obtained any.

III. Second Order Transitions

Second order phase transitions can be studied by the same method. By definition, such transitions do not occur when $\partial p(\mu,0+)/\partial\mu$ and $\partial^2 p(\mu,0+)/\partial\mu^2$ are single valued (i.e. when they exist). We deduce from (1.4) the following :

Criterion 2. A sufficient condition for the absence of both first and second order transitions for a given value of μ is that both $n^*(\underset{\sim}{y},\mu)$ and $\varphi(\underset{\sim}{y},\mu) \equiv \partial n^*(y,\mu)/\partial\mu$ be unique in the sense of Criterian 1.

To apply this criterion we differentiate both sides of

(2.2) with respect to μ. Let us assume that $\mu^{\circ}(\rho)$ is differentiable and its derivative is non-zero for all ρ, which implies that the reference system has no first or second order transitions. Setting $\sigma^{\circ}(\rho) \equiv [\partial\mu^{\circ}(\rho)/\partial\rho]^{-1}$, (which is ρ^2 times the compressibility of the reference system) we obtain[1]

$$\varphi(\underset{\sim}{y}) = \sigma^{\circ}[n^{*}(\underset{\sim}{y})] + \int d\underset{\sim}{y}'\varphi(\underset{\sim}{y}')K^{*}(\underset{\sim}{y},\underset{\sim}{y}'), \tag{3.1}$$

where $$K^{*}(\underset{\sim}{y},\underset{\sim}{y}',\mu) = -\sigma^{\circ}[n^{*}(\underset{\sim}{y},\mu)]K(\underset{\sim}{y}-\underset{\sim}{y}') . \tag{3.2}$$

Equation (3.1) is an inhomogeneous Fredholm integral equation of the second kind for φ. By Fredholm's theorem [2], the solution φ is unique if the kernel K^{*} does not have the eigenvalue unity. One can express this concisely in the form

$$\mathcal{D}^{*}(1,\mu) \neq 0 \tag{3.3}$$

where $\mathcal{D}^{*}(\lambda,\mu)$ is the Fredholm determinant of the kernel K^{*}.

We have not yet obtained any new results using (3.3). Only for a uniform fluid phase where $n^{*} = \rho(\mu,0+)$ have we been able to calculate $\mathcal{D}^{*}$. In this case we easily find $\mathcal{D}^{*}(\lambda,\mu) = 1 + \lambda\alpha\sigma^{\circ}[\rho(\mu,0+)]$, so that (3.3) becomes

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[1] The same equation is considered by Tricomi [2], and references cited therein, in connection with the bifurcation points of a Hammerstein equation closely related to (2.3).

$(\sigma^o)^{-1}_+ \alpha \neq 0$. Since $a(\rho,0+) = a^o(\rho) + \frac{1}{2}\alpha\rho^2$ in this case, the condition can be written $\partial^2 a(\rho,0+)/\partial\rho^2 \neq 0$, which implies the absence of a first order transition.

IV. Bounds on n^* and $\rho(\mu,0+)$.

Finally we show that van Kampen's equation (2.2) can be used to obtain bounds on $n^*(\underset{\sim}{y},\mu)$ and $\rho(\mu,0+)$. Assuming for simplicity that $\rho^o(\mu)$ is singlevalued, we can write (2.2) in the form

$$n^*(\underset{\sim}{y},\mu) = \rho^o[\mu - \int d\underset{\sim}{y}' n^*(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}')]. \tag{4.1}$$

Since $0 \leqq n^*(\underset{\sim}{y}) \leqq \rho_c$, we have

$$\left|\int d\underset{\sim}{y}' n^*(\underset{\sim}{y}')K(\underset{\sim}{y}-\underset{\sim}{y}')\right| \leqq \rho_c \int d\underset{\sim}{s}\,|K(\underset{\sim}{s})| \ ,$$

and because ρ^o is non-decreasing we deduce that, for all $\underset{\sim}{y}$,

$$\rho^o[\mu - \rho_c\int d\underset{\sim}{s}\,|K(\underset{\sim}{s})|\,] \leqq n^*(\underset{\sim}{y},\mu) \leqq \rho^o[\mu + \rho_c\int d\underset{\sim}{s}\,|K(\underset{\sim}{s})|]. \tag{4.2}$$

This shows that n^* is in fact bounded away from 0 and ρ_c for all μ . Also, by (1.4), $\rho(\mu,0+)$ has the same bounds.

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