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We establish the existence of the infinite volume (thermodynamic) limit for the free energy density of a system of charged particles, e.g., electrons and nuclei. These particles, which are the elementary constituents of macroscopic matter, interact via Coulomb forces. The long range nature of this interaction necessitates the use of new methods for proving the existence of the limit. It is shown that the limit function has all the convexity (stability) properties required by macroscopic thermodynamics. For electrically neutral systems, the limit functions are domain-shape independent, while for systems having a net charge the thermodynamic free energy density is shape dependent in conformity with the well-known formula of classical electrostatics. The analysis is based on the statistical mechanics ensemble formalism of Gibbs and may be either classical or quantum mechanical. The equivalence of the microcanonical, canonical and grand canonical ensembles is demonstrated.

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I. Introduction

In this paper we present a proof of the existence of the thermodynamic limit for Coulomb systems. A statement of the main results appeared in Lebowitz and Lieb (1969) and an outline of the proof is to be found in Lebowitz and Lieb (1972).

We start with a brief overview of the paper and defer precise definitions to later sections, mainly Section II.

A. Perspective

Statistical Mechanics as developed by Gibbs and others rests on the hypothesis that the equilibrium properties of matter can be completely described in terms of a phase-space average, or canonical partition function \( Z = \text{Tr}(\exp(-\beta H)) \), with \( H \) the Hamiltonian and \( \beta \) the reciprocal temperature. It was realized early that there were grave difficulties in justifying this assumption in terms of basic microscopic dynamics. These questions, which involve the time evolution of macroscopic systems, have still not been satisfactorily resolved, but the great success of equilibrium statistical mechanics in offering qualitative and quantitative explanations of such varied phenomena as superconductivity, specific heats of crystals, chemical equilibrium constants, etc., have left little doubt about the essential correctness of the partition function method. However, since \( Z \) cannot be evaluated explicitly for any reasonable physical Hamiltonian \( H \), comparison with experiment always involves some uncontrolled approximations. Hence, the following problem deserves attention: Is it true that the thermal properties of matter obtained from an exact evaluation of the partition function would be extensive and otherwise have the same form as those postulated in the science of thermodynamics? In particular, does the thermodynamic, or bulk limit exist for the Helmholtz free energy/unit volume derived from the canonical partition function, and, if so, does it have the appropriate convexity, i.e., stability properties?

To be more precise: Let \( \{ A_j \} \) be a sequence of bounded open sets (domains) in \( \mathbb{R}^d \) with \( A_j \) becoming infinitely large as \( j \to \infty \) in some "reasonable way" which will be specified later. [We shall be concerned primarily with \( d = 3 \) but many of our results are valid for all \( d \). For some results on classical Coulomb systems in \( d = 1 \) and 2, cf. Lenard (1961), Hisa Hauge and Hemmer (1972).] The volume of \( A_j \) will be denoted by \( V(A_j) \) and \( V(A_j) \to \infty \) as \( j \to \infty \). Consider now a sequence of systems consisting of \( S \) species of particles contained in the domains \( \{ A_j \} \). Let \( N_j = (N_{j1}, ..., N_{jS}) \) be the particle number vector specifying the system in \( A_j \), i.e., \( N_{ji} \) is a nonnegative integer and is the number of particles of species \( i \) contained in \( A_j \). The canonical partition function of the \( j \)-th system at reciprocal temperature \( \beta \) is then given by

\[
Z(\beta, N_j ; A_j) = \text{Tr} \ e^{-\beta H} = \sum_{\epsilon = 0}^\infty \exp(-\beta E_\epsilon(N_j ; A_j)) = \exp[V(A_j) g(\beta, \rho_j ; A_j)], \tag{1.1}
\]

where \( E_\epsilon(N_j ; A_j) \) are the energy levels of the \( j \)-th system, \( \rho_j = N_j / V(A_j) \) is the particle density vector, and \( -\beta^{-1} g(\beta, \rho_j ; A_j) \) is the Helmholtz free energy per unit volume of the \( j \)-th system. According to statistical mechanics, knowledge of \( g \) determines all the equilibrium properties of this system. The question to be studied is the following: Given a sequence of particle density vectors \( \{ \rho_j \} \) which approach a limit \( \rho \) as \( j \to \infty \), does \( g(\beta, \rho_j ; A_j) \) approach a limit \( g(\beta, \rho) \) as \( j \to \infty \), and is this limit independent in some sense of the particular sequence of domains \( \{ A_j \} \) and density vectors \( \{ \rho_j \} \) used in going to the limit? If so, does the limiting free energy density have, as a function of \( \rho \) and \( \beta \), the convexity properties required for thermodynamic stability, i.e., is \( g(\beta, \rho) \) convex in \( \beta \) and concave in \( \rho \)? With regard to \( \beta \), we see from (1.1) that each \( g(\beta, \rho_j ; A_j) \) is convex in \( \beta \). Therefore, if the limit \( g(\beta, \rho) \) exists, it will automatically be convex in \( \beta \). Consequently, we can set \( \beta = 1 \) and omit mention of \( \beta \), and shall do so henceforth.

In addition to proving the above, one also wants to show that the "same" thermodynamic results are obtained from the microcanonical and grand canonical partition functions (to be defined later). This program is referred to as proving the existence of the thermodynamic limit.

Various authors have evolved a technique for establishing the existence of this limit for systems whose Hamiltonians satisfy certain conditions. [The different names associated with this development are: Van Hove, Lee and Yang, van Kampen, Wils, Mazur and van der Linden, Griffiths, Dobrushin, and in particular, Ruelle and Fisher. The reader is referred to Fisher (1964) and Ruelle (1969) for an exposition and references. For a synopsis and more references see also Lebowitz (1968) and Griffiths (1971).] These Hamiltonians are the sum of kinetic energies of the individual particles plus an interaction potential energy among the particles, the latter depending only on the particle coordinates. There are two basic conditions required by the above authors on the interaction
among the particles constituting the microscopic units of macroscopic matter.

The first of these requirements is that the interaction be short-range or tempered. The requirement of tempering unfortunately excludes the Coulomb potential which is the true potential relevant for real matter. That thermodynamics is applicable to systems with Coulomb forces is a fact of common experience, but the proof that it does so is a much more subtle matter than for short-range forces. It is screening, brought about by the long-range nature of the Coulomb force itself, that causes the Coulomb force to behave as if it were short-range. This has the consequence, as we shall prove in this paper, that for a sequence of systems, each of which is overall neutral, the approach of \( g(\rho_j; A_j) \) to its limit \( g(\rho) \) and the properties of \( g(\rho) \) are the same as those obtained for systems with tempered interactions (except that the \( \rho^i, i = 1, \ldots, S \) are constrained by the neutrality requirement). In particular, \( g(\rho) \) is the same for different "shapes" of the domains \( \{A_j\} \). This shape independence disappears when the constraint of charge neutrality is lifted and systems with a "nonnegligible" amount of net charge are considered. The true long-range nature of the Coulomb force now becomes manifest, leading in some cases to a shape dependent limit of the free energy density and in other cases (when the excess charge is too large) to an infinite limit.

The second basic requirement, which is essential also for Coulomb systems, is a stability criterion on the \( N \)-body Hamiltonian \( H \). It is that there exists a constant \( B < \infty \) such that for a system of \( N \) particles, \( H > -BN \). We shall refer to this condition as \( H \)-stability. Heuristically, \( H \)-stability insures against collapse of the system. Mathematically, it provides an upper bound to the sequence \( \{g(\rho_j; A_j)\} \) and this bound plays an essential role in the proof. It should be emphasized, however, that \( H \)-stability does not in itself imply a thermodynamic limit. As an example, it is trivial to prove \( H \)-stability for charged particles all of one sign, and it is equally obvious that the thermodynamic limit does not exist in that case. Since the kinetic energy is positive, it is clearly sufficient for \( H \)-stability that the interaction energy is \( H \)-stable by itself. For classical systems this is also a necessary condition since the kinetic energy can be arbitrarily small. While it is not too difficult to prove classical \( H \)-stability for a wide variety of interaction potentials [cf. Ruclle (1969)], it is clear that classical \( H \)-stability will not hold for a system composed of positive and negative point charges. Even for a single pair, the Coulomb energy in three dimensions, \(-1/r\), is unbounded below. Interestingly, though, if the charged particles have hard cores, classical \( H \)-stability is satisfied, as shown by Onsager (1939).

Onsager's results were generalized by Fisher and Ruelle (1966). Their work, however, still left open the question of whether a quantum system of point Coulomb charges, which may be taken as the building blocks of real matter, is \( H \)-stable. Now when dealing with a quantum system of charges, the nonexistence of a lower bound to \(-1/r\) might not appear as serious as in the classical case since we expect that the Heisenberg uncertainty principle, which prevents particles from having their positions "close to each other" without also having a large kinetic energy, will insure the existence of a lower bound to the Hamiltonian. This is indeed the case for any finite system, \((-13.5 \text{ eV for a system composed of one electron and one proton})\), and generally \( H > \infty \) for any \( N \) (cf. Simon, Appendix B to this paper). We need, however, a lower bound proportional to \( N \) and this, it turns out, the uncertainty principle alone cannot provide. The required result was proved by Dyson and Lenard (1967, 1968), who showed that \( H \)-stability holds for a system of point charges in three dimensions when all species with negative and/or positive charges are fermions. This is happily the case in nature where the electrons are fermions. (When neither of the charges are fermions, Dyson (1967) found an upper bound to the ground state energy that is proportional to \(-N^{7/2}\); hence such a system will not be thermodynamically stable). The Dyson–Lenard theorem is as fundamental as it is difficult.

We note here that Griffiths (1969), found a way to extend the "canonical" proof to electrically neutral systems with Coulomb forces under the restrictive assumption of complete charge symmetry, i.e., that positive and negative particles have the same mass, spin, etc., but this is clearly insufficient for nuclei and electrons. Also, in a recent paper, Penrose and Smith (1972) established the existence of the thermodynamic limit for classical systems with electromagnetic interactions (including external fields) when the systems are confined in superconducting like containers which modify the electromagnetic interaction among the constituent particles.

This paper deals with the general nonrelativistic, classical or quantum mechanical Coulomb system without restriction. We do not consider any relativistic effects, such as spin–spin and spin–orbit couplings; the simple spin–spin dipolar coupling containing an \( r^{-3} \) interaction is not \( H \)-stable even for two particles. However, if the particles have a hard core, the dipolar interaction is \( H \)-stable and, although it is not tempered,
it can be satisfactorily treated [Griffiths (1969); cf. also Remark (ii) after Theorem 2.6 in Section II].

Needless to say, we also do not deal with the strong (nuclear) and weak interactions. As pointed out by Dyson (1967), the magnitude of the nuclear forces is so large that they would give completely different binding energies for molecules and for crystals if they played any role in the thermal properties of ordinary matter. We are also neglecting gravitational forces which certainly are important for large aggregates of matter and thus might be thought important in the thermodynamic limit. To quote Onsager (1967), "The common concept of a homogeneous phase implies dimensions that are large compared to the molecules and small compared to the moon." When we speak of the thermodynamic limit, which is mathematically the infinite system limit, we have in mind its physical application to systems containing $10^{22} \sim 10^{28}$ particles, i.e., systems which are large enough for surface effects to be negligible and yet small enough for internal gravitational effects also to be completely negligible.

B. Outline and Summary of Results

In Section II we establish the basic notation and definitions, and list some inequalities needed in the sequel. Here we rely heavily on Appendix B contributed by Simon to whom we are indebted. The proof of the existence of the thermodynamic limit proceeds, as in the tempered case, by first establishing the limit for a standard sequence of domains. The limit for an arbitrary sequence of domains is then easily arrived at by packing those domains with the standard ones. The usual choice for the standard domains is a sequence of cubes $\{I_j\}$ of sides essentially $2^j$. These have the desirable geometric property that $I_{j+1}$ can be packed with $2^d$ copies of $I_j$. For the Coulomb case we find it necessary to use balls $\{B_j\}$, and Section III is devoted to showing that the unit ball can be packed efficiently with a sequence of balls of decreasing diameter.

In Section IV we combine the results of Sections II and III to establish the existence of the thermodynamic limit of $g(p; B_j)$ defined in (1.1), when each system in the sequence is overall strictly neutral. Section V generalizes this result to arbitrary domains, while keeping the condition of strict neutrality. The limiting free energy $g(p)$ is found to be shape-independent.

Section VI is devoted to systems that are not overall neutral and we establish the fundamental fact of electrostatics that in the thermodynamic limit the free energy is the sum of the neutral system free energy and $\frac{1}{2}Q^2/C$, where $Q$ is the surplus charge and $C$ is the (shape-dependent) capacity. For technical reasons, we are able to do this only for a sequence of domains whose shapes are essentially ellipsoidal.

Section VII deals with the grand canonical ensemble. We prove the existence of the thermodynamic limit for the grand canonical pressure and show that the thermodynamic properties are the same as for the neutral canonical ensemble, i.e., nonneutral systems make a vanishingly small contribution to the grand canonical pressure regardless of the choice of the chemical potentials of the different species. This is a very special feature of the Coulomb potential.

The microcanonical ensemble is treated in Section VIII. For simplicity, and not for any reason of technical difficulty, we consider only neutral systems in balls. We make use of a microcanonical partition function that is a little different from the usual ones, but has the virtue of satisfying a minimax principle. This ensemble, the usual microcanonical ensembles, and the canonical ensemble are shown to have the same thermodynamic properties in the limit.

II. Basic Definitions and Inequalities

A. Description of Systems

The particles comprising our system will consist of $S$ different species and we shall denote the number, charge, and mass of species $i$ by $N^i$, $e_i$, and $m_i$. For convenience, we write $N = (N^1, \ldots, N^S)$, $E = (e_1, \ldots, e_S)$ and $M = (m_1, \ldots, m_S)$. A neutral system is one for which $N \cdot E = 0$. $E$ and $M$ are fixed. The $e_i$ are real numbers (including zero). Since the $N^i$ are nonnegative integers, the possibility of having a neutral system (which is essential in our analysis) requires that the charges be not all of the same sign. We also want, for simplicity, to be able to make neutral systems from any combination of positively and negatively charged species. This requires that the ratios of the $e_i$'s be rational. We may thus choose appropriate units in which the $e_i$ are all integers. In nature all elementary charges are, in fact, integral multiples of the electron charge. The $m_i$ are strictly positive. We shall use $N = N^1 + \cdots + N^S$ to be the total number of particles, and we shall denote the particle coordinates, without regard to species, by $x_i \in \mathbb{R}^d$, $i = 1, \ldots, N$ and $X = (x_1, \ldots, x_N)$. In like manner, we shall denote the individual charges and masses by $e^i$ and $m^i$, respectively, $i = 1, \ldots, N$.

A domain $\Lambda$ is a bounded open set in $\mathbb{R}^d$. It is not necessarily connected.
The volume (Lebesgue measure) of \( A \) will be denoted by \( V(A) \), or simply \( V \). The particle density in \( A \) will be denoted by \( p = (p^1, ..., p^d) \), where \( p^i = N_i^i/V(A) \). We shall also write \( \rho = N/V(A) \) for the total density. Using (1.1) with \( \beta \) set equal to one, we make the further definition
\[
\tilde{g}(N/V(A); A) = \tilde{g}(N; A).
\] (2.1)

**Statistics.** Each particle species will be assumed to be either a boson or a single component fermion, or a physical two-component fermion. To say that species \( i \) is a boson, resp. single-component fermion, means that in considering the domain of the Hamiltonian we shall restrict our attention to the subset of \( L^2(\mathbb{R}^d) \) consisting of functions which are either symmetric, resp. antisymmetric, under permutation of all the coordinates of particles of species \( i \). The two-component fermion is more complicated. The Hilbert space is \( L^2(\mathbb{R}^{2d}) \otimes (\mathbb{C}^2)^N \) instead of \( L^2(\mathbb{R}^d) \). In other words, the "coordinate" of particle \( k \) of species \( i \) is in \( A \times Z_2 \), i.e., \( x_k \rightarrow (x_k, s_k) \), \( s_k \in \{-1, 1\} \), where \( x_k \) is the spatial coordinate and \( s_k \) is the spin coordinate of the \( k \)-th particle. Again, the functions of interest are required to be antisymmetric under permutation of the coordinates \( (x, s) \) of particles of species \( i \). To avoid needless repetition, in the sequel we shall indicate only the spatial coordinate, \( x_k \in \mathbb{R}^d \), and the reader can interpolate the obvious necessary changes to include the spin coordinates of the two-component fermions. In all cases, the Hamiltonian is assumed to be symmetric under permutation of the (space-spin) coordinates of the particles of each species.

**The Hamiltonian.** To describe the Hamiltonian of the \( N \) particles we refer to the Appendix by Simon. It suffices to say here that
\[
H(N; A) = T(N; A) + U(N; X),
\] (2.2)
where \( T(N; A) \) is the kinetic energy operator and \( U(N; X) \) is the potential energy, or interaction. (These are denoted by \( H_0 \) and \( V \) in Appendix B).
\[
T(N; A) = -\frac{1}{2} \hbar^2 \sum_{i=1}^{N} (m_i)^{-1} \Delta_i,
\] (2.3)
with \( \hbar \) being \((2\pi)^{-1}\) Planck's constant. The eigenfunctions of \( H(N; A) \) vanish on the boundary of \( A \).

We regard the potential as defined for all \( X \in \mathbb{R}^{Nd} \), and to describe it we write
\[
U(N; X) = U^C(N; X) + U^T(N; X),
\] (2.4)
where
\[
U^C(N; X) = \sum_{1 \leq i < j \leq N} e^{i\phi(|x_i - x_j|)},
\] (2.5)
and \( \phi(r) \) is the Coulomb potential \( \phi(r) = r^{-1} \) for \( d = 3 \). \( U^T(N; X) \) is a tempered interaction (to be defined presently) which can depend upon the particle composition, but must be symmetric under interchange of (space-spin) coordinates of particles of the same species. In real matter it is absent, provided we assume that the electromagnetic interaction is purely Coulombic. We include it, however, because one may wish to consider a model system in which the constituent particles are not elementary but instead are composite, for example, ionized atoms. If there are \( N_i \) two-component fermions, then \( U^T(N; X) \) is to be interpreted as a linear operator (matrix) on \( (\mathbb{C}^2)^{N_i} \) which depends on the spatial coordinates of all \( N_i \) particles, i.e., it is a multiplication operator on \( L^2(\mathbb{R}^{Nd}) \). Clearly, \( U^C(N; X) \rightarrow U^C(N; X)1 \), where \( 1 \) is the identity operator on \( (\mathbb{C}^2)^{N_i} \).

**The tempered interaction.** We shall assume that \( U^T(N; X) \) satisfies three conditions:

1. **Stability.** There exists a constant \( B \), independent of \( N, X \), and the particle composition such that
\[
U^T(N; X) \geq -BN, \quad \text{all } X \in \mathbb{R}^{Nd},
\] (2.6)
where \( 1 \) is the identity operator on \( (\mathbb{C}^2)^{N_i} \).

2. **Tempering.** Let \( P_N \) be a partition of the \( N \) particles into several disjoint sets \( S_1, ..., S_K \) containing \( N_1, ..., N_K \) particles, respectively. Denoting the coordinates of the particles in the several sets by \( X_1, ..., X_K \), we define the inter-set potential energy \( W \) by
\[
W(N, P_N; X) = U(N; X) - \sum_{i=1}^{K} U(N_i; X_i).
\] (2.7)

For each pair of sets, \( S_a \) and \( S_b \), let
\[
r_{ab}(N, P_N; X) = \min\{|x_i - x_j| : i \in S_a, j \in S_b\}.
\]
The **tempering condition** states that there exists a distance \( r_0 \geq 0 \), a constant \( w \geq 0 \) and a constant \( c > 0 \), all independent of \( N, P_N, X_i, K \).
and the particle composition, such that whenever $r_{ab}(N, P_N; \mathbf{X}) \geq r_0$ for all $\alpha, \beta$, then

$$W(N, P_N; \mathbf{X}) \leq w \sum_{1 \leq a < b \leq K} N_{a\beta} r_{ab}(N, P_N; \mathbf{X})^{-d-\frac{1}{2}},$$

(2.8)

with $I$ being the identity operator on $(\mathbb{C}^3)^K$. If $w = 0$ we say that $U^I$ is strongly tempered; otherwise, $U^I$ is weakly tempered. For examples of stable, tempered potentials and for sufficiency conditions see Ruelle (1969). One thing is clear: the Coulomb potential is not tempered regardless of the signs of the charges. This is the reason that the standard proof of the existence of the thermodynamic limit is not applicable in this case.

3. Translation and rotation invariance. If $G$ is any translation or proper rotation of $\mathbb{R}^d$ we require that

$$U^I(N; x_1, \ldots, x_N) = U^I(N; Gx_1, \ldots, Gx_N).$$

(2.9a)

When there are two-component fermions,

$$U^I(N; x_1, \ldots, x_N) = \Psi_G^* U^I(N; Gx_1, \ldots, Gx_N) \Psi_G,$$

(2.9b)

where $\Psi_G$ is a unitary operator on $(\mathbb{C}^6)^K$. The physical content of (2.9b) is that the Hamiltonian is invariant under simultaneous space and spin rotation. The spin–spin dipolar interaction has this property, and so does $U^C(N; \mathbf{X})$. The condition (2.9) excludes any position- or orientation-dependent external potential such as a magnetic field.

H-Stability. We say that the Hamiltonian is H-stable (quantum mechanically) if for all $\Psi \in L^2(\mathbb{R}^{3d})$ of the appropriate symmetry and in the form domain of $H(N; A)$,

$$(\Psi, H(N; A)\Psi)(\Psi, \Psi) > -NB$$

(2.10)

for some $B$ independent of $N$ and $A$.

We say that the potential is H-stable if $U(N; \mathbf{X})$ is stable, i.e., if it satisfies (2.6). (This is the same as classical H-stability.) As $T(N; A)$ is positive, classical H-stability implies quantum mechanical H-stability, but the converse is not true. It is also clear that if $T(N; A) + U^C(N; \mathbf{X})$ is H-stable, then so is $H(N; A)$.

Stability of the Coulomb potential with hard cores. The Coulomb potential is not, by itself, a stable potential (unless all the charges are of one sign), but it is possible that the total $U(N; \mathbf{X})$ is. One way to achieve this is to include a hard core in $U^I(N; \mathbf{X})$, i.e., there are $\frac{1}{2}S(S + 1)$ positive reals $a_{ab} = a_{ba}$, $\alpha, \beta = 1, \ldots, S$ such that $U^I(N; \mathbf{X}) = +\infty$ if $|x_i - x_j| \leq a_{ab}$ for any $x_i$ of species $\alpha$ and $x_j$ of species $\beta$ and for all $\alpha, \beta$. [Note: If there are hard cores, the domain to consider is, as mentioned in Appendix B, not $\mathbb{R}^{3d}$ (or $A^N$) but rather the complement of the hard-core region wherein $U^I(N; \mathbf{X}) = +\infty$.] The fact that $U(N; \mathbf{X})$ is stable under these conditions was proven by Onsager (1939) and we give the proof here in a form communicated to us by Penrose for $d = 3$.

Let $R = \min_{\alpha, \beta} a_{ab}$. Since $U^I(N; \mathbf{X})$ is stable, it is sufficient to show that $U^C(N; \mathbf{X})$ satisfies (2.6) in the subset $D$ of $\mathbb{R}^{3N}$ where $|x_i - x_j| > R$, all $i, j$. Concentric with each coordinate $x_i$, construct a closed ball $B_i(x_i)$ of radius $\frac{1}{2}R$ and fill it uniformly with a total charge equal to the given charge of particle $i$. For $\mathbf{X} \in D$, these balls are disjoint. According to Newton’s (1687) theorem (cf. Theorem 2.5), the mutual electrostatic potential energy of $B_i(x_i)$ and $B_j(x_j)$ is exactly $e^2|e| \sum_{i < j} e^2 |x_i - x_j|^{-1}$. Introducing the electric field vector $\mathbf{E}(\mathbf{x})$ determined by the balls, we can prove stability by using the well-known electrostatic formula

$$\sum_{i < j} e^2 |x_i - x_j|^{-1} = (8\pi\epsilon)^{-1} \int |\mathbf{E}(\mathbf{x})|^2 d^n\mathbf{x} = \sum_{i = 1}^N \text{(self-energy of } B_i) \geq -NB,$$

(2.11)

where $B$ is the maximum electrostatic self-energy of any one ball. This same proof is applicable to the spin–spin dipolar interaction, Griffiths (1969).

If $U(N; \mathbf{X})$ is bounded below, we can define the classical (configurational) partition function as

$$Z(N; A) = \prod_{i = 1}^S \left[ (N_i!)^{-1} \int_{A^N} \exp[-U(N; \mathbf{X})] d^n\mathbf{x} \right].$$

(2.12)

The theorems we prove in this paper concern $\ln Z$, whether defined by (1.1) or by (2.12). Although we shall always make statements in terms of the quantum mechanical $Z$, (1.1), it will be clear that these theorems hold for (2.12) as well when $U(N; \mathbf{x})$ is stable.

The H-stability of the purely Coulomb Hamiltonian, i.e., $U^I(N; \mathbf{X}) = 0$, was proved by Dyson and Lenard (1967, 1968) [cf. also Lenard (1972)].

Theorem 2.1 (Dyson–Lenard). The Coulomb Hamiltonian

$$H(N; A) = T(N; A) + U^C(N; \mathbf{X})$$

is
is $H$-stable in three dimensions provided that either all the positively charged particles or all the negatively charged particles are fermions.

In this paper we shall adopt the convention that all the negative particles are fermions, as they are in real matter.

B. Upper Bound on $g(\rho; A)$

**Theorem 2.2.** There exists a finite function $h(\rho)$ such that for all $A$, $g(\rho; A) \leq h(\rho)$.

**Proof.** Consider the $H$-stable Hamiltonian

$$H(N; A) = \frac{1}{2}T(N; A) + U(N; X)$$

in $A$, so that

$$H(N; A) = H'(N; A) + \frac{1}{2}T(N; A).$$

The factor $\frac{1}{2}$ in $H'(N; A)$ is equivalent to doubling all the masses and, using Theorem 2.1, $H'(N; A) \geq -NB^2$. Therefore,

$$\ln Z = \ln \text{Tr} \exp[-H(N; A)] \leq \ln \text{Tr} \exp[-\frac{1}{2}T(N; A)] + \frac{1}{2}NB^2$$

$$= V(A) \{ g_0(\rho; A) + \frac{1}{2}B^2 \}. \quad (2.13)$$

Independent of statistics (Bose or Fermi) there exists a finite function $h'(\rho)$ such that $g_0(\rho; A) \leq h(\rho)$ (see Fisher (1964)).

Theorem 2.2 is the only place where $H$-stability will be used. The rest of the proof of the existence of the thermodynamic limit essentially consists of a demonstration that $g(\rho; A)$ is increasing in $A$. The upper bound $h(\rho)$ then guarantees the existence of a limit.

C. Useful Inequalities

**Theorem 2.3** (Peierls). Let $A$ and $B$ be self-adjoint operators on a Hilbert space $\mathcal{H}$ with domains $D(A)$ and $D(B)$ and let $\mathcal{S} = \{ f_i \}$ be a finite or countably infinite set of orthonormal vectors in $D(A) \cap D(B)$. Then,

$$\text{Tr}[e^{A+B}] \geq \sum_i \langle f_i, e^{A+B}g_i \rangle \geq \sum_i \langle f_i, (A+B)f_i \rangle$$

$$\geq \sum_i \exp(\langle f_i, Af_i \rangle) \exp\langle B \rangle_{A,\mu}, \quad (2.14)$$

where

$$\langle B \rangle_{A,\mu} = \sum_i \langle f_i, Bf_i \rangle \exp(\langle f_i, Af_i \rangle) \sum_i \exp(\langle f_i, Af_i \rangle). \quad (2.15)$$

**Proof.** The first inequality in (2.14) follows from the fact that the trace is the sum over a complete set of vectors, the second and third inequalities follow essentially from the convexity of the exponential function [see Ruelle (1969) and Wehrl (1972)].

**Remarks.**
1. If $A$ has a complete orthonormal set of eigenvectors in $D(A) \cap D(B)$, then

$$\text{Tr}[e^{A+B}] \geq \text{Tr}[e^A \exp(\langle B \rangle_A)]. \quad (2.16)$$

where

$$\langle B \rangle_A = \text{Tr}[B e^A]/\text{Tr}[e^A]. \quad (2.17)$$

2. If $\{ f_i \}$ consists of a single vector $\Psi \in D(A) \cap D(B)$, then

$$\ln \text{Tr}[e^{A+B}] \geq \langle \Psi, (A+B)\Psi \rangle. \quad (2.18)$$

Now let $\{ \Psi_n \}_{\alpha = 1}^J$ be a set of $J$ normalized vectors (not necessarily orthogonal) in $D(A) \cap D(B)$, and take the mean of (2.18):

$$\ln \text{Tr}[e^{A+B}] \geq J^{-1} \sum_{\alpha=1}^J \langle \Psi \alpha, (A+B) \Psi \alpha \rangle. \quad (2.19)$$

We shall need this result in Section VI.

The next inequality is the domain partition theorem. This is proved in Appendix B, Theorem 8, and we repeat it here with a slightly different wording:

**Theorem 2.4.** Let $A_1$ and $A_2$ be two disjoint domains in $\mathbb{R}^d$ and let $A \supset A_1 \cup A_2$. Let $S_1$, $S_2$ be a partition of the $N$ particles. (This means that the particles are split into two groups). Define $H(N_1, N_2; A_1, A_2)$ to be (2.2) but with the domain of the functions to be the subset of $\mathbb{R}^{N_d}$ where $x_1, \ldots, x_N \in A_1$ and $x_{N+1}, \ldots, x_N \in A_2$ with $\Psi = 0$ on the boundary of $A_1 \cup A_2$. Then

$$\text{Tr} \exp[-H(N; A)] \geq \text{Tr} \exp[-H(N_1, N_2; A_1, A_2)] \quad (2.20)$$

The right-hand side of (2.20) is to be interpreted as follows: While
the two groups of particles in the two domains still interact with each other via the potential \( U(N; X) \), the two groups are independent as far as statistics is concerned, i.e., the trace is over functions that are symmetric (or antisymmetric) under separate permutations of the coordinates of the \( N_\alpha^i \) particles of species \( i \) in \( A_\alpha \) and the \( N_\beta^i \) coordinates in \( A_\beta \). It is as though there are altogether 2S species: \( S \) in \( A_\alpha \) and \( S \) in \( A_\beta \). To justify this we first apply Theorem 8, Appendix B to the subdomain \((A_\alpha \cup A_\beta)^N \subset A^N\). Then we apply it again to the disjoint union of the \( K = \prod_{i=1}^N (N_\alpha^i) \) permutation copies of \( D_k = X_{k-1}(A_\alpha^{N_\alpha^k} \times A_\beta^{N_\beta^k}) \). Call these domains \( D_k \), \( i = 1, \ldots, K \). Any function which has the correct symmetry properties in \( D_k \) can be extended in an obvious and unique way to a statistically correct function in \( \bigcup D_k \). If \( \Psi_i \) and \( \Psi_j \) have supports in \( D_i \) and \( D_j \), respectively, the crucial observation is that \((\Psi_i^*, H \Psi_j) = 0\), and hence we can take the trace on the right side of (2.20) over \( L^2(D_\alpha) \) only. This argument also holds for two-component fermions. For further elucidation, cf. Fisher (1964).

D. The Newton Theorem

Finally, we need the fundamental electrostatic theorem due to Newton (1687).

**Theorem 2.5 (Newton).** Let \( B \) be an open ball in \( \mathbb{R}^d \) of radius \( r \), centered at the origin. Let \( f \in L^1(B) \) be such that \( f \) is rotation invariant (i.e., \( f(x) = F(|x|) \)). Then

\[
\int_B f(x) \phi(|x - y|) \, dx = \left[ \int_B f(x) \, dx \right] \phi(|y|), \quad \text{for } |y| > r, \tag{2.21}
\]

where \( \phi \) is the Coulomb potential, \( \phi(r) = r^{-1} \) for \( d = 3 \).

**Corollary.** Let \( B \) and \( f \) be as above, let \( \Lambda \) be a measurable set in \( \mathbb{R}^d \) such that the distance from \( B \) to \( \Lambda \) is positive and let \( g \in L^1(\Lambda) \). Then

\[
\int_B dx \int_\Lambda dy f(x) g(y) \phi(|x - y|) = \int_B f(x) \, dx \int_\Lambda \phi(|y|) g(y) \, dy. \tag{2.22}
\]

E. Application of Inequalities

Consider a domain \( A' \) such that \( A' \supset B \cup A \) where \( B \) is an open ball centered at the origin, \( A \) is a domain, and the distance from \( A \) to \( B \) is a positive number \( r \), \( r \geq r_0 \) with \( r_0 \) defined in (2.8). Consider a partition of a set of \( N \) particles into two sets \( N_B \) and \( N_A \) confined to \( B \) and \( A \), respectively, and \( N = N_B + N_A \).

First we apply Theorem 2.4 to this case. Next, we use Theorem 2.3 in the following way: Let \( \{\Psi_i^b\} \), respectively \( \{\Psi_i^a\} \), be complete orthonormal sets of eigenfunctions of \( H(N_B; B) \) in \( L^2(B^N_B) \), respectively \( H(N_A; A) \) in \( L^2(A^N_A) \). The existence of these functions and the relevant domain questions are discussed in Appendix B. Choose \( \mathcal{S}' \) in Theorem 2.3 to consist of functions of the form \( \Psi_i^b \otimes \Psi_j^a \) in \( L^2(B^N_B) \otimes L^2(A^N_A) \). Writing

\[
H(N_B; N_A; B; A) = H(N_B; B) + H(N_A; A) + \tilde{W} = \tilde{H} + \tilde{W},
\]

in \( Z(N; A') \geq \overline{Z}(N_B; B) + \overline{Z}(N_A; A) - \overline{\langle \tilde{W} \rangle} \), \( \overline{\langle \tilde{W} \rangle} \) the expectation value of \( \tilde{W} \) in the canonical ensemble of a system with Hamiltonian \( \tilde{H} \).

Now \( \overline{\langle \tilde{W} \rangle} \) consists of two terms: the contribution of \( U \), \( \overline{\langle \tilde{W} \rangle}_U \), and the contribution of the Coulomb potential, \( \overline{\langle \tilde{W} \rangle}_C \). The first can be bounded, using (2.8), as

\[
\overline{\langle \tilde{W} \rangle}_U \leq w_N N_B^{d-a} r^{-d}. \tag{2.24}
\]

To obtain a bound on \( \overline{\langle \tilde{W} \rangle}_C \), we note (cf. Appendix B, Theorem 9) that

\[
\overline{\langle \tilde{W} \rangle}_C = \sum_{i=1}^{N_B} \sum_{j=1}^{N_A} \int_B dx_i \int_A dx_j f(x_i, x_j) \rho_{ij}(x_i, x_j),
\]

where \( i \) indexes the set \( N_B \), \( j \) the set \( N_A \), \( f(x_i, x_j) = e^{i \phi(|x_i - x_j|)} \) and \( \rho_{ij}(x_i, x_j) \) is the joint probability density for the \( i \)-th particle in \( B \) and the \( j \)-th particle in \( A \). The probability density \( \rho_{ij} \) is computed from the canonical ensemble for a system with the Hamiltonian \( \tilde{H} \), which contains no interaction between the particles in \( B \) and the particles in \( A \). Hence \( \rho_{ij}(x_i, x_j) = \rho_B^a(x_i) \rho_A^b(x_j) \) and \( \rho_B^a(x_i) \) is rotation invariant (by rotational invariance of \( H(N_B; B) \) and uniqueness of \( \rho_B^a(x) \)). Also \( \int_B \rho_B^a(x) \, dx = 1 = \int_A \rho_A^b(x) \, dx \). Upon introducing the functions

\[
\rho_B^a(x) = \sum_{i=1}^{N_B} e^{i \phi(x_i)} \quad \text{for } x \in B
\]

and

\[
\rho_A^b(x) = \sum_{i=1}^{N_A} e^{i \phi(x_i)} \quad \text{for } x \in A,
\]
and using Theorem 2.5, we see that

$$\langle \hat{H} \rangle^c = \int_B \rho^n(x) \, dx \int_A \rho^d(y) \, d\phi(y) \, dy.$$  \hfill (2.25)

Note that \( \int_B \rho^n(x) \, dx = Q_B = N_B \cdot E \) where \( Q_B \) is the total charge of the particles in the ball. Thus we have proved

**Theorem 2.6.** If \( A' \supset B \cup A \) with \( B, A, N_B \) and \( N_A \) as described above and if \( N_B \cdot E = 0 \) then

$$\ln Z(N; A') \geq \ln Z(N_B; B) + \ln Z(N_A; A) + w N_B N_A d^{-d - \epsilon}.$$  \hfill (2.26)

**Remarks.** 1. \( (2.25) \) and \( (2.26) \) obviously hold even for two-component fermions.

2. If we add to \( H \) in \( (2.2) \) a (nontempered) spin–spin dipolar interaction \( \hat{U}^\alpha \), and if we assume that the particles have hard cores so that the Hamiltonian is \( H \)-stable (Griffiths, 1969) then \( (2.26) \) remains true. The reason is that \( \langle \hat{U}^\alpha \rangle = 0 \) because an analog of Newton's theorem holds. Spin inversion symmetry of \( H \), as used by Griffiths (1969), is not required.

**F. Basic Strategy**

Theorem 2.6 is the central fact used in our proof of the existence of the thermodynamic limit for Coulomb systems; it overcomes the lack of tempering of the Coulomb potential. Using Theorem 2.6 we are able to construct a standard sequence of increasing domains \( \{A_j\}_j \) with \( V(A_j) \to \infty \), for which \( g(\rho; A_j) \) is essentially monotonically increasing. Theorem 2.2 then guarantees that the \( g(\rho; A_j) \) have a limit as \( j \to \infty \).

For the domains \( A_j \), we have to use balls \( B_j \) rather than cubes \( \Gamma_j \), as is the case in the proofs for tempered potentials. The ball \( B_j \) will in turn have to be packed with balls \( B_{j-1}, B_{j-2}, \ldots, B_0 \), rather than just with balls \( B_{j-1} \) (the ability to pack \( \Gamma_j \) with just cubes \( \Gamma_{j-1} \) is what makes the standard proofs simple). To do so effectively, and also to be able then to prove the limit for a sequence of general domains \( \{A_j\}_j \), we must be able to decompose a given domain into a decreasing sequence of balls efficiently, and this geometric packing problem is the subject of the next section. In connection with Theorem 2.6 we note that it can be used repeatedly to give a bound when \( A' \) contains the union of \( K \) disjoint, separated subdomains, so long as all but one of the domains are balls and the balls contain a neutral mixture of particles.

**III. On Packing a Domain With Balls**

In this section we address ourselves to a geometric construction which is fundamental to our proof of the existence of the thermodynamic limit, namely, the possibility of packing a ball or a cube by smaller balls, such that the packing is both complete and rapid. Our main results are Theorems 3.1 and 3.2.

If \( A \subset \mathbb{R}^d \) is a domain and \( B = \{B_i\}_i \) is a denumerable family of domains such that \( B_i \subset A \) for all \( i \) we shall say that \( B \) is packed in \( A \) if the \( \{B_i\}_i \) are disjoint. The packing is complete if \( \sum_i V(B_i) = V(A) \).

**Definition.** For a domain \( A \subset \mathbb{R}^d \) and a real number \( h \) we define

\[ A_h = \{ r; r \in A, d(r; \sim A) < h \} \quad \text{for} \quad h > 0 \]

\[ = \{ r; r \in \sim A, d(r; A) \leq -h \} \quad \text{for} \quad h \leq 0, \quad (3.1) \]

where \( d(\cdot) \) is the distance function and \( \sim \) denotes complement. We also define \( V_h(A) \) to be the volume of \( A_h \).

**Lemma 3.1.** Let \( A \) be a domain in \( \mathbb{R}^d \) and consider any covering of \( A \) by closed cubes of side \( x \) having disjoint interiors (e.g., the cubes may themselves be arranged in a cubic array). Let \( n \) be the number of cubes whose interiors are contained entirely in \( A \). Then the volume of \( A \) not covered by these cubes,

\[ \Delta V = V(A) - nx^d \]

is less than \( V(x \sqrt{d}; A) \).

This is Lemma 2 in Section 8 of Fisher (1964). It follows from the observation that if \( A \) is first covered by closed cubes having disjoint interiors, and if the interiors of the cubes that intersect \( \sim A \) are then removed, the subset of \( A \) which is uncovered is contained in \( A_x \sqrt{d} \). It follows from this that the number \( N_y \) of cubes of side \( 2y \) that can be packed in \( A \) satisfies the inequality

\[ N_y \geq (2y)^{-d} [V(A) - V(2y \sqrt{d}; A)]. \quad (3.2) \]

**Definition.** Let \( \sigma_d \) be the volume of a ball of unit radius in \( \mathbb{R}^d \).
\[ \sigma_d = 2^{-d/2} \sigma_d \]

is the fraction of the volume of a cube of side \( 2y \) filled by a ball of radius \( y \) when the ball is packed in the cube. We also define \( \alpha_d \equiv (2^d - 1) 2 \sqrt{d} \). Ball always means open ball.

**Lemma 3.2.** Let \( B \subset \mathbb{R}^d \) be a ball of radius \( r \) and let \( y \) be such that
\[ y \geq 2y \sqrt{d} \geq 0. \]
Then
\[ V(2y \sqrt{d}; B) \leq V(-2y \sqrt{d}; B) \leq \alpha_d \sigma_d (d-3) y. \]  
(3.3)

Proof. Clearly, for \( 0 \leq h \leq r \),
\[ V(h; B) = \alpha_d [r^d - (r - h)^d] \leq V(-h; B) = \alpha_d [(r + h)^d - r^d]. \]
Let \( f(\epsilon) = (1 + \epsilon)^d - 1 \). Since \( f(\epsilon) \) is convex,
\[ f(\epsilon) \leq f(0) + \epsilon [f(1) - f(0)] = \epsilon [2^d - 1] \quad \text{for} \quad 0 \leq \epsilon \leq 1. \]

Applying this inequality proves the lemma.

The main theorem we wish to prove is that we can find a sequence of balls of decreasing radius, of which the \( j \)-th type has radius \( r_j = r^j \) (with \( r < 1 \)), such that we can completely pack a unit \( d \)-dimensional ball with these and, moreover, we can do this rapidly.

**Theorem 3.1.** Let \( p \) be a positive integer and, for all positive integers \( j \), define radii \( r_j = (1 + p)^{-j} \) and integers \( n_j = p^{j-1}(1 + p)^{(d-1)} \). Then if \( 1 + p \geq \alpha_d + g_d^2 \) it is possible to pack \( \bigcup_{j=1}^{n_0} n_j r_j^d \) in a unit \( d \)-dimensional ball. The packing is complete since \( n_j r_j^d = 1 \).

Proof. We shall give an explicit construction for accomplishing the packing stated in the theorem by using Lemmas 3.1 and 3.2. First cover the unit ball by a cubic array of cubes of side \( 2r_1 \). We shall show that there are \( n_j \) of these cubes which are contained in the unit ball. We can place a ball of radius \( r_1 \) at the center of each of these cubes. We then cover the unit ball by a cubic array of cubes of side \( 2r_2 \) and show that there are \( n_2 \) of these cubes which are contained in the unit ball and which do not intersect the first \( n_1 \) cubes. The argument is repeated inductively. Thus, we have to show that after placing all balls up to and including those of radius \( r_j \) we can pack \( n_j n_{j+1} \) balls of radius \( r_{j+1} \) in a cubic array into \( \Omega_j \), which is the interior of the unfilled portion of the unit ball. (We must prove this for \( j \geq 0 \), with \( r_0 = 0 \).) For \( j \geq 0 \),
\[ V(\Omega_j) = \sigma_d - \sigma_d \sum_{k=0}^{j} n_k r_k^d = \sigma_d \left( \frac{p^j - 1}{p + 1} \right)^j. \]

Clearly, \( V(2 \sqrt{d} r_{j+1}; B) \) is bounded above by \( M_j \) which is the sum of the \( V(-2 \sqrt{d} r_{j+1}; B) \) for each ball of \( \bigcup_{j=0}^{j} n_j (r_j \) balls of radius \( r_j \)) separately

plus \( V(2 \sqrt{d} r_{j+1}; B) \) for the unit ball. Thus, by Lemma 3.2, if \( 2 \sqrt{d} r_{j+1} < r_j \) (which is true when \( p \) satisfies the hypothesis)
\[ V(2 \sqrt{d} r_{j+1}; \Omega_j) \leq M_j \leq \alpha_d \sigma_d (d-3) \left( 1 + \sum_{k=0}^{j} n_k r_k^d \right) \]
\[ = (p^j + p - 2)(p - 1)^{-1}(1 + p)^{-(j+1)}\alpha_d \sigma_d = M_j. \]

Using (3.2) it is sufficient to show that
\[ (2r_{j+1})^d n_{j+1} \leq [V_j - M_j] \leq [V(\Omega_j) - V(2 \sqrt{d} r_{j+1}; \Omega_j)]. \]

Inserting the relevant quantities, we require that
\[ 1 \leq g_d \left[ p + 1 - \alpha_d \frac{1 + p^{-j}(p - 2)}{p - 1} \right] \]
for all \( j \geq 0 \). By the hypothesis \( p \geq 2 \). Then \( p^{-j}(p - 2) \leq (p - 2) \) and hence it is sufficient that
\[ 1 \leq g_d (p + 1 - \alpha_d), \]

which agrees with the hypothesis.

It is amusing to compute the minimum ratio of successive radii required by this construction:
\[ d \quad 1 \quad 2 \quad 3 \quad 10 \quad 27. \]
\[ (1 + p) \geq 3 \]

We note that the fraction of volume of the unit ball occupied by all the balls of radius \( r_j \) is
\[ f_j = n_j r_j^d = p^{-j} \gamma^j, \]
(3.5)

where
\[ \gamma = p(1 + p)^{-1} < 1. \]

Moreover, the fraction of volume left unfilled after the balls of type \( j \) have been packed is \( \gamma^j \). This implies that the packing is "exponentially fast". It is not claimed that it is impossible to pack the unit ball "exponentially fast" with a smaller value of \( p \), nor do we claim that our particular packing is the fastest possible for a given \( p \).

The following, which is similar to Theorem 3.1, will be needed in Section V.
THEOREM 3.2. Let $\Gamma_d$ be an open cube in $\mathbb{R}^d$ of volume $\alpha_d$, i.e., of side $(\alpha_d)^{1/d}$. Then Theorem 3.1 remains true if "unit d-dimensional ball" is replaced by "cube $\Gamma_d$".

Proof. If we can show that the estimate (3.4) remains valid the rest will follow. To do so, we have to show that $V\left(2\sqrt{d}\, y; \Gamma_d \right) \leq \alpha_d y^d$. As $\Gamma_d$ has $2d$ faces, $V\left(h; \Gamma_d \right) < 2dh(\alpha_d)^{1-1/d}$ for $h > 0$. Hence, we require that $2d \leq (2d - 1)(\alpha_d)^{1/d}$, which is true.

IV. THERMODYNAMIC LIMIT FOR SPHERICAL DOMAINS

In this section we shall prove the existence of the thermodynamic limit for a standard sequence of balls. To do so we shall define a sequence of standard balls $\{B_j\}$ of increasing radii $\{R_j\}$, $j = 0, 1, \ldots$. To avoid confusion, it should be noted that these balls are geometric objects only and are independent of the manner in which we shall later choose to fill them with particles. The motivation for our choice of the $\{B_j\}$ and for Lemma 4.1 will become apparent later.

A. THE STANDARD SEQUENCE

Definition. Let $1 + p$ satisfy the condition of Theorem 3.1 and be even. (The fact that $1 + p$ is even will not be used until Theorem 4.3.) For a suitable choice of an $R_0' > 0$ and $0 \leq \theta < 1$, the balls $B_0$, $B_1$, ..., forming the standard sequence, are chosen to have the radii

$$R_j = R_0' (1 + p) (1 - \frac{1}{2} \theta^j).$$

(4.1)

The choice of $R_0'$ and $\theta$ depends upon the type of potential being considered.

(i) For pure Coulomb potentials, $R_0'$ is arbitrary and $\theta = 0$. In this case we always interpret $r_0$, where it appears in the sequel as zero.

(ii) For strongly tempered potentials (in addition to the Coulomb potential), characterized by a distance $r_0$ beyond which the tempered potential is nonpositive, we choose $\theta = (1 + p)^{-1}$ and $R_0' > 2r_0 (1 - \theta)^{-1}$.

(iii) For weakly tempered potentials (in addition to the Coulomb potential), characterized by an $r_0$ and by a decay parameter $\epsilon$ (Eq. (2.8)) we choose $\theta = (1 + p)^{-1/2\epsilon}$ and $R_0' > 2r_0 (1 - \theta)^{-1}$.

In Fisher's (1964) terminology, the standard balls, $\{B_j\}$, would be called the "free volumes", i.e., these are the domains to which the particles are confined. It is also convenient to define "nominal volumes" which are balls $B_j'$ with radii

$$R_j' = R_0'(1 + p)^j.$$

The volumes of the above balls will be denoted by $V_j$ and $V_j'$, respectively.

Let $n_j = 2^{d-1} (1 + p)^{jd/\gamma}$ with $\gamma = p/(1 + p)$ as in Eq. (3.6) and Theorem 3.1.

LEMMA 4.1. For all $K > 0$ it is possible to pack a ball $B_K$ (or a cube $\Gamma_K$ of the same volume) with $\bigcup_{j=0}^{K-1} (n_{K-j} B_j)$, such that the distance between every ball of type $j$ and every ball of type $k$, $0 \leq j, k \leq K - 1$, is at least $d_{jk} = b(t^j + t^k)$ where $b = \frac{1}{2} R_0'(1 - \theta) > r_0$ and $t = (p + 1)\theta$. (Note that $d_{jk} > 2r_0$ since $t \geq 1$.) Furthermore, the distance between every ball of type $j$ and the boundary of $B_K$ or $\Gamma_K$ is at least $bt^j > r_0$.

Proof. Consider a sequence of balls $B_j'$ of radii

$$R_j' = R_j'(1 - \frac{1}{2} \theta^j) \geq R_j \quad \text{for} \quad 0 \leq j \leq K.$$

Since $R_K' = R_K$ and $R_{j+1}' - R_j' = 1 + p$ for $j < K$, we can pack $B_K$ or $\Gamma_K$ with the required number of $B_j'$ balls according to Theorems 3.1 and 3.2. Concentric with each $B_j'$, place a ball $B_j$. The distance between two balls $B_j$ and $B_k$ is not less than

$$R_j' + R_k' - (R_j + R_k) = \frac{1}{2} R_j'(\theta^j - \theta^k) + \frac{1}{2} R_k'(\theta^k - \theta^k)$$

and since $\theta^k \leq \theta^j$ for $0 \leq j \leq K - 1$ the first part of the lemma is proved. The distance of a ball $B_j$ to the boundary is not less than $R_j' - R_j = \frac{1}{2} R_0' t^j (1 - \theta)$.

The above packing will be referred to as the standard packing of the ball $B_K$ (or cube $\Gamma_K$) with balls $\{B_j\}$, $j = 0, 1, \ldots, K - 1$.

The following subsection B is relevant only when weakly tempered potentials are present. Otherwise it may be omitted and the constant $A$, appearing in all subsequent energy estimates, set equal to zero. This is so because Lemma 4.1 implies that the particles in different balls of a standard packing have zero as an upper bound for their interactions via strongly tempered potentials.
B. Upper Bound on Tempered Interactions

Suppose that in each ball of type \( j \) in a standard packing of \( B_k \) or \( \Gamma_k \) we place at most \( N_j = \rho V_j \) particles, for some \( \rho \geq 0 \). We recall that the tempering condition states that the tempered (non-Coulombic) part of the potential energy of two sets of \( N_a \) and \( N_b \) particles separated by a distance \( r > r_0 \), is bounded above by \( w N_a N_b r^{-(d+\epsilon)} \) with \( w \geq 0 \).

Let \( U_j \) be an upper bound to the tempered interactions of the particles in any one ball \( B_j \) with the particles in all other balls of types \( k \leq j \). Then, by counting the positive bounds to the interactions of balls of equal type twice we obtain an upper bound on the total tempered interaction energy between particles in different balls \( B_j \) contained in \( B_k \)

\[
U_k \leq \sum_{j=0}^{k-1} n_{k-j} U_j .
\]  

(4.3)

To find \( U_j \), consider some particular ball \( B_j \), and around it construct spheres of radii \( L_k = R_j(k - \frac{1}{2}b^{j+1}) \) for all \( k \geq 1 \). Since \( L_1 = R_j + \beta r' \), with \( \beta = \frac{1}{4}R_0(1 - \theta) \) and \( t = (\rho - 1)\theta \), it follows from Lemma 4.1, and the fact that \( R_j' \geq R_j \), that each of the other balls \( B_j \) with \( l \leq j \) is contained entirely in some shell of inner radius \( L_k \) and outer radius \( L_{k+1} \) for some \( k \geq 1 \). Hence the total volume of such balls in that shell is less than the volume of the shell, namely,

\[
v_k = \sigma_d(R_j')^d ((k + 3 - \frac{1}{2}b^{j+1})^d - (k - \frac{1}{2}b^{j+1})^d)
\leq 3d\sigma_d(R_j')^d (k + 3)^{-1}.
\]  

(4.4)

(Here, we have used the convexity argument \( f(y + x) - f(y) \leq f'(y + x) \) for \( f \) convex.) The number of particles in these balls does not exceed \( \rho v_k \) and since \( R_j'(k - \frac{1}{2}b^{j+1}) \geq R_j'k(1 - 1)^{-1} \) we have

\[
U_j \leq N_j \rho w \left\{ \sum_{k=2}^{\infty} v_k [(k - 1)(R_j')^{-1}(d+\epsilon)]^{-d} + v_1 (\beta r')^{-d}(d+\epsilon) \right\}
\leq 3dN_j \rho w \sigma_d (u_k (R_j')^{-1} + 4^{-1}(R_j')^d (\beta r')^{-d(d+\epsilon)}),
\]  

(4.5)

where

\[
u_k = \sum_{k=2}^{\infty} [(k + 3)^{d-1} (k - 1)^{-d-\epsilon}] < \infty.
\]  

(4.6)

We can now insert (4.5) into (4.3). If we recall that the volume of \( B_j' \) is \( V_j' = \sigma_d(R_j')^d \), that \( N_k u_{k-j} = p^{-1} p r^{k-j} V_j', \) and that \((R_j'/R_n')^d t^{-j(d+\epsilon)} = (1 + p)^{-j(b^{j+1})} = (1 + p)^{-j(b^{j+1})}, \) then we have the following:

\[
\text{LEMMA 4.2. If a standard ball } B_k \text{ or cube } \Gamma_k \text{ be packed with smaller balls in the standard way (as in Lemma 4.1) and if the smaller balls } B_j \text{ have particle numbers not exceeding } N_j = \rho V_j' \text{ for some } \rho \geq 0, \text{ then there exist constants } A \geq 0 \text{ and } B \geq 1 \text{ depending on } \rho, d, \epsilon \text{ and } w \text{ but not on } K \text{ or } \rho \text{ such that the tempered potential energy } U \text{ is bounded by}
\]

\[
U_k \leq \rho^2 V_k' AB^{-k}.
\]

(4.7)

C. Filling of Balls with Particles

In the following we shall fill the standard balls with particles in various ways. However, we shall always observe the following conventions:

1. Each ball will have charge neutrality. We shall assume that there is a fundamental multiplet of particles of the various species which is charge neutral and this will be used as the fundamental unit and will be referred to simply as a multiplet. Densities and particle numbers will be in terms of this unit. The only effect of this convention is to modify the value of \( A \) of Lemma 4.2. Later, in subsection F we shall generalize our results to arbitrary, but neutral, mixtures of particles. In subsections C, D and E, \( \rho \) is not a vector but a number.

2. For convenience, free energies and densities for the standard balls will be referred to the nominal volume \( V_j' \), rather than to the true volume \( V_j \). Since \( V_j' / V_j \downarrow 1 \) as \( j \uparrow \infty \) this creates no problem. Thus, we define

\[
g(p) = (V_j')^{-1} \ln Z(N = \rho V_j'; \beta_i),
\]

where \( N \) is the number of multiplets.

Since \( N \) must be an integer, an obvious restriction is thereby placed on \( \rho \). However, following Fischer (1964) we can define \( g \) for all \( \rho \) by linear interpolation as follows:

DEFINITION. Let \( f(N) \) be a function from the integers to the reals. If \( n = N + \eta \), with \( N \) an integer and \( 0 \leq \eta \leq 1 \), we extend \( f(\cdot) \) to the reals by \( f'(n) \equiv f(N) + \eta [f(N + 1) - f(N)] \).

The usefulness of this definition is made manifest by the following lemma.
Lemma 4.3. Let \( \mathcal{N}_0 \) be the nonnegative integers, \( \mathbb{R}^+ \) the nonnegative reals, and \( \mathbb{R} \) the reals. Let \( f, h_1, h_2, \ldots, h_M \) be functions from \( \mathcal{N}_0 \) to \( \mathbb{R}^+ \) and let \( f', h_1', \ldots, h_M' \) be the extended functions from \( \mathbb{R}^+ \) to \( \mathbb{R} \) as in the above definition. Let \( N_j \in \mathcal{N}_0 \) and \( n_j \in \mathbb{R}^+ \). If \( f(\sum_{1}^{M} N_j) \geq \sum_{1}^{M} h_j(N_j) \) for all \( \{N_j\} \) then \( f'(\sum_{1}^{M} n_j) \geq \sum_{1}^{M} h_j'(n_j) \) for all \( \{n_j\} \).

Proof. We use induction on \( M \). The case \( M = 1 \) is obvious and \( M = 2 \) is proved in Fisher (1964, footnote 25). Assume the lemma for \( M \) and define \( G(N) = \max \sum_{1}^{M} h_j(N_j) \), where the maximum is with respect to all \( \{N_j\} \) whose sum is \( N \). Then \( G'(\sum_{1}^{M} N_j) \geq \sum_{1}^{M} h_j'(N_j) \). For \( M + 1 \), let \( \sum_{1}^{M} N_j = B_1 \) and \( N_{M+1} = B_2 \). Then the hypothesis of the theorem states that \( f(B_1 + B_2) \geq G(B_1) + h_{M+1}(B_2) \). Application of the \( M = 2 \) case to this inequality proves the lemma.

Let us now consider a standard packing of \( B_K \) with \( N_j \) multiplets placed in all balls of type \( j, j = 0, 1, \ldots, K - 1 \). The total number of multiplets in \( B_K \) is then

\[
N = \sum_{0}^{K-1} N_j p_{K-j},
\]

(4.9)

so that

\[
\rho = N/V_K' = p^{-1} \sum_{0}^{K-1} \rho_j p^{K-j}.
\]

(4.10)

Our fundamental inequalities of Section II on the partition function of a subdivided domain, together with the bound of Lemma 4.2 on the tempered potential, the vanishing of the average interdomain Coulomb interaction for neutral balls, and the fact that \( \max_j \rho_j^2 \leq \sum_{0}^{K-1} \rho_j^2 \) implies that

\[
g_k(N/V_K') \geq \sum_{j=0}^{K-1} \left\{ n_{K-j} V_j' / V_K' \right\} g_k(n_j/V_j) - AB^{-K} \left( \frac{N_j}{V_j'} \right)^2.
\]

(4.11)

An obvious application of Lemma 4.3 [noting there that if \( f(N) = N^a \) then \( f'(n) \leq n(n + 1) \)] leads to

Theorem 4.1. Let \( \rho_1, \ldots, \rho_{K-1} \) be nonnegative reals and let

\[
\rho = p^{-1} \sum_{0}^{K-1} \rho_j p^{K-j}.
\]

Then there exist \( A \geq 0 \) and \( B > 1 \), independent of \( K \) and \( \rho_1, \ldots, \rho_{K-1} \), such that

\[
g_k(\rho) \geq \frac{1}{p} \sum_{j=0}^{K-1} \gamma^{K-j} g_j(\rho_j) - AB^{-K} \sum_{j=0}^{K-1} \rho_j (\rho_j + (V_j')^{-1}).
\]

(4.12)

Remark. Theorem 4.1 raises the specter that we are placing fractional numbers of multiplets in the various balls. This is not the case. What has been done is to extend the definition of \( g \) to noninteger multiplet numbers by linear interpolation so that when the multiplet number is integral the extended \( g \) is the same as the primitive \( g \). Despite the apparent simplicity of Lemma 4.3, (4.12) is really derived from a complicated summation of inequalities involving only integral particle numbers.

D. Limit of \( g_k(\rho) \) as \( k \to \infty \)

Our next task is to use Theorem 4.1 to establish the thermodynamic limit of \( g_k(\rho) \) for the standard sequence of balls.

One source of annoyance is the possibility that the particles may have hard cores. Consequently, when we fill the balls with multiplets we must be careful to avoid overfilling the smaller balls, otherwise some \( g_j \) will be \(-\infty\) and Theorem 4.1 will be meaningless. The difficulty arises because, owing to the imperfection of the filling at each stage, the true density in the smaller balls must always be greater than the limit density, and we want to be able to make the latter arbitrarily close to the close-packing density.

Definition. For the fundamental multiplet, let \( \rho_c \) be the maximum (i.e., close packing) density for an infinitely large ball. If the particles do not have hard cores, then \( \rho_c = +\infty \).

Definition. Standard filling of the standard sequence of balls for a given density \( \rho < \rho_c \). Let \( t \) be a positive integer such that \( (1 - \gamma^t) \rho_c > \rho \). Define \( M_t \) to be the maximum number of multiplets that can be packed into \( B_t \) such that there is a minimum distance \( \delta > 0 \) between the hard cores of any pair of particles and a distance \( \delta/2 \) between the hard core of any particle and the boundary of \( B_t \), i.e., if the hard core diameter of each particle is increased by \( \delta \) then \( M_t \) would be the maximum number of multiplets which could be packed in \( B_t \). We can and do choose \( \delta > 0 \) such that the infinite volume close packing density for these “swollen”
particles, \( \lim_{\rho \to 0} M_j/V_j = \tilde{\rho}_c \), satisfies \( \rho_c > \tilde{\rho}_c > \rho(1 - \gamma')^{-1} \). Hence, there exists a smallest positive integer \( K \), such that \( M_j/V_j > \rho(1 - \gamma')^{-1} \) for all \( j \geq K \). Although \( t \), \( \delta \) and \( \{M_j\} \) cannot be chosen independent of \( \rho \) for all \( \rho < \rho_c \), we can clearly choose them to be independent of \( \rho \) in any interval \( 0 \leq \rho \leq \tilde{\rho} \) where \( \tilde{\rho} < \rho_c \). In particular, when \( \tilde{\rho} = \frac{1}{2}(1 - \gamma)\rho_c \) we can choose \( t = 1 \). Now, let \( L = K + t - 1 \). For each \( j \geq 0 \) we define a standard density sequence (depending on \( \rho \)) as follows: \( \rho_j = \rho \) for \( j > L; \rho_j = \rho(1 - \gamma')^{-1} \) for \( K \leq j < L; \rho_j = 0 \) for \( 0 < j < K \).

**Remarks.** (i) We note that the quantities \( \rho_j V_j \) are always less than \( M_j \). Since \( g_j(\rho) \) is defined by linear interpolation, the maximum number of multipliers we ever have to consider in \( B_j \) is just \( M_j \). In that case a lower bound on the partition function can be obtained from our fundamental inequality by confining each particle in \( B_j \) to a ball whose diameter exceeds the particle’s hard core diameter by \( \delta \). This permits the center of each particle to move within a ball of diameter \( \delta \), giving it a finite kinetic energy and thus giving a lower bound to \( Z \).

(ii) It is understood that when \( \rho = 0 \), \( g_j(0) = 0 \);

(iii) Equations

\[
\rho_k = \rho^{-1} \sum_{j=0}^{k-1} \rho_j \gamma^{k-j} \tag{4.13}
\]

\[
\rho(t + (V_j)^{-1}) + k - L - 1 \geq \sum_{j=0}^{k-1} \rho_j \gamma^{k-j} \tag{4.14}
\]

are true for all \( k > L \).

With \( \rho \) held fixed, let us denote \( g_j(\rho_j) \) simply by \( g_j \). Then, from Theorem 4.1,

\[
ge_k = \sum_{j=K}^{k-1} \gamma^{k-j} \delta_k + c_k \tag{4.15}
\]

for \( k > L \), and where

\[
\delta_k = AB^{-k} \sum_{j=0}^{k-1} \rho_j \gamma^{k-j} \tag{4.16}
\]

and \( c_k \) is a nonnegative real number.

We shall use (4.15) to establish that \( g_j \) has a limit. That such a limit exists follows from the general theory of the renewal equation, but since it is possible to solve (4.15) explicitly there is no need to avail ourselves of general theorems. The solution to (4.15), valid for \( k > L \), is easily proved by induction to be

\[
ge_k = \gamma(c_k - \delta_k) + (1 - \gamma) \sum_{j=L+1}^{k} (c_j - \delta_j)
\]

\[
+ (1 - \gamma) \sum_{j=K}^{L} \gamma^{L-j} g_j, \tag{4.17}
\]

Equation (4.17) establishes a limit for \( g_k \) because (a) The terms involving \( \delta_k \) clearly have a limit from (4.14) and (4.16); (b) The last sum in (4.17) is a fixed finite number since each \( g_j \) is finite; (c) As each \( c_j \geq 0 \), and as we know that \( g_k \) has an upper bound by \( H \)-stability, the sum involving the \( c \)'s must converge. This implies that \( c_k \to 0 \) and hence (4.17) must have a limit. We shall call this limit \( g(\rho) \).

Further examination of (4.17) leads to a lower bound for \( g \) which is proportional to \( \rho \) for sufficiently small \( \rho \). It is easily verified from (4.17) that the sequence \( h_k = g_k + \gamma(\delta_k - c_k) + (1 - \gamma) \sum_{j=L+1}^{k} \delta_j \) is non-decreasing for \( k > L \). Hence,

\[
g(\rho) + (1 - \gamma) \sum_{j=L+1}^{K} \delta_j \geq h_{L+1} = g_{L+1} + \delta_{L+1} - \gamma c_{L+1}
\]

\[
\geq (1 - \gamma) g_{L+1} + \gamma^2 \sum_{j=K}^{L} \gamma^{L-j} g_j. \tag{4.18}
\]

The left side of (4.18) is \( g(\rho) + a_{\rho} + a_{\rho}^2 \), so that our aim is then to show that the right side is suitably bounded. Referring to the definition of the standard filling, let \( \rho \) be in the interval \( (0, \frac{1}{2}(1 - \gamma)\rho_c) \) so that \( t = 1 \) and \( M_j \) is independent of \( \rho \). Then let \( J = \min\{j : M_j > 0\} \) and let \( \psi = \inf\{M_j/V_j : j \geq J\} \). Since \( M_j/V_j \to \tilde{\rho}_c > 0 \), it follows that \( \psi > 0 \). Define the nonempty open interval \( I \) by

\[
I = \{\rho : 0 < \rho < \min\{\frac{1}{2}(1 - \gamma)\rho_c, (1 - \gamma)\psi, (V_{j+1})^{-1}\}\}. \tag{4.19}
\]

From these definitions, it follows that if \( \rho \in I \) then the \( K \) and \( L \) values appropriate to all such \( \rho \) satisfy \( K = L = J \). Thus, if \( \rho \in I \), the right side of (4.18) is \( (1 - \gamma) g_{L+1}(\rho) + \gamma^2 \rho g(\rho) \). Since \( \rho < (V_{j+1})^{-1} < (V_j)^{-1} \), the linear interpolation definition of \( g \) states that these two terms are a linear combination of the four quantities \( Z(N = 0, B_j) \) and \( Z(N = 0, B_{j+1}) \).
In $Z(N = 1, B_j)$ and $\ln Z(N = 1, B_{j+1})$. The first two are zero. The
latter two refer to a system with one unit multiplet. Nevertheless,
these latter two quantities are finite numbers independent of $\rho$ so that
when they are inserted into the right side of (4.18) they will give a lower
bound proportional to $\rho$. We also recall that $g(\rho = 0) = 0$.

Our analysis of (4.15) has thus led us to

**Theorem 4.2.** Let $\rho < \rho_c$ be a fixed multiplet density and let each ball
$B_k$ of the standard sequence have the density $\rho_k$ of a standard filling appro-
riate to $\rho$. Then

$$g(\rho) = \lim_{k \to \infty} g_k(\rho_k)$$

exists and is finite. Furthermore, there exists a $\rho_1 > 0$ such that for $\rho$ in the
closed-open interval $[0, \rho_1)$, $g(\rho)$ is bounded below by $\lambda \rho$ with $\lambda$ finite and independent of $\rho$.

**Remark.** For a given $\rho$ the standard filling is not uniquely determined.
However, all standard fillings have the property that $\rho_j = \rho$ for $j$
sufficiently large. Hence the function $g(\rho)$ in Theorem 4.2 is independent of
the standard filling and what Theorem 4.2 really says is that $g(\rho) = \lim_{k \to \infty} g_k(\rho)$.

**E. Convexity of the Free Energy**

With the limit $g(\rho)$ in hand we can next establish convexity. [Note: The
following theorem actually proves the concavity of $g(\rho)$. The word
convexity is sanctioned by historical usage, however, because the free
energy/unit volume, $-\beta^{-1} g$, is the quantity of physical interest and is
convex if $g$ is concave.]

It is here that we use the fact that $1 + p$ was chosen to be even.

**Theorem 4.3.** Let $\rho'$ and $\rho^*$ be any two numbers in the interval $[0, \rho_c)$.
Then the limit function of Theorem 4.2 satisfies

$$g(l \rho' + \frac{1}{2} \rho^*) \geq \frac{1}{2} g(\rho') + \frac{1}{2} g(\rho^*).$$

(4.20)

**Proof.** In a standard packing of $B_k$, the number of balls $B_j (0 \leq j \leq k)$
that are used is $n_k = p^{k-j} (1 + p)^{(k-j)(d-1)}$ and this is even for all $j$
d $d \geq 2$. [The one-dimensional case can be handled separately, but
we shall not bother to do so here.] For each $j$ fill half the balls $B_j$ with
a density $\rho_j'$ appropriate to the standard filling for $\rho'$. Fill the remaining
half with the corresponding density $\rho_j^*$. An obvious extension of the
argument leading to Theorem 4.1 shows that (using the notation of (4.16), with $\rho_j'$ and $\rho_j^*$)

$$g_k(\rho_k) \geq \frac{1}{2p} \sum_{j=0}^{k-1} \gamma^{k-j} [g_j' + g_j^*] - \delta_j' - \delta_j^*$$

with

$$\tilde{\rho}_k = \frac{1}{2p} \sum_{j=0}^{k-1} \gamma^{k-j} (\rho_j' + \rho_j^*)$$

and $g_j' = g(\rho_j')$; $g_j^* = g(\rho_j^*)$.

Let $L'$ and $L^*$, respectively, be the $L$ values associated with the standard
filling for $\rho'$ and $\rho^*$. Then, for $k \geq \max(L', L^*)$, $\tilde{\rho}_k = \frac{1}{2} (\rho' + \rho^*) = \rho$. 

Let $L$ be the $L$ value associated with the standard filling for $\rho$ so that for
$k \geq \max(L, L', L^*)$ we also have $\rho_k = \rho$ and hence $g_k(\rho_k) = g_k$. Let $c_k'$ and $c_k^*$ be the corresponding numbers defined in (4.15), whence, for
$k \geq \max(L, L', L^*)$, $g_k \geq \frac{1}{2} [g_k' + g_k^*] - \frac{1}{2} (c_k' + c_k^* + \delta_k' + \delta_k^*)$. Taking
the limit $k \to \infty$ proves the theorem.

If we now appeal to Sections 3.5–19 of Hardy, Littlewood and Polya (1959), especially Theorem 111, we can combine Theorem 4.3 with the lower bound of Theorem 4.2 to yield

**Corollary.** In the closed-open interval $[0, \rho_c)$, the limit function $g(\rho)$ is
continuous and is concave in the sense that

$$g(l \rho' + (1 - l) \rho^*) \geq l g(\rho') + (1 - l) g(\rho^*)$$

for all $0 \leq l \leq 1$ and all $\rho'$, $\rho^* \in [0, \rho_c)$. In the open interval $(0, \rho_c)$, $g(\rho)$
has everywhere left-hand and right-hand derivatives; the former is never
less than the latter and both derivatives decrease with $\rho$.

**Remark.** Strictly speaking, the theorems in Hardy, Littlewood and Polya (1959) do not establish continuity at the end point $\rho = 0$. However,
for small $\rho$, our fundamental upper bound for $g(\rho)$ is proportional to
$-\rho \ln \rho$ and our lower bound of Theorem 4.2 is proportional to $\rho$. Since
$g(0) = 0$, we also have continuity at $\rho = 0$.

The continuity of $g(\rho)$ leads to the following theorem on the uniformity
of the thermodynamic limit.

**Theorem 4.4.** Let $\rho \in [0, \rho_c)$ and let $\{\rho_j^*\}$, $j = 0, 1, \ldots$, be a sequence
of nonnegative reals such that $\lim_{j \to \infty} \rho_j^* = \rho$. Then
Then

(i) $\lim_{j \to \infty} g_j(\rho) = g(\rho)$ uniformly on compact subsets of $[0, \rho_0]$;

(ii) $\lim_{j \to \infty} g_j(\rho) = g(\rho)$.

Proof. (ii) is a trivial consequence of (i) since

$$|g(\rho) - g_j(\rho)| \leq |g(\rho) - g(\rho_*)| + |g(\rho_*) - g_j(\rho_*)|.$$

The first term goes to zero by the continuity of $g(\rho)$ and the second term goes to zero by (i).

We shall prove (i) on an interval $[0, \tilde{\rho}]$ with $\tilde{\rho} < \rho_0$. As already stated, we can choose the parameters $t, \delta, K$ (and hence $L$) to be independent of $\rho$ when $\rho \leq \tilde{\rho}$. This implies two things: $\rho_j(\rho)$ of the standard filling is a continuous function of $\rho$ for each $j$ and $\rho_0(\rho) = \rho$ for $\rho > L$. Consequently all the quantities in (4.15) and (4.17) are continuous functions of $\rho$. Since the $\varepsilon_{\rho}(\rho)$ are nonnegative, (4.17) states that the functions

$$h_k(\rho) = g_k + \gamma(\delta_k - \varepsilon_k) + (1 - \gamma) \sum_{L_k=1}^{k} \delta_j$$

and

$$h_k'(\rho) = g_k + (\delta_k - \varepsilon_k) + (1 - \gamma) \sum_{L_k=1}^{k-1} \delta_j$$

are continuous functions which converge to the same continuous function monotonically. By Dini’s theorem the convergence is uniform for $0 \leq \rho \leq \tilde{\rho}$. Hence,

$$h_k(\rho) - \gamma h_k'(\rho) = (1 - \gamma) g_k + (1 - \gamma)^2 \sum_{L_k=1}^{k-1} \delta_j + (1 - \gamma) \delta_k$$

also converges uniformly. As $\delta_k \to 0$ and as the sum $\sum_{L_k=1}^{k-1} \delta_j$ obviously converges uniformly to a continuous function, we conclude that $g_k \to g(\rho)$ uniformly.

F. Multicomponent Systems

Thus far we have established the limit and the convexity of the free energy/unit volume for a system composed of a single kind of charge-neutral multiplet of the various charged particles. This meant dealing with the multiplet as though it were a single particle and no consideration had to be given to the internal constitution of that multiplet.

Here we wish to investigate the properties of the free energy/unit volume when the multiplet is treated as having variable but neutral constitution or, in other words, when the density is treated in its proper role as a vector quantity. Our goal is to show that the free energy/unit volume is convex in the vector density, that is, it is a convex function of $S$ variables simultaneously.

For tempered potentials, the extension to a vector density is trivial. For Coulomb systems the requirement of charge neutrality in the filling of each of the standard domains is a complicating feature because we are constrained to a hyperplane, and this interferes with our interpolation formula of subsection (C) for defining $g$ for nonintegral particle numbers.

To solve this problem we first show that the particle number vector can be expressed in terms of a finite number of neutral multiplets. We then establish the relevant theorems in terms of these multiplets and, finally, show that these results can be translated back into true particle densities.

We should like to have a linear representation of the vectors $N$ in terms of a spanning set of neutral multiplets and this possibility is given by

**Lemma 4.4.** Let $E = (e_1, ..., e_S)$ be an $S$-dimensional vector such that all $e_i$ are integers and they are not all of one sign. Let $A$ be the space of $S$-dimensional vectors such that $N = (N_1, ..., N_S) \in A$ if and only if $A$ are nonnegative integers, and $N \cdot E = 0$. Then there exists a finite spanning set of vectors $M_1, ..., M_r \in A$ such that for each $N \in A$ there is a representation $N = \sum_{l=1}^{r} a^l M_l$ with all $a^l$ nonnegative integers. Conversely, $\sum_{l=1}^{r} a^l M_l \in A$ when all $a^l$ are nonnegative integers.

Proof. It is sufficient to consider the case where all $e_i \neq 0$, because if, for example, $e_1 = 0$ take $M_1 = (1, 0, ..., 0)$ and deal with the remaining $S - 1$ dimensional space. Suppose $e_1, ..., e_a > 0$ and $e_{a+1}, ..., e_S < 0$ with $0 < a < S$. Define $W_+ = \sum_{i=1}^{a} e_i$ and $W_- = \sum_{j=1}^{S-a} e_j$. Let $C \subset A$ be the set of vectors $N$ such that $N_i < W_+$ for $i = 1, ..., a$ and $a < N_i < W_-$ for $i = a + 1, ..., S$. C is clearly a finite set. For $j \leq a$ and $k > a$ let $V_{jk} \in A$ be the vector with components $V_{jk} = [e_k], V_{jk} = e_j$ and $V_{jk} = 0$ otherwise. Then we claim that the finite set $C \cup \{V_{jk}\}$ is a spanning set. Let $N \in A$ and $N \not\in C$ and suppose, for example, that $N_k > W_-$ for some $k > a$. Then $\sum_{i=1}^{a} N_i e_i = \sum_{i=1}^{a} N_i e_i > |e_k| W_+ = |e_k| |\sum_{i=1}^{a} e_i|$. Thus, for at least one $0 < j \leq a$, $N_j \geq |e_j|$. Hence, $N - V_{jk} \in A$. A finite number of repetitions of this process yields the desired result. The converse is trivial.
The conclusion to be drawn from Lemma 4.4 is that instead of considering particle numbers \(N^1, \ldots, N^8\) subject to the annoying restriction of neutrality \(N \cdot E = 0\), we may instead think in terms of multiplet numbers \(\alpha = (\alpha^1, \ldots, \alpha^r)\) subject to no restriction other than the usual one that all \(\alpha^i\) are nonnegative integers. Thus, in a domain \(A\), we may extend the function \(g(N; A)\) to
\[
G(\alpha; A) = g\left(\sum_{i=1}^{r} \alpha^i M_i; A\right). \tag{4.21}
\]
Each point in multiplet space corresponds to a unique point in particle number space. The fact that the converse is not true is a matter we shall deal with later in this section.

We first direct our attention to obtaining a theorem on the existence and concavity of a limiting \(G\) function. To do so merely requires generalizing the foregoing theorems and lemmas to vector quantities (multiplet numbers and densities). Since the steps are simple and well known, we shall only outline them here, cf. Fisher (1964).

1. Define the multiplet density vector (for a ball \(B_j\)) as \(R_j = (V_j')^{-1} \alpha\) and define \(G_j(R_j) = g(\sum_{i=1}^{r} R_j^i M_i)\).

2. The critical density (for an infinitely large sphere) is no longer a single number but is a surface in the \(T\)-dimensional multiplet density space and this, in turn, corresponds to a surface in the \((S-1)\)-dimensional particle density space of vectors \(\rho\) such that \(\rho \cdot E = 0\). The crucial point is that in either space the critical density surface bounds a convex set of vectors with nonnegative components. The critical surface will be denoted by \(R_\rho\) (resp. \(\rho_\rho\)); \(\rho \leq R_\rho\) (resp. \(\rho \leq \rho_\rho\)) will mean that \(R\) (resp. \(\rho\)) is inside the set. As before, one first introduces an interior surface \(R\) (resp. \(\rho\)) and then passes to the limit \(R \rightarrow R_\rho\) after continuity has been established from concavity plus boundedness.

3. The function \(G(\alpha; A)\) is defined for nonintegral values of the \(\alpha^i\) by simultaneous linear interpolation on each variable separately. Thus, for a vector \(A = \alpha + \eta\) with \(\alpha\) integral and \(0 \leq \eta_i \leq 1\), we define
\[
G(A; A) = \sum_{\{\alpha\}} \prod_{i=1}^{r} \nu_i(\alpha^i) \left| G(\alpha + \sigma; A) \right|,
\]
where \(\{\alpha\}\) is the set of vectors of the form \(\alpha^i = 0\) or \(1\) for \(i = 1, \ldots, T\) and \(\nu_i(0) = 1 - \eta^i; \nu_i(1) = \eta^i\). With this definition, Lemma 4.3 immediately generalizes to functions of \(T\) variables. (The proof is obtained by first applying Lemma 4.3 to \(\alpha^i\) keeping \(\alpha^1, \ldots, \alpha^{i-1}, \alpha^{i+1}, \ldots, \alpha^T\) as fixed integers. Next, the lemma is applied to \(\alpha^i\) with \(\alpha^1, \alpha^2, \ldots, \alpha^{i-1}, \alpha^{i+1}, \ldots, \alpha^T\), fixed, and so on.) It should be pointed out that the linear interpolation of \(G\) does not induce any kind of unique interpolation of \(g\) as a function of \(N\) because a noninteger vector \(N\) corresponds to several vectors \(A\). We shall return to this point in the sequel to Theorem 4.5.

With the above outline we are led to the generalization of Theorems 4.3 and 4.4 in multiplet space.

**Theorem 4.5.** Let \(\{R_j\}\) be a sequence of multiplet density vectors such that \(\lim_{j \to \infty} R_j = \mathbf{R} \) with \(|\mathbf{R}| < R_\rho\). Then

(i) \(\lim_{j \to \infty} G_j(R_j) = G(\mathbf{R})\) exists and is independent of the particular sequence;

(ii) \(G\) is continuous in the convex space \(|\mathbf{R}| < R_\rho\) and it is concave, i.e., \(G(\lambda \mathbf{R} + (1 - \lambda) \mathbf{R}' ) \geq \lambda G(\mathbf{R}) + (1 - \lambda) G(\mathbf{R}')\) for all \(0 \leq \lambda \leq 1\) and all \(\mathbf{R}, \mathbf{R}'\) with \(|\mathbf{R}| < R_\rho\) and \(|\mathbf{R}'| < R_\rho\);

(iii) \(G(0) = 0\);

(iv) If \(R_j = \mathbf{R}\) for all \(j\), the convergence in (i) is uniform on compact subsets of \(|\mathbf{R}| < R_\rho\).

**Corollary.** Let \(\mathbf{R}\) and \(\mathbf{R}'\) be two multiplet density vectors such that
\[
\sum_{i=1}^{T} R^i M_i^l = \sum_{i=1}^{T} R'^i M_i^l \quad \text{for all } l = 1, \ldots, S.
\]
Then \(G(\mathbf{R}) = G(\mathbf{R}')\).

**Proof.** Define integral multiplet numbers by \(\alpha_j = [V_j/\mathbf{R}]^*\) and \(\alpha_j' = [V_j/\mathbf{R}']^*\), where [ ] denotes "integral part" and [ ]* denotes "next greater integral part." Thus \(\alpha_j = V_j^i \mathbf{R} + \alpha_j\) and \(\alpha_j' = V_j^i \mathbf{R}' - \alpha_j'\) where \(\alpha_j\) and \(\alpha_j'\) are vectors with components in \([0, 1]\). For any multiplet vector \(\alpha\) there is a particle vector \(N = \alpha \cdot M\) (i.e., \(N^i = \sum_{i=1}^{T} \alpha^i M_i^l\)). Thus,
\[
N_j = \alpha_j \cdot M = V_j^i \mathbf{R} \cdot M + \alpha_j \cdot M = V_j^i \mathbf{R}' \cdot M + \alpha_j \cdot M
\]
\[
= \alpha_j' \cdot M + (\alpha_j + \alpha_j') \cdot M = N_j + (\alpha_j + \alpha_j') \cdot M.
\]
Define
\[
R_j = (V_j')^{-1} \alpha_j, \quad R_j' = (V_j')^{-1} \alpha_j'.
\]
and
\[ R_j' = R_j' + (V_j')^{-1} (\sigma_j + \alpha_j') \cdot M. \]

Thus, \( G_j(R_j') = g_j((V_j')^{-1} N_j) = G_j(R_j) \). Since \( R_j' \to R \) and \( R_j \to R \) as \( j \to \infty \) we have
\[
G(R) = \lim_{j \to \infty} G_j(R_j') = \lim_{j \to \infty} G_j(R_j) = G(R).
\]

Theorem 4.5 leads easily to our main theorem which is the generalization of Theorems 4.3 and 4.4.

**Theorem 4.6.** (i) Let \( \{N_j\} \) be a sequence of non-negative, integer valued particle number vectors satisfying \( N \cdot E = 0 \) and let \( \rho_j = (V_j')^{-1} N_j \).

If \( \lim_{j \to \infty} \rho_j = \rho \) with \( |\rho| < \rho_c \) then \( \lim_{j \to \infty} g_j(\rho_j) = g(\rho) \) exists independently of the particular sequence. Furthermore, \( g(\rho) \) is continuous and concave on the convex domain \( D = \{ \rho : |\rho| < \rho_c \} \cap \{ \rho : \rho \cdot E = 0 \} \).

(ii) Let \( K \) be a compact subset of \( D \). Suppose that for each \( \rho \in K \) we have a sequence \( \{N_j(\rho)\} \) and the corresponding sequence \( \{\rho_j(\rho)\} \), as in part (i), with the additional hypothesis that \( \lim_{j \to \infty} \rho_j(\rho) = \rho \) uniformly in \( K \). Then \( g_j(\rho_j(\rho)) \to g(\rho) \) uniformly on \( K \).

(iii) \( g(0) = 0 \).

**Proof of (i).** For each \( N_j \) we can choose a multiplet density \( R_j = (V_j')^{-1} \alpha_j \) such that \( \rho_j = R_j \cdot M \). We may assume that \( |\rho_j| < \rho_c \) and \( |R_j| < \rho_c \). Let \( B = [R : R \cdot M = \rho, |R| < \rho_c] \). The set of points \( \{R_j\} \), together with \( B \), obviously lie in a compact subset of \( R \)-space (even if \( \rho_c = \infty \)). Hence, every subsequence of \( \{R_j\} \) has a convergent subsequence. Moreover, if \( R \) is the limit of any convergent subsequence of \( \{R_j\} \) then \( R \in B \) since \( R \cdot M = \rho \). By Theorem 4.5 and its corollary, \( G(R) \) is a constant on \( B \) which we shall define to be \( g(\rho) \). Hence \( g_j(\rho_j(\rho)) = G_j(R_j) \to g(\rho) \). The continuity and concavity of \( G(R) \) imply the same properties for \( g(\rho) \).

**Proof of (ii).** Let \( || \) be the uniform norm on \( K \). Then
\[
|| g_j(\rho_j(\rho)) - g(\rho) || \leq || g(\rho_j(\rho)) - g(\rho) || + \| g_j(\rho_j(\rho)) - g(\rho_j(\rho)) \|.
\]
The first term goes to zero by the uniform continuity of \( g(\cdot) \) on \( K \). The second term is \( || G_j(R_j(\rho)) - G(R_j(\rho)) || \). This also goes to zero by part (iv) of Theorem 4.5 because we can always choose \( \{R_j(\rho) : \rho \in K, j = 0, 1,...\} \) to lie in a compact subset \( K' \) of \( |R| < \rho_c \).

V. **Thermodynamic Limit for Neutral Systems in General Domains**

In Section IV we established the existence and convexity of the thermodynamic limit of the free energy for a particular sequence of balls \( \{B_j\} \) with radii \( R_j \) given by (4.1). In this section we shall show that the same limit \( g(\rho) \) is attained for a general sequence of domains tending to infinity in a reasonable way. The proof follows closely that given in Fisher (1964, Section 9), and we shall stress here only the modifications necessitated by the Coulomb potential.

The following are conditions on a sequence of domains in \( \mathbb{R}^d \):

A. A sequence of domains \( \{A_j\} \) tends to infinity in the sense of Van Hove if \( V(A_j) \to \infty \) and \( V(h_j ; A_j) / V(A_j) \to 0 \) as \( j \to \infty \) for each fixed \( h \). (For definitions see (3.1)). This is condition D of Fisher (1964).

B. A sequence of domains \( \{A_j\} \) satisfies the **ball condition** if there exists a \( \delta > 0 \) such that
\[
V(A_j) / V(B_j) \geq \delta,
\]
where \( B_j \) is the ball of smallest radius containing \( A_j \).

C. A sequence of domains \( \{A_j\} \) tends to infinity in the sense of Fisher if \( V(A_j) \to \infty \) and if there exists a continuous function \( \pi : \mathbb{R}^d \to \mathbb{R}^d \), with \( \pi(0) = 0 \) such that
\[
V(\pi[V(A_j)]^{1/4}; A_j) / V(A_j) \leq \pi(\alpha)
\]
for all \( \alpha \) and all \( j \). This is condition \( D^* \) of Fisher (1964).

Obviously, condition C implies A. It also implies condition B if each \( A_j \) is connected, as shown in Appendix A. On the other hand, neither condition A nor B implies the other, nor do conditions A and B together imply C.

**Definition.** A regular sequence of domains \( \{A_j\} \) in \( \mathbb{R}^d \) is one satisfying conditions A and B if only strongly tempered potentials (in addition to the Coulomb potential) are present. If weakly tempered potentials are also present then the stronger condition C must be satisfied.

Clearly, our standard sequence of balls is always regular.

The only departure from Fisher's (1964) conditions is the replacement of his E by our B. Condition B is a bit more restrictive than Fisher's
condition E which requires only that \( V(A_j)/V(\Pi_j) \geq \delta \) where \( \Pi_j \) is any parallelepiped, not necessarily a cube, containing \( A_j \). Thus, the example given by Fisher of a sequence of parallelepipeds \( A_j \) in which the length of the first edge increases at a rate \( j \) while the other edges increase as \( j^\alpha \) would satisfy Fisher's E but not our B. It is not clear to us at present whether this is just a technical flaw in our method or whether the intrinsic long range nature of the Coulomb potential would prevent the approach to the thermodynamic limit for such a "cigar shaped" domain, even when only strongly tempered potentials are present in addition to the Coulomb potential.

We turn now to the generalization of Theorem 4.6 to regular sequences of domains.

**Theorem 5.1.** Let \( \{A_j\} \) be a regular sequence of domains. Let \( \{N_j\} \) be a sequence of nonnegative, integer valued particle number vectors satisfying the neutrality condition, \( N_j \cdot E = 0 \), and let \( \rho_j = V(A_j)^{-1}N_j \). If \( \lim_{j \to \infty} \rho_j \to \rho_e \), with \( |\rho| < \rho_e \), then \( \lim_{j \to \infty} g(\rho_j; A_j) = g(\rho) \) exists and is independent of the sequence. In particular, \( g(\rho) \) is the same as that for the standard sequence of balls. Furthermore, on any compact subset of \( |\rho| < \rho_e \), the convergence of \( g(\rho; A_j) \) to \( g(\rho) \) is uniform.

**Proof.** We shall give the proof for strongly tempered potentials and refer the reader to Fisher (1964, Section 9) for the general case. The strongly tempered potential case illustrates the modifications necessitated by the presence of the Coulomb potential.

**Preliminary Remarks.** The discussion of the multicomponent systems at the end of Section IV is clearly applicable to general domains because the geometry of balls was not used there. It suffices, therefore, to prove the theorem for \( G(R; A_j) \), which is just \( g(\rho_j; A_j) \) expressed in terms of multiplet densities instead of particle densities (which means that we must consider \( R_e \) instead of \( \rho_e \)). We remind the reader that \( R = V(A_j)^{-1}\alpha \), where \( \alpha \) is the multiplet vector. Likewise, the function \( G(R; A_j) \) is defined by dividing \( R \) by the true volume \( V(A_j) \). However, for the standard balls \( \{B_k\} \) used in the proof, our convention of Section IV uses \( V_{k'} > V_k = V(B_k) \) both for the density and the normalization of \( G_k(R) \). We shall denote \( V_{k'}/V_k \) by \( x_k \). Clearly, \( x_k \downarrow 1 \) as \( k \uparrow \infty \).

As before, we define \( G(R; A_j) \) for all \( R \) by linear interpolation. Since the limiting function \( G(R) \) for balls is continuous, it is clearly sufficient to prove the theorem (which includes the uniformity of the limit) when \( \mathbf{R}_j = \mathbf{R} \), independent of \( j \). We denote the compact subset in the last line of the theorem by \( C \) and note that for sufficiently small \( \Delta > 0 \), \( C_{\Delta} = \{(1 + \Delta)C \} \) is also a compact subset of \( \{R < R_e \} \). The proof consists of two parts: (a) give any \( \varepsilon > 0 \) we find a lower bound of the form \( G(R; A_j) \geq G(R) - \varepsilon \) when \( j \geq J \) for all \( R \in C \) and some \( J \); (b) we find an upper bound of the form \( G(R; A_j) \leq G(R) + \varepsilon \) when \( j \geq J \) for all \( R \in C \) the dependence of \( J \) on \( \varepsilon \) in parts (a) and (b) need not be the same.

Finally, we introduce a sequence of open cubes \( \{T_k\} \) whose volumes are the same as those of \( \{B_k\} \).

(a) Lower bound. Consider a maximal packing of \( A_j \) by \( n_{jk} \) cubes \( T_k \). Each cube, in turn, is packed in the standard manner with balls of type \( B_{k-1}, \ldots, B_{k-m} \) for some \( m, 0 < m < k \). By Lemma 4.1, the distance between every pair of balls is at least \( 2R_0 \). Hence, if the multiplets are constrained to lie in these balls, the inter-ball, strongly tempered interaction is nonpositive and we obtain

\[
G(R; A_j) \geq (1 - \xi_{j,k}) x_k \sum_{i=1}^{m} f_i G_{k-i}(\mathbf{R}),
\]

(5.3)

where \( G_{k-i} \) refers to the standard balls, \( f_i = p^{i-1} \gamma^{i-1} \) as in Section III, \( \xi_{j,k} = 1 - n_{jk} V_{B_k}/V(A_j) \), \( 0 \leq \xi_{j,k} \leq 1 \), and

\[
\mathbf{R} = \mathbf{R} x_k (1 - \xi_{j,k}) \sum_{i=1}^{m} f_i - x_k (1 - \xi_{j,k}) (1 - \gamma^m) \mathbf{R}.
\]

From the properties of the \( G_n(R) \) and its limit \( G(R) \) we can

1. Find a constant \( G \) such that \( |G(R)| < G \) for \( R \in C \);
2. Find an integer \( M \) such that \( G_n(R) - G(R) \leq \varepsilon/5 \) when \( n \geq M \) and \( R \in C \);
3. Find a \( \Delta' \), with \( 0 < \Delta' < \Delta \), such that

\[
|G((1 + \alpha)R) - G(R)| \leq \varepsilon/5
\]

when \( R \in C \) and \( |\alpha| \leq \Delta' \);

4. Find an integer, \( M' \), such that \( (1 - (1 - \gamma^m)^2) G \leq \varepsilon/5 \) and \( (1 - \gamma^m)^{-2} \leq 1 + \Delta' \) when \( m \geq M' \);
5. Find an integer, \( M'' \), such that \( (x_m)^{-1} \geq 1 - \Delta' \), \( x_m \leq 2 \), and \( (x_m^{-1} - 1) G \leq \varepsilon/5 \) when \( m \geq M'' \).

Now, in (5.3) set \( m = \max(M, M', M'') \) and let \( k = 2m \). By condition A,
\( \zeta_{jk} \to 0 \) as \( j \to \infty \). Hence, there exists a \( J \) such that, for \( j \geq J \),

\( (1 - \zeta_{jk})^{-2} \leq 1 + \Delta' \) and \( [1 - (1 - \zeta_{jk})^3] G \leq \epsilon/5 \). Under these circumstances, \( \bar{R} = (1 + a)\bar{R} \) with \( |a| \leq \Delta' \). Rewriting (5.3) as

\[
G(\bar{R}; A_j) \geq (1 - \zeta_{jk}) x_k \sum_{i=1}^{m} f_i [G_{k-i}(\bar{R}) - G(\bar{R})] + G(\bar{R}) - G(\bar{R}) + G(\bar{R}) ,
\]

we obtain \( G(\bar{R}; A_j) \geq x_k (1 - \gamma^m) (1 - \zeta_{jk}) G(\bar{R}) - 4\epsilon/5 \) and then \( G(\bar{R}; A_j) - G(\bar{R}) \geq -\epsilon \).

(b) Upper bound. We define integers \( K(j) \) such that \( B_{K(j)} \) is the smallest standard ball containing \( A_j \). By considering \( A_j \) as a subdomain in a packing of \( B_{K(j)} \), we can obtain an upper bound on \( G(\bar{R}; A_j) \) from a lower bound on \( G_{K(j)}(\bar{R}') \) for some appropriate \( \bar{R}' \). To this end, consider a maximal packing of \( B_{K(j)} \) by \( n_{jk} \) cubes \( \Gamma_k \) and pack these, in turn, in the standard manner with balls of type \( B_{K(j)} \) of the same kind, namely, \( \bar{R}' \). Thus,

\[
G_{K(j)}(\bar{R}') \geq W_j G(\bar{R}; A_j) + W_{jk} x_k \sum_{i=1}^{m} f_i G_{K(i)}(\bar{R}) ,
\]

(5.4)

where \( W_j = V(A_j)/V_{K(j)} \leq 1 \), \( W_{jk} = n_{jk} V_{k}/V_{K(j)} < 1 \), and

\[
\bar{R}' = W_j \bar{R} + W_{jk} (1 - \gamma^m) x_k \bar{R}' = W_j [1 - W_{jk} x_k + \gamma^m x_k W_{jk}]^{-1} \bar{R} .
\]

Let \( \bar{B}_j \) be the (nonstandard) ball referred to in condition \( B \), so that \( B_{K(j)} \subset \bar{B}_j \subset B_{K(j)} \). Hence,

\[
W_j = [V(A_j)/V(\bar{B}_j)][V(\bar{B}_j)/V_{K(j)}] \geq \delta, \quad (5.5)
\]

where \( \delta \) is a positive constant (approximately \( (1 + p)^{-d} \) when \( K(j) \) is large) which can be chosen independent of \( j \). Also, by condition \( A \), \( W_j + W_{jk} \to 1 \) as \( j \to \infty \) with \( k \) fixed, but for every \( j \) and \( k \), \( W_j + W_{jk} \leq 1 \).

As in part (a), we choose \( k = 2m \) and let \( m \) be fixed, but sufficiently large. The crucial observation is that (5.5) tells us that \( W_{jk}/W_j \) is bounded above by \( (\delta \delta)^{-1} \) independent of \( j \) and \( k \). This, in turn, tells us that \( (1 - W_{jk}/W_j) \to 1 \) for \( k \) fixed and \( j \to \infty \). With the help of these facts, the proof is the same as in part (a).

VI. Systems with Net Charge

In the last two sections we showed that a sequence of systems of charged particles has a thermodynamic limit when the finite systems in the sequence have no net charge, that is, \( \mathbf{N}_j \cdot \mathbf{E} = 0 \). The free energy density in this limit \( -g(\rho) \), is independent of the shape of the domains \( A_j \) and depends only on the limit of the particle density vector \( \mathbf{N}_j/V(A_j) \). The above proof fails if there is any charge imbalance, no matter how small, in the sequence of particle numbers \( \{\mathbf{N}_j\} \).

It is intuitively clear that this condition of strict charge neutrality, \( \mathbf{N}_j \cdot \mathbf{E} = 0 \), is unnecessarily restrictive. We expect that a "small" amount of uncompensated charge will have no effect on the free energy density in the thermodynamic limit while a "large" amount of uncompensated charge will lead to a divergent free energy density in that limit. The dividing line between "small" and "large" should be when the excess charge \( Q_j \), in a domain \( A_j \), increases in proportion to the "surface area" of \( A_j \) as \( j \to \infty \). In this case we expect the thermodynamic limit of the free energy density to exist but that its value depends also on the limiting shape of the domains \( A_j \).

These expectations come from macroscopic electrostatic theory (Kellog, 1929), which shows that the lowest energy configuration for any net charge \( Q \) confined to a domain \( A \) is obtained when \( Q \) is concentrated at the boundary of \( A \). This configuration of the charge is described in electrostatics by a two-dimensional charge density \( \sigma(x) \), \( x \in S_{\rho} \), where \( S_{\rho} \) is the surface of \( A \). (We shall only consider three-dimensional systems here, that is \( A_j \subset \mathbb{R}^3 \)). This surface charge density will be such as to make the electrostatic potential constant in the interior of \( A \), i.e., there will be no electric field in \( A \). The electrostatic energy of this surface layer is equal to \( \frac{1}{2} \mathcal{O}^j \mathcal{C}(A) \), where \( \mathcal{C}(A) \) is the capacitance of \( A \).

For "reasonable" domain shapes, \( \mathcal{C}(A) \) is proportional to \( [V(A)]^{1/2} \) and the electrostatic energy per unit volume will thus be proportional
to \([Q_j/V^{3/3}]^3\), the square of the “average surface charge density”. Hence for a sequence of domains \(\{A_j\}\) with volumes \(V_j\) and capacitances \(C_j\) each containing a net charge \(Q_j\), such that, as \(j \to \infty\), \(V_j \to \infty\), \(C_j/V_j^{1/3} \to c\) and \(Q_j/V_j^{2/3} \to \sigma\), the minimum electrostatic energy per unit volume, \(\tilde{\varepsilon}_j\), will also approach a limit:

\[
\tilde{\varepsilon} = \lim_{j \to \infty} \tilde{\varepsilon}_j = \frac{1}{2} \sigma^2/c.
\]  

(6.1)

Note that (6.1) refers solely to the macroscopic electrostatic energy per unit volume of the charge \(Q\) in the domain \(A\) or on the surface \(S_A\). We shall now prove a theorem which shows that in the thermodynamic limit the difference between the free energy densities of a neutral system, obtained in Sections IV and V, and of a system containing some extra charged particles is given precisely by (6.1).

For technical reasons the theorem will be proved only for a sequence of domains whose shapes approach ellipsoids in the sense defined below. This is more restrictive than is desirable or (probably) necessary as will be clear from the derivation of the theorem.

**Definition.** Let \(E\) be an open ellipsoid of unit volume and capacity \(c_E\). A sequence of domains \(\{A_j\}\), \(j = 1, 2, \ldots\) will be called asymptotically similar to \(E\) if \(V(A_j) \to \infty\) and if there exist ellipsoids \(\{E_j^+\}\) and \(\{E_j^-\}\) similar to \(E\) such that \(E_j^+ \subset A_j \subset E_j^-\) and \(V(E_j^+)/V(E_j^-) \to 1\) as \(j \to \infty\). The capacity of \(A_j\) will clearly lie between the capacities of \(E_j^+\) and \(E_j^-.\) These latter capacities are \(c_E[V(E_j^+)]^{1/3}\) and \(c_E[V(E_j^-)]^{1/3}\) respectively.

**Theorem 6.1.** Let \(\{A_j\}\) be a sequence of domains asymptotically similar to an ellipsoid \(E\), and let \(\{N_j\}\) and \(\{n_j\}\) be sequences of integer particle number vectors such that \(N_j \cdot E = 0\), \(n_j \cdot E = Q_j\) and

\[
\lim_{j \to \infty} N_j/V(A_j) = \rho, \quad \lim_{j \to \infty} n_j/V(A_j) = 0, \quad \lim_{j \to \infty} Q_j[V(A_j)]^{-2/3} = \sigma.
\]

Then,

\[
\lim_{j \to \infty} g[(N_j + n_j)/V(A_j); A_j] = g(\sigma) - \frac{1}{2} \sigma^2/c_E.
\]

**Proof (Preliminary remarks).** (i) Since \(E_j^+ \subset A_j \subset E_j^-\), it follows from our basic inequality that \(Z(N_j + n_j; E_j^-) \geq Z(N_j + n_j; A_j) \geq Z(N_j + n_j; E_j^+)\). Moreover, since \(V(E_j^+)/V(E_j^-) \to 1\) as \(j \to \infty\) it is sufficient to prove the theorem for a sequence of ellipsoids \(\{E_j^+\}\) similar to \(E\), whose volumes are the same as that of the \(\{A_j\}\). With each \(E_j\) we associate a pair of concentric ellipsoids, \(E_j^-\) and \(E_j^+\) homothetic to \(E_j\) such that \(E_j^- \subset E_j \subset E_j^+\) and \(V(E_j^+)/V(E_j^-) \to 1\) as \(j \to \infty\). The volumes and capacities of \(E_j^-\), \(E_j^+\), and \(E_j\) will be denoted by \((Q_j)^-\), \((Q_j)^+\), \((Q_j)^\alpha\) and \((Q_j)^\beta\), \(C_j^-\), \(C_j^+\), \(C_j\), respectively. Clearly \(C_j^- = c_EQ_j^-\) and \(C_j = c_EQ_j\). The interiors of the ellipsoidal shells \(E_j^+\backslash E_j\) and \(E_j\backslash E_j^-\) will be called \(D_j^+\) and \(D_j^-\), respectively.

(ii) A sequence of domains asymptotically similar to \(E\) is also a regular sequence satisfying condition C of Section V.

(iii) The reason for the introduction of ellipsoidal domains is their well-known electrostatic property (Kellog, 1929), that a uniform three-dimensional charge density \(\tau\) in an ellipsoidal shell such as \(D_j^+(\text{defined above})\) has a self-energy \(\frac{1}{2} V(D_j^+)\tau^2/C_j\) and produces a constant potential \(\tau V(D_j^+)/C_j\) in the interior of \(E_j\), with \(c_EQ_j^- \leq C_j \leq c_EQ_j^+\). This fact will enable us to obtain bounds on the partition functions for the domains \(E_j\) in a simple manner. Identical methods would work also for any other sequence of domains for which there are shell domains surrounding each \(A_j\) with the above mentioned properties of the shells \(D_j\).

(iv) We shall assume that the particles interact only with strongly tempered potentials in addition to the Coulomb potential.

(v) The proof of Theorem 6.1 will proceed by establishing bounds on the free energies of these systems. For this we shall need the free energies of two kinds of neutral systems: The first kind consists of \(N_j\) particles in \(E_j^-\); the second kind is a system in \(E_j^+\) which contains an additional species of particles so that it has altogether \(S + 1\) species. The new specie, which, following Aristotle, we shall call hyle will be labeled by the index zero. Its charge \(e_0\) will be \(\pm 1\) (in units in which all \(e_i, i = 1, \ldots, S\) are integers). The sign of \(e_0\) will be chosen as the opposite to the sign (which we shall take to be independent of \(j\)) of the excess charge \(Q_j\), that is \(e_0Q_j < 0\). The new neutral system will have an \(S + 1\) component particle number vector

\[
N_j + n_j + n_j^0 = (N_j^+, N_j^+ + n_j^0, \ldots, N_j^S + n_j^S) \quad \text{with} \quad n_j^0 = |Q_j|,
\]

\(n_j^0 e_0 = -Q_j\) so that the system is overall neutral. The hyle particles will only have Coulomb interactions and will be one component fermions in order to comply with the Dyson–Lenard theorem.
A. Lower Bound on the Partition Functions of Charged Ellipsoids

As in part (a) of Theorem 5.1 we consider a packing of $E_j^-$ with balls and we distribute the $N_j$ particles, $N_j \cdot E = 0$, among the balls such that each ball is neutral and call the resulting partition function $Z(N_j; \beta(E_j^-))$. The remaining $n_j$ particles we place in $D_j^-$. It then follows from our basic inequality that

$$Z(N_j + n_j; E_j) \geq Z(N_j; \beta(E_j^-)) Z(n_j; D_j^-),$$

(6.2)

since each ball is neutral and the separation between the particles in $B(E_j^-)$ and those in $D_j^-$ is at least $r_0$. Taking the logarithm of (6.2) and dividing by $V(E_j)$ yields, as in section V,

$$\lim_{n \to \infty} \frac{\ln g((N_j + n_j)/V(E_j); E_j) - \ln Z(N_j; D_j^-)}{\ln Z(n_j; D_j^-)} \geq g(\phi).$$

(6.3)

Let $n_j = \sum_{i=1}^J n_j^i$ be the total number of particles which contribute to the excess charge and label the coordinates and charges of these particles by $x_1, \ldots, x_{n_j}, q_1, \ldots, q_{n_j}$, respectively. The Hamiltonian of these $n_j$ particles in the domain $D_j^-$ will be written in the symbolic form $H'(n_j) + U(n_j)$, where $H'(n_j)$ contains the kinetic energy and the strongly tempered interaction and $U(n_j)$ is the Coulomb interaction.

To obtain a lower bound on $Z(n_j; D_j^-)$ we use the inequality (2.19)

$$\ln Z(n_j; D_j^-) \geq -1/J \sum_{a=1}^J \left( \Psi_a, [H'(n_j) + U(n_j)] \Psi_a \right),$$

(6.4)

where $\{\Psi_a\}, \alpha = 1, \ldots, J$ is any properly symmetrized and normalized set of functions of the $n_j$ particles coordinates and spins which vanishes unless $x_i \in D_j^-$ for $i = 1, \ldots, n_j$. Preliminary to our choice of $\{\Psi_a\}$ we shall establish the following proposition.

**Proposition 6.1.** Let $\mathbb{R}^3$ be covered by cubes $\Gamma$ of sides $2y = r_0 + 2b$, for some arbitrary but fixed $b > 0$, arranged in a cubic array. Let $M_j^\pm$ be the number of cubes lying entirely inside $D_j^\pm$ and let $n_j$ satisfy the hypothesis of Theorem 6.1. Then we can choose the ellipsoids $E_j^\pm$ in such a way that $M_j^\pm(2y)^3/V(D_j^\pm) \to 1$ and $M_j^\pm/n_j \to \infty$ as $j \to \infty$.

**Proof.** By Lemma 3.1 (2y)^3M_j^\pm/V(D_j^\pm) \to 1 whenever $|L_j - L_j^\pm| \to \infty$. Hence, whenever $n_j/L_j^\pm \to 0$ as in Theorem 6.1 we can choose the $L_j^\pm$ in such a way that $|L_j - L_j^\pm| \to \infty$, $L_j - L_j^\pm/|L_j| \to 0$ and $V(D_j^\pm)/n_j \to \infty$. For example, we can choose $|L_j - L_j^\pm|/|L_j| \sim [n_j/|L_j^\pm|^\gamma]$ with $0 < \gamma < \frac{1}{2}$.

**Remark.** We shall assume from now on that we begin our sequence with sufficiently large domains for $M_j^\pm$ to be larger than $n_j$ and $|D_j^-|$. We are now ready to choose $\{\Psi_a\}$. Let $q(r)$ be a $C^\infty$ normalized function of $r = |r|$ vanishing for $r > b$. Let $\{X_i\}, \ell = 1, \ldots, M_j^\ell$ be the center of the cubes $\{\Gamma_i\} \subset D_j^-$. From these $M_j^\ell$ cubes we now choose a subset of $n_j$ cubes $\{\Gamma^i_n\}, i = 1, \ldots, n_j$, and define $\Psi_a(x_1, \ldots, x_{n_j})$ to be the appropriately symmetrized product, $\prod_{i=1}^{n_j} \varphi(x_i - X_i)$. The number of different configurations $a$ is clearly equal to

$$M_j^-! / [(M_j^- - n_j)! \prod_{i=1}^{n_j} n_j^i!] = J.$$

Using this set $\{\Psi_a\}$ in (6.4) it is readily verified that

$$(\Psi_a, H'(n_j) \Psi_a) \leq K n_j,$$

(6.5)

with $K$ a constant independent of $j$ or $\alpha$. Owing to the spherical symmetry of $\varphi(x - X_i)$ about $X_i$, the expectation value of the Coulomb interaction for the wavefunction $\Psi_a$ will be

$$(\Psi_a, U(n_j) \Psi_a) = \frac{1}{2} \sum_{i=1}^{n_j} \sum_{l=1}^{n_j} (q_{i} q_{l} |X_i - X_l|)^3 - 1.$$

(6.6)

When doing the sum in (6.4) of the right hand side of (6.6) over different configurations $\alpha, \alpha' = 1, \ldots, J$, a particular interaction term such as $q_i q_j |X_i - X_j|^{-3}$, $\nu, \nu' = 1, \ldots, J$, $\nu \neq \nu'$, will occur

$$(M_j^- - 2)! / [(M_j^- - n_j)! \prod_{i=1}^{n_j} (n_j^i - 1)! (n_j^i - 1)!]$$

times for $\nu \neq \nu'$

and

$$(M_j^- - 2)! / [(M_j^- - n_j)! \prod_{i=1}^{n_j} (n_j^i! - 2)!]$$

times for $\nu = \nu'$.

Hence

$$J^{-1} \sum_{a=1}^J (\Psi_a, U(n_j) \Psi_a) = \frac{1}{2} \sum_{i=1}^{n_j} \sum_{l=1}^{n_j} |X_i - X_l|^{-3}$$

$$+ \frac{1}{2} \sum_{i=1}^{n_j} \sum_{l=1}^{n_j} \sum_{\nu=1}^{n_j} q_i^\nu q_j^\nu |X_i - X_l|^{-3} q_i^\nu q_j^\nu$$

$$\leq \Omega^2 J^{-1} \sum_{i=1}^{n_j} \sum_{l=1}^{n_j} |X_i - X_l|^{-3}.$$

(6.7)
The extreme right hand side of (6.7) corresponds to the interaction energy of \( M_j^- \) equal charges of magnitude \( \tilde{q}_j = Q_j/M_j^- (M_j^- - 1)^{-1/3} \) which are located at the centers of the \( M_j^- \) cubes packed in \( D_j^- \). As \( j \to \infty \) and \( \bar{q}_j \to 0 \), the sum in this term will go over into an integral. This becomes apparent when we make a scale transformation of \( \mathbb{R}^3: x \to xL_j \). This transformation takes \( E_j \) into the unit ellipsoid \( E \) and \( D_j^- \to D_j^+ \) where \( D_j^+ \) is an ellipsoidal shell inside \( E \) of volume \( V(D_j^+) = V(D_j^-)L_j^3 \). The right side of (6.7) divided by \( V(E_j) \) now becomes

\[
\frac{1}{2} \left[ \frac{Q_j^2}{V(E_j)^{1/2}} \right]^2 \left[ \frac{V(D_j^-)^{-1}}{M_j^- (M_j^- - 1)} (2y)^9 \right] \\
\times \left\{ V(D_j^+) - \sum_{l=1}^{M_j^- - M_j^-} \sum_{k=1}^{M_j^-} |Y_l - Y_k|^{-1} \Delta_l^3 \right\}. \tag{6.8}
\]

The sum in the last bracket is over all cubical cells of volume \( \Delta_l^3 = (2y)^9 L_j^3 \) arranged in a cubic lattice, which are packed in the domain \( D_j^+ \). As \( j \to \infty \) the last bracket approaches an integral which, by Remark (ii) after Theorem 6.1, is the self-energy \( \frac{1}{2} e_0^{-1} \) of a unit charge distributed on the surface of \( E \) in such a way as to make the electrostatic potential in the interior of \( E \) equal to \( e_0^{-1} \). Also \( Q_j^9 V(E_j)^{1/2} \to 2^{10} \alpha^2 \) and, by Proposition 6.1, the second bracket \( [ ] \) in (6.8) \( \to 1 \). Combining Eqs. (6.3)-(6.8) yields

\[
\lim_{j \to \infty} g([N_j + n_j]; V(E_j); E_j) \geq g(\rho) - \frac{8}{3} \alpha^2 a_0. \tag{6.9}
\]

### B. Upper Bound on the Partition Functions of Charged Ellipsoids

Let \( Z(N_j + n_j; E_j) \) be the partition function of a system in the domain \( E_j \) having \( S + 1 \) species with \( n_j^0 = |Q_j| \) hyle particles of charge \( e_0 = -Q_j/|Q_j| \), as in Remark (iv) after Theorem 6.1. The masses \( m_0 \) of the hyle particles may be chosen arbitrarily positive.

Applying the inequality (2.23) after adding \( W_j = \sum_{i=1}^{S+a} w_i(x_i) \) (to be defined presently) to the Hamiltonian of the hyle particles and subtracting it from the interdomain interaction, we obtain

\[
Z(N_j + n_j; E_j) \geq Z(N_j + n_j; E_j) Z(n_j^0; D_j^+; W_j). \tag{6.10}
\]

Here \( Z(n_j^0; D_j^+; W_j) \) is the partition function of \( n_j^0 \) particles of species zero whose Hamiltonian consists of a kinetic energy term \( T(n_j^0) \), a Coulomb pair interaction term \( U(n_j^0; W_j) \), and an external one-body electrostatic potential \( \omega_i(x_i), i = 1, \ldots, n_j^0 \), produced by the (canonical ensemble) average charge density of the \( N_j + n_j \) particles in \( E_j \) which we shall denote by \( q(x; N_j + n_j; E_j) \). Obviously, \( \int_{E_j} q(x; N_j + n_j; E_j) dx = Q_j \).

The electrostatic potential is

\[
\omega_i(x) = e_0 \int_{E_j} d\mathbf{x}' q(x'; N_j + n_j; E_j) \left| \mathbf{x}' - \mathbf{x} \right|^{-1}, \quad \mathbf{x} \in D_j^+. \tag{6.11}
\]

Taking logarithms in (6.10) and dividing by \( V(E_j) \) gives the upper bound

\[
\lim_{j \to \infty} \frac{g([N_j + n_j]; V(E_j); E_j)}{[V(E_j)]^{-1}} \ln Z(n_j^0; D_j^+: W_j) \leq g(\rho). \tag{6.12}
\]

To obtain a lower bound on \( Z(n_j^0; D_j^+; W_j) \) we shall again use the inequality (2.19)

\[
\ln Z(n_j^0; D_j^+; W_j) \geq -\frac{1}{2} \sum_{\alpha=1}^{S+a} \left( \Psi_{\alpha}^*, T(n_j^0) + U(n_j^0) + W_j \right) \Psi_{\alpha}. \tag{6.13}
\]

The expectation value of the potential energy term \( W_j \) in (6.13) will have the form

\[
(\Psi_{\alpha}^*, W_j \Psi_{\alpha}) = \int_{D_j^+} d\mathbf{x} \omega_i(x) q_i(x; n_j^0, D_j^+), \tag{6.14}
\]

with

\[
q_i(x; n_j^0, D_j^+) = n_j^0 \int_{D_j^+} |\Psi_{\alpha}(x, x_2, \ldots, x_{n_j^0})|^2 dx_2 \cdots dx_{n_j^0}
\]

and

\[
\int_{D_j^+} q_i(x; n_j^0, D_j^+) dx = -Q_j.
\]

The wavefunctions \( \{\Psi_{\alpha}\} \) of the coordinates of the hyle particles will be of the same form as the corresponding functions in part (a) above. That is \( \Psi_{\alpha} \) will be a normalized antisymmetric product of one-particle functions \( \varphi(x - X_{\alpha}^i), i = 1, \ldots, n_j^0 \) with the \( X_{\alpha}^i \in D_j^+ \) lying on the vertices of a cubic lattice of spacing \( 2y \) such that the distance between \( X_{\alpha}^i \) and the boundary of \( D_j^+ \) is at least \( y \). (Since the hyle particles interact only via the Coulomb potential, we are free to choose \( y = b \) in Proposition 6.1.) The \( \{X_{\alpha}^i\} \) will again be chosen as all possible subsets of a larger set of points \( \{X_i\}, i = 1, \ldots, M_j \), which lie on the vertices of a
cubic lattice defined in Proposition 6.1. (The ratio $M_j/M_{j+}$ will be shown to approach unity as $j \to \infty$ and hence we can choose our domains such that $M_j \geq n_j^0$ for all $j$.) While in part (a) we could choose the points $\{X_i\}$ simply as the centers of all cubes $I$ lying entirely in $D_j^+$ and did not have to specify the orientation or origin of the cubic lattice, we shall have to make our choices more carefully now as will be described presently. The basic construction is, however, the same as in (a) so that we find, in analogy with Eqs. (6.6) and (6.7), that

$$ (\Psi^*_a, T(n_j^0) \Psi_a) \leq Kn_j^0, \quad (6.15) $$

and

$$ J^{-1} \sum_{n=1}^J (\Psi^*_a, [U(n_j^0) + W_j] \Psi_a) \leq \frac{\beta}{2} \omega^2 [M_j(M_j - 1)]^{-1} \sum_{\xi, \eta} |\xi - \eta|^{-1} $$

$$ + n_j^0 (M_j - 1) \sum_{l=1}^{M_j} \omega(X_l). \quad (6.16) $$

The right side of (6.16) is (except for the trivial difference between $M_j$ and $M_j - 1$ in the denominator of the first term) the total electrostatic energy of $M_j$ particles, each having a charge $q_j = Q_j/M_j$, which are located at the positions $\{X_l\}, X_l \in D^+_j$, forming part of a cubic lattice. This energy is the sum of the self-energy of these charges and of their external energy in the electrostatic potential produced by the charge density $g(x; N_j + n_j, E_j)$ in $E_j$.

To obtain an upper bound on the right side of (6.16) we shall now prove a lemma which will show that we can choose the cubes $\{I_l\}$ and the corresponding $X_l, l = 1, \ldots, M_j$, in such a way as to make the external energy term in (6.16) less than $-Q_j^2 [\epsilon \rho L_j]^{-1}$. The self-energy term will be estimated in the same way as in (a), leading finally to an upper bound on the free energy density of the charged system identical to the lower bound in (6.9).

**Definition.** Let $D_j \subset D_j^+$ be an elliptoidal shell which is homothetic and concentric with $D_j^+$ and which is constructed in such a way that the minimum distance between a point in $D_j$ and the boundary of $D_j^+$ is equal to $y$, where $2y$ is the side of a cube $I$ defined in Proposition 6.1.

**Lemma 6.1.** It is possible to find $M_j$ points, $X_1, \ldots, X_{M_j} \in D_j$ which lie on the vertices of a cubic lattice of size $2y$ such that

(i) $\sum_{i=1}^{M_j} w_j(X_i) \leq -[Q_j/(C_j^+)] V(D_j)/[M_j(2y)^3]$

(ii) $\lim_{j \to \infty} V(D_j)/[M_j(2y)^3] = 1$.

**Proof.** Let $V(D_j)/C_j$ be the constant electrostatic potential (see Remark (ii) after Theorem 6.1) produced in $E_j$ by a uniform unit charge density in $D_j, C_j < C^+$. The interaction energy $I_j$ of such a unit charge density in $D_j$ (having the same sign as $e_0$) with the charges in $E_j$ is therefore

$$ I_j = \int_{D_j} w_j(x) \, dx = -V(D_j)/C_j. \quad (6.17) $$

Let $\{R_i\}$ denote the vertices of the lattice of Proposition 6.1 and let $w_j(x) = w_j(x)$ for $x \in D_j$, and $w_j(x) = 0$ otherwise. Consider now all translations of this lattice by $\xi, \xi \in I$. The integral in (6.17) can then be written in the form $\int_{I} \sum_i w_j(\xi + R_i) \, d\xi$. There must therefore be some value of $\xi$ for which $\sum_i w_j(\xi + R_i)(2y)^3 \leq -V(D_j)/C_j$, where the sum on $i$ is over all vertices $\xi + R_i \in D_j$. Calling the number of such vertices $M_j$, and identifying $\xi + R_i$ with $X_i$, proves part (i) of Lemma 6.1. Using the choice of $L_j^+$ given in Proposition 6.1, the proof of (ii) is trivial.

The wavefunctions $\{\Psi_a\}$ will now be as in part (a), i.e., antisymmetrized products of $g(X_l, x)$ with the $\{X_l\}, l = 1, \ldots, M_j$, as in Lemma 6.1. The support of the $\Psi_a(X_l, \ldots, X_{M_j})$ will lie entirely in $D_j^+$ since the points $\{X_l\}$ are at least a distance $y$ (where $y$ is the same as in $b$ in Proposition 6.1) from the boundary of $D_j^+$. (This was the reason for defining $D_j$ in the first place and is clearly a minor point which could have been handled in various ways.) Combining Eqs. (6.13)–(6.16) gives the bound

$$ -\ln Z(n_j^0; D_j^+ : W_j) \leq \frac{\beta}{2} \omega^2 [M_j(M_j - 1)]^{-1} \sum_{l=1}^{M_j} \sum_{k \neq l}^{M_j} |X_l - X_k|^{-1} $$

$$ -Q_j^2 [C_j^+]/[V(D_j)/M_j(2y)^3] + Kn_j^0. \quad (6.18) $$

As $j \to \infty$ the sum in the first term on the right side of (6.18) goes over into an integral as in part (a) so that (6.12) gives the upper bound

$$ \lim_{j \to \infty} g([N_j + n_j]/V(E_j); E_j) \leq g(e_0) - \frac{\beta}{2} \omega e_0. \quad (6.19) $$

Combining (6.19) with (6.9) proves Theorem 6.1.
Remark. When \( \lim_{j \to \infty} |Q_j| V(A_j)^{-a/b} \to \infty \), and \( \{A_j\} \) is any regular sequence of domains, not just ellipsoidal domains, then the free energy per unit volume approaches \( \infty \) as \( j \to \infty \), cf. Lemma 7.3.

VII. Grand Canonical Ensemble

The grand canonical partition function for a system of \( S \) species in a domain \( A_j \) with chemical potentials \( \mu_i \), \( i = 1, \ldots, S \), is defined as

\[
\mathcal{Z}(\mu; A_j) = \sum_{N_1=0}^\infty \cdots \sum_{N_S=0}^\infty \exp[\mu \cdot N] Z(N; A_j),
\]

where \( \mu = (\mu_1, \ldots, \mu_S) \), and we have set \( \beta = 1 \). The grand canonical pressure is defined as

\[
\pi(\mu; A_j) = V(A_j)^{-1} \ln \mathcal{Z}(\mu; A_j).
\]

We also define the neutral grand canonical partition function \( \mathcal{Z}' \) by restricting the summations in the right side of (7.1) to neutral systems for which \( N \cdot E = 0 \). The function \( \mathcal{Z}' \) will clearly depend only on that part of the vector \( \mu \) which is perpendicular to \( E \), i.e., on \( \mu' = \mu - (\mu \cdot E) E / (E \cdot E) \), and will thus be a function of only \( S - 1 \) independent variables,

\[
\mathcal{Z}'(\mu; A_j) = \mathcal{Z}'(\mu'; A_j) = \sum_{|N| = 0} \exp[\mu' \cdot N] Z(N; A_j).
\]

Similarly,

\[
\pi'(\mu; A_j) = \pi'(\mu'; A_j) = V(A_j)^{-1} \ln \mathcal{Z}'(\mu'; A_j)
\]

is the neutral grand canonical pressure.

As in Section VI, we shall confine our attention here to domains \( A_j \subset \mathbb{R}^3 \).

Remark. It is well known that if \( \mu > 0 \), the grand canonical partition function of an ideal Bose gas \( \mathcal{Z}_0(\mu; A_j) \) (the superscript indicating Bose statistics) is infinite for large \( j \) (Bose–Einstein condensation). One can prove (Ruelle, 1963) that if the particles interact with a tempered superstable potential then \( \mathcal{Z}(\mu; A_j) \) and \( \pi(\mu) = \lim_{j \to \infty} \pi(\mu; A_j) \) do exist for all \( \mu \) and all statistics. For bosons with a tempered potential which is only stable, \( \mathcal{E}(\mu) \) will be bounded only for small values of \( \mu \) (depending on \( \beta \)), i.e., \( \mu < \beta \).

For Coulomb systems to be H-stable the Dyson–Lenard theorem requires that all negative (or positive) charges be fermions so that all charged bosons have charges of the same sign. We shall show that, for charged systems satisfying this requirement, the strength with which the Coulomb potential inhibits deviations from charge neutrality prevents the ideal gas type of Bose–Einstein condensation. Large numbers of bosons must be accompanied by large numbers of fermions and this is energetically unfavorable at all values of \( \mu \). Thus if the only bosons present are charged ones, then \( \lim_{j \to \infty} \pi(\mu; A_j) \) exists for all values of the \( \{\mu_i\} \), \( -\infty < \mu_i < \infty, \ i = 1, \ldots, S \). If, however, our system contains some species of neutral bosons, then the corresponding \( \mu_i \)’s will have to be appropriately small (unless the tempered potentials involving these uncharged particles satisfy some super-stability condition). Since the part of the proof which involves the uncharged components does not differ from the standard one we shall assume from now on that all the species are charged with \( e_1, \ldots, e_S > 0 \) and \( e_{S+1}, \ldots, e_8 < 0 \), and that species \( a+1, \ldots, S \) are fermions while some or all of species \( 1, \ldots, a \) may be bosons.

We shall now state the main theorem of this section.

**Theorem 7.1.** For any regular sequence of domains \( \{A_j\} \), \( \pi(\mu) = \lim_{j \to \infty} \pi(\mu; A_j) = \lim_{j \to \infty} \pi'(\mu'; A_j) = \pi'(\mu') \) exists and is related to the Helmholtz free energy density by

\[
\pi'(\mu') = \sup_{|\varphi| \leq \varepsilon} [\varphi \cdot \mu' + g(\varphi)],
\]

the supremum being taken only over values of \( \varphi \) for which \( \varphi \cdot E = 0 \).

**Proof.** The proof we shall give that \( \lim_{j \to \infty} \pi'(\mu'; A_j) \) exists and is given by (7.5) is analogous to Fisher’s (1964) proof of a similar result for one component systems interacting only with tempered potentials, with the additional result that the \( \mu_i \) are arbitrary even if some of the components are bosons. The new element entering Theorem 7.1 is the equality of \( \pi(\mu; A_j) \) and \( \pi'(\mu'; A_j) \) in the thermodynamic limit. This means, in essence, that the terms in the grand partition function for which \( N \cdot E \neq 0 \) do not contribute to the pressure in this limit and hence \( \lim_{j \to \infty} \pi(\mu; A_j) \) depends only on \( S - 1 \) variables. Now since \( \pi(\mu; A_j) \geq \pi'(\mu'; A_j) \), the proof will involve showing that the sum of those terms in
(7.1) for which \( \mathbf{N} \cdot \mathbf{E} \neq 0 \) do not contribute too much, i.e., \( \pi(\mathbf{n}; A_j) \leq \pi'(\mathbf{n}'; A_j) + \delta_j \) with \( \delta_j \to 0 \) as \( j \to \infty \). The proof will be accomplished with the help of the following lemmas:

**Lemma 7.1.** Let \( \mathbf{M} = (M^1, ..., M^q) \) be an integer particle number vector such that \( \mathbf{M} \cdot \mathbf{E} = Q \). It is then possible to decompose \( \mathbf{M} \) into a “neutral” part \( \mathbf{N} \) and a “charged” part \( \mathbf{n} \) with \( \mathbf{M} = \mathbf{N} + \mathbf{n} \) such that (i) \( \mathbf{N} \) and \( \mathbf{n} \) are both integer particle number vectors; (ii) \( \mathbf{N} \cdot \mathbf{E} = 0 \) and \( \mathbf{n} \cdot \mathbf{E} = Q \); (iii) it is impossible to decompose \( \mathbf{n} \) into a nonzero neutral part and a charged part; (iv) \( n = \sum_{i=1}^{q} n_i \leq \lambda |Q| \) with \( \lambda \) a constant independent of \( \mathbf{M} \).

**Proof.** The decomposition of \( \mathbf{M} \) can be carried out explicitly using Lemma (4.4) on the representation of any neutral vector \( \mathbf{N} \) in the form \( \sum_{i=1}^{q} \alpha_i \mathbf{M}_i \) where the \( \alpha_i \) are nonnegative integers and the \( \mathbf{M}_i \) (not to be confused with \( M^i \)) are neutral multiplet vectors. Given \( \mathbf{M} \), we first find the largest integer \( \alpha_1 \) such that \( \mathbf{M} - \alpha_1 \mathbf{M}_1 \) is an integer particle number vector. Having chosen \( \alpha_1 \) we then repeat this procedure and find the largest integer \( \alpha_2 \) such that \( \mathbf{M} - \alpha_1 \mathbf{M}_1 - \alpha_2 \mathbf{M}_2 \) is an integer particle number vector. This decomposition clearly satisfies parts (i), (ii) and (iii) of the lemma.

The proof of part (iv) of the lemma is similar to the proof of Lemma 4.4. Using units in which all the \( |e_j| \) are positive integers, we set

\[
W_+ = \sum_{j=1}^{S} |e_j| \geq 1, \quad W_- = \sum_{i=1}^{a} e_i \geq 1, \quad (7.6)
\]

\[
q_+ = \sum_{i=1}^{a} u_i e_i \geq \sum_{i=1}^{a} n_i = n^+, \quad (7.7)
\]

\[
q_- = \sum_{i=1}^{S} n_i \geq \sum_{i=1}^{S} n_i = n^-, \quad (7.7)
\]

and consider, for definiteness, the case where \( Q \) is positive, so that \( Q = q_+ - q_- \geq 1 \). It follows from the requirement that \( \mathbf{n} \) does not contain any neutral part that for some \( i \), \( 0 < i \leq S \), \( n^i \geq W_+ \). Hence if \( q_+ \geq W_- W_+ \) (which implies that \( n^i \geq W_+ \) for some \( i \leq a \)), then \( q_- < W_- W_+ \), and vice versa. For

\[
Q > 0, \text{ we also have that } q_- < W_- W_+ \text{ if } q_+ < W_- W_+. \quad (7.8)
\]

Since for \( Q = 0 \), \( n = 0 \) and otherwise \( |Q| > 1 \) we have generally that \( n \leq (1 + 2W_- W_+) |Q| = |\lambda Q| \).

**Lemma 7.2.** Let \( \{A_j\} \) be a regular sequence of domains with \( V(A_j) = V_j \) and let \( K \) be a compact subset of \( \{ \rho : |\rho| < \rho_0 \} \). Let \( \mathbf{P} \) be a fixed chemical potential. Then there exists a sequence of numbers \( \{\epsilon_j\} \) (depending on \( K \) and \( \mathbf{P} \)), tending to zero as \( j \to \infty \), such that

\[
A(\mathbf{N}, \mathbf{n}; A_j) = \mu \cdot \mathbf{n} V_j^{-1} + g(\mathbf{MV}_j^{-1}; A_j) - g(\mathbf{NW}_j^{-1}; A_j) \leq \epsilon_j, \quad (7.9)
\]

whenever \( \mathbf{MV}_j^{-1} \in K \) and \( \mathbf{M} = \mathbf{N} + \mathbf{n} \) as in Lemma 7.1.

**Proof.** Let \( R_j \) be the radius of the ball \( B_j \) referred to in (5.1) and let \( B_j^+ \) be a ball concentric with \( B_j \) having a radius \( R_j = R_j + dR_j^{1/2} \) with \( d > 0 \) a constant. The spherical shell \( B_j^+ \backslash B_j \) will be denoted by \( D_j \), the domain \( A_j \cup D_j \) by \( A_j' \), and we shall set \( V_j' = V(D_j) \), so that \( V_j' = V(A_j') = V_j + V_j^+ \). Clearly, \( \{A_j'\} \) is a sequence of regular domains with \( V_j' V_j \to \infty \) as \( j \to \infty \). At this point we again make use of the construction involving hyde particles introduced in Section VI. We consider a neutral system of \( \mathbf{N} + \mathbf{n} + \mathbf{n}^0 \) particles in \( A_j' \) (with \( n^0 = |Q| \) the number of hyde particles). Since \( D_j \) is here a spherical shell, the charge distribution of the \( n^0 \) hyde particles in \( D_j \) will be spherically symmetric and will produce a constant electrostatic potential \(-Q/R_j' \). \( R_j < R_j' \leq R_j^+ \), in \( A_j' \). Application of inequalities analogous to (6.10) readily yields

\[
A(\mathbf{N}, \mathbf{n}; A_j) \leq \mu \cdot \mathbf{n} V_j^{-1} + (V_j'/V_j) g[\mathbf{N} + \mathbf{n} + \mathbf{n}^0]/V_j'; A_j' |g(\mathbf{N}/V_j'; A_j) - g(\mathbf{N}/V_j; A_j) - Q^g(V_j R_j')^{-1} - V_j^{-1} \ln Z(n^0; D_j). \quad (7.10)
\]

An upper bound to (7.10) is now obtained by combining the following observations:

(i) Let \( \rho = \mathbf{N}/V_j \), \( \rho^* = (\mathbf{n} + \mathbf{n}^0)/V_j' \), \( \rho^* = (\mathbf{N} + \mathbf{n} + \mathbf{n}^0)/V_j' = (V_j'/V_j) \rho + \rho^* \).

\[
(7.11)
\]
and consider $\rho$ and $\rho'$ to be particle density vectors in $\mathbb{R}^{s+1}$ (with $\rho^0 = 0$). By the condition of the lemma, both $\rho$ and $\rho'$ will be in $K'$ where $K'$ is a compact subset of $\{ |\xi| < \rho_c, \xi \in \mathbb{R}^{s+1} \}$. $K'$ is the product of $K$ and the interval $[0, \max_{\xi} |Q|/V_j^{-1}]$. The uniform convergence of the neutral $g(\rho; A_j)$ to $g(\rho)$ implies that

$$|g(\rho; A_j) - g(\rho)| \leq \varepsilon_j', \quad |g(\rho'; A_j) - g(\rho')| \leq \varepsilon_j', \quad (7.12)$$

where $\varepsilon_j' \to 0$ as $j \to \infty$ and is independent of $\rho$ and $\rho'$ for $\rho$ and $\rho'$ in $K'$.

(ii) By Theorem 5.1 $g(\rho)$ is continuous in $K'$. Hence given any $\varepsilon > 0$, there exists a $\delta > 0$ such that

$$|g(\rho) - g(\rho')| \leq \varepsilon \quad \text{if} \quad |\rho - \rho'| \leq \delta, \quad (7.13)$$

with $\rho$ and $\rho'$ in $K'$, $\chi$ and $\delta$ are constants and $\delta \to 0$ as $\varepsilon \to 0$.

(iii) By part (iv) of Lemma 7.1 $\rho^0 \leq (\lambda + 1) |Q|/V_j$. Combining these remarks and remembering that $[V_j'/V_j - 1] = \varepsilon_j' \to 0$ as $j \to \infty$, we readily see that for sufficiently large $j$,

$$[(V_j'/V_j), g(V_j'/V_j) \rho + \rho'; A_j)] - g(\rho; A_j) \leq \varepsilon_j + 2\varepsilon, \quad \text{if} \quad (\lambda + 1)|Q|/V_j' < \delta,$$

$$\varepsilon_j + \varepsilon + \varepsilon_j, \quad \text{if} \quad (\lambda + 1)|Q|/V_j' \geq \delta, \quad (7.14)$$

with $\varepsilon_j \to 0$ as $j \to \infty$.

To obtain an upper bound on $-V_j^{-1} \ln Z(n^0; D_j)$ we again use the inequality (6.4) with the functions $\psi_\lambda$ constructed as in Section VI. We must, however, be careful with the choice of the size of the cubes $2y$, so that the number of cubes $M_j$ in $D_j$ satisfies the condition $M_j \geq n^0 = |Q|$. Now the volume of $D_j$ grows as $R_j^{y/2}$. We shall therefore choose the length of the side of the cubes $L$, $2y$, as $y = \min(\gamma_0, K_1 R_j^{5/6}|Q|^{-1/3})$, with $\gamma_0$ and $K_1$ constants chosen to insure that $M_j \geq |Q|$. Since the kinetic energy of a particle in a ball of radius $y$ is proportional to $y^2$, we find that

$$-\ln Z(n^0; D_j) \leq J^{-1} \sum_{a=1}^J (\psi_\lambda, [T(n^0) + U] \psi_\lambda) \leq \max[B \big| Q \big|, C \big| Q \big|^{5/3} R_j^{-3/5}] + \frac{1}{2} Q n^0 R_j^{-1} (1 + \gamma_j), \quad (7.15)$$

where $T(n^0)$ is the kinetic energy operator and $U$ is the Coulomb energy of the hyle particles, $B$ and $C$ are constants and $\gamma_j \to 0$ as $j \to \infty$. The first term on the right side of (7.15) is a bound on the kinetic energy, while the factor $\gamma_j$ in the second term represents the difference between the Riemann sum (cf. (6.8)) and the integral for the Coulomb self-energy. Finally we note that

$$|\mu \cdot n_j V_j^{-1}| \leq \lambda |\mu| |Q| V_j^{-1}, \quad (7.16)$$

where $|\mu| = \sum_{j=1}^s |\mu_j|$. Substituting the bounds (7.14), (7.15) and (7.16) into (7.10) we obtain

$$A(N, n; A_j) \leq \varepsilon_j + \frac{1}{2} |Q| V_j^{-1} (B' + C |Q|^{5/3} R_j^{-1/5})$$

$$- \frac{1}{2} |Q| V_j^{-1} (1 - \gamma_j - 2(R_j^0 - R_j)/R_j^0)$$

$$+ \frac{1}{2} |Q| V_j^{-1} \geq \delta(\lambda + 1)^{-1}, \quad (7.17)$$

where $B'$ is again some constant.

We now take $n_j$ sufficiently large so that $[1 - \gamma_j - 2(R_j^0 - R_j)/R_j^0] \geq 4/5$ and divide up the possible value of $|Q|$ into two ranges: (a) $|Q| \leq V_j^{1/3}$, and (b) $|Q| > V_j^{1/4}$. In case (a), the second term in (7.17) vanishes as $j \to \infty$ and $|Q| V_j^{-1} \leq 2\lambda(\lambda + 1)^{-1}$ for any $\varepsilon > 0$. In case (b), the right side of (7.17) is negative for sufficiently large $j$; indeed this will be true if we replace the $1/2$ in front of the $Q^2 V_j R_j^{-1}$ term by $\frac{1}{3}$. Since $\varepsilon$ can be made arbitrarily small, this yields

$$A(N, n; A_j) \leq \varepsilon_j - \frac{1}{2} \frac{Q^2}{V_j R_j} \leq \varepsilon_j - \frac{\lambda}{2} \frac{n^0}{V_j R_j}, \quad (7.18)$$

where $\varepsilon_j \to 0$ and is independent of $N$ and $n$ for $(N + n) V_j^{-1} \in K$, which proves the lemma.

**Lemma 7.3.** Let $\{A_j\}$ be a regular sequence of domains as in Lemma 7.2. Then there exist some fixed, strictly positive constants $c$, $k$ and $\alpha$ independent of $j$ such that

$$Z(M; A_j) \leq \left\{ \prod_{t=0}^s (M_t)^{-1} [V_j M_t] \right\} \times \exp \left\{ c V_j + k \sum_{t=0}^s M_t - \alpha V_j^{-1} \psi(M \cdot E)^{a} \right\} \quad (7.19)$$

for $j$ sufficiently large.
Proof. Using the same notation as in Lemmas 7.1 and 7.2, with $M = N + n$, we have

$$Z(M; A_j) \leq Z(N + n + n^0; A_j)[Z(n^0; D_j)]^{-1} \exp[-Q^*]$$

$$= Z(N + n + n^0; A_j) \exp[k_1 |Q| - \alpha V_j^{1/3}Q^*]$$

(7.20)

with $k_1$ and $\alpha$ some constants and we have used (7.15). Applying (2.13) yields

$$Z(N + n + n^0; A_j) \leq \exp \left[ \frac{1}{2} \left( \sum_{i=1}^{s} M'_i + |Q| \right) B_i \right] \prod_{i=1}^{s} Z_{0,0}(M'_i; A_j) Z_{0,0}(n^0; A_j),$$

with $Z_{0,0}(M'_i; A_j)$ the ideal gas partition of the $i$-th species (with masses $m_i' = 2m_i$) and $Z_{0,0}(n^0; A_j)$ the ideal gas partition function of the hyle particles (which are fermions).

The ideal gas partition functions of $N$ fermions or bosons with mass $m$ in a domain $A$ satisfy the following inequalities (Fisher, 1964; Ruelle, 1969):

$$Z_0^-(N; A) \leq Z_0^+(N; A),$$

(7.21)

$$Z_0^-(N; A) \leq \nu^N(N) - 1 [V(A)]^N = Z_0^+(N; A),$$

(7.22)

$$Z_0^+(N; A) \leq \theta^{-N(1 - \theta^{-1})}, \quad \text{for all } \theta, 0 < \theta < 1,$$

(7.23)

where the superscripts $-$, $+$, $cl$ refer to fermions, bosons and classical particles, respectively, $\nu \equiv (2\pi m^0h^0)^{3/2}$. Noting now that (i) $|Q| \leq w \sum_{i=1}^{s} M_i$ where $w = \max\{|e_i|: i = 1,\ldots, S\}$; (ii) $(V_j/V_j) < \delta$, $\delta$ fixed; and (iii) that by assumption species $a + 1,\ldots, S$ are fermions, proves the lemma.

**Lemma 7.4.** Let $\{A_j\}$ be as in Lemma 7.2. Then there exists a positive number (density) $\gamma$ independent of $j$ (but depending on $\nu$) such that the sum of all the terms in the grand partition function $\Xi(\nu; A_j)$, defined in (7.1), for which $\max[M^+ = \sum_{i=1}^{s} M_i', M^- = \sum_{i=0}^{s} M_i'] > 2\gamma V_j$ approaches zero as $j \to \infty$, i.e.,

$$\Xi(\nu; A_j; : \nu) = \sum_{\nu} \exp[\nu \cdot M] Z(M; A_j) \to 0$$

(7.24)

as $j \to \infty$ for $\nu > \gamma$ and the star indicates that the sum is taken only over those $M'_i$ which satisfy the inequality $M^+ > 2\nu V_j$ or $M^- > 2\nu V_j$.
Since the sum in (7.30) is symmetric in the $M^i$, $i = a + 1, \ldots, S$, we obtain an upper bound on the sum if we carry out an unrestricted sum on $M^{a+1}, \ldots, M^{S-1}$ (over all nonnegative integers), but require that $M^S \geq \nu V_j [w(S-a)]^{-1}$ and then multiply by $(S-a)$. This yields, with $b = b(1 + w)$,

$$
\mathcal{E}_3(\mu; A_j : v) \leq \exp[(c + v b + (S - a - 1) e^0) V_j] \sum_i (N_i)^{-1} [V_j e^0]^N_i, \tag{7.31}
$$

with $b = k + |\mu| + a$. The last sum is over all integers

$$
N \geq \nu V_j [w(S-a)]^{-1}.
$$

It has the upper bound

$$
[w(S-a)[\exp(b + 1)]\nu^{-1} r V_j[w(S-a)]^{-1}]
\times \sum_i \{\nu^{-1} r w(S-a)[\exp(b + 1)]\nu^{-1}\}^i,
$$

since $N! \geq (N/e)^N$. Summing this series (for $\nu$ sufficiently large) and substituting the result in (7.31) gives an upper bound of the form

$$
\mathcal{E}_4(\mu; A_j : v) \leq (1 - K_1/\nu)^{-i} (K_2/\nu)^r V_j[w(S-a)]^{-1}, \tag{7.32a}
$$

with $K_1$, $K_2$ some constants independent of $j$ or $\nu$ (but depending on $\mu$). Choosing $\nu > K_1$ and $\nu = \eta$, the right side of (7.32) will approach zero as $j \to \infty$.

To obtain an upper bound on (7.26), we again use (7.19), noting that for all the terms in the sum in (7.26), $[Q_+ - Q_-]^a \geq [\nu V_j]^a + [Q_+ - Q_- - \nu V_j]^a$. Hence,

$$
\mathcal{E}_3(\mu; A_j : v) \leq \exp\left[-\alpha \nu^{1/2} V_j^{1/2} + c V_j\right]
\times \sum_{i=0}^{\infty} \{\sum_{N=1}^{\infty} \cdots \sum_{N=S}^{\infty} \exp \left[ b \left( Q_+ + \nu V_j + N + \sum_{i=a+1}^{S} M^i \right) \right]
\times \prod_{i=a+1}^{S} (M^i)^{-1} V_j^{(N)^2}) \exp\left[-\alpha V_j^{1/2} N^2\right]
\times \exp\left[ -\alpha \nu^{1/2} V_j^{1/2} + V_j(c + (S-a) \exp[(1 + w)b])\right]
\times \sum_{N=0}^{\infty} \exp[b N - \alpha V_j^{1/2} N^2], \tag{7.32b}
$$

where we have set $N = Q_+ - Q_- - \nu V_j$, and have performed the summation over $M^i$, $i = 1, \ldots, a$, for each $N$. Due to the $V_j^{1/2}$ term in the exponent the right side of (7.32) will clearly approach zero as $j \to \infty$ proving the lemma.

**Lemma 7.5.** With $\{A_j\}$ as before and for $j$ large enough

$$
\mathcal{E}(\mu; A_j) \leq \mathcal{E}(\mu; A_j) \leq 2\mathcal{E}(\mu; A_j), \tag{7.33}
$$

where

$$
\mathcal{E}(\mu; A_j) = \sum_{M} \cdots \sum_{M} \exp[\mu \cdot M] Z(M; A_j) = \exp[V_j \mathcal{E}(\mu; A_j)]. \tag{7.34}
$$

The prime on the summation indicates that the sum is restricted to values of $M$ for which $M^+ \leq 2\eta V_j$ and $M^- \leq 2\eta V_j$.

**Proof.** The first inequality is obvious and the second follows from Lemma 7.4 and the observation that $Z(0; A_j) = 1$.

It is clearly sufficient to deal from now on with $\mathcal{E}(\mu; A_j)$. Note that the sum in (7.34) contains no more than $(1 + 2\eta V_j)^{2}$ terms. In particular, therefore, for all terms in (7.34) $M V_j^{-1}$ will lie in a compact set $K$ of $\rho$.

When some (or all) of the species have hard cores, there will be a critical surface $\rho_c$ (cf. Section IV) such that for sufficiently large $j$, $Z(M; A_j) = 0$ if $|M| V_j^{-1} \geq (1 + \epsilon)\rho_c$, i.e., $M V_j^{-1}$ is outside $(1 + \epsilon)\rho_c$, with $\epsilon > 0$, arbitrary.

**Definition.** We shall denote by $K_c$ the compact set $\{\rho : \rho \in K, |\rho| \leq (1 + \epsilon)\rho_c\}$, and by $\mathcal{E}_c(\mu; A_j)$ the sum in (7.34) when $M V_j^{-1}$ is restricted to be in $K_c$ (with a corresponding meaning for $\mathcal{E}(\mu; A_j)$). The symbols $\mathcal{E}(\mu; A_j)$, $\mathcal{E}_c(\mu; A_j)$, $\hat{\mathcal{E}}(\mu; A_j)$ and $\hat{\mathcal{E}}_c(\mu; A_j)$ will denote the same quantities as those without primes except that the summation in (7.34) will now be restricted to neutral systems $M \cdot E = 0$, which implies that $M V_j^{-1} \in K_c' = \{\rho : \rho \cdot E = 0\} \cap K_c$.

**Lemma 7.6.** (i) $\lim_{j \to \infty} \hat{\mathcal{E}}(\mu; A_j) = \max_{\rho \in K_c'} [\mu' \cdot \rho + g(\rho)] = \hat{\mathcal{E}}(\mu) = \hat{\mathcal{E}}(\mu')$ where $\mu' = \mu - (\mu \cdot E) E(E \cdot E)$.

(ii) $\lim_{j \to \infty} \hat{\mathcal{E}}_c(\mu; A_j) = \hat{\mathcal{E}}_c(\mu) = \hat{\mathcal{E}}(\mu)$. 

Lemma 7.7. (i) \( \lim_{j \to \infty} \hat{\Psi}(\mu; A_j) = \hat{\Psi}(\mu) \).

(ii) \( \lim_{j \to \infty} \hat{\theta}(\mu; A_j) = \hat{\theta}(\mu) \).

Proof. As we already noted, given any \( \epsilon > 0 \), \( \mathbf{Z}(\mathbf{M}; A_j) = 0 \) for sufficiently large \( j \) if \( |\mathbf{M} V_j^{-1} | \geq 1 + \epsilon | \mathbf{p}_0 | \). Hence for larger \( j \), the only nonzero contributions to the sum in (7.34) will come from those values of \( \mathbf{M} \) for which \( \mathbf{M} V_j^{-1} \in K_{\epsilon} \), where \( K_{\epsilon} = \{ \mathbf{p} \in K \mid |\mathbf{p}| < 1 + \epsilon \} \). Now it is readily seen that to any domain \( A_j \) (with \( j \) sufficiently large), we can associate (e.g., by expanding \( A_j \) uniformly) a larger domain \( A_j \supset A_j \), having a volume \( V(A_{\delta}) = V_j \), and \( V_{\epsilon} \leq (1 + \delta) V_j \) where \( \delta \) is independent of \( j \) and depends on \( \epsilon \) in such a way that \( \delta \to 0 \) as \( \epsilon \to 0 \). The domain \( A_j \) has the property that whenever \( \mathbf{M}_j V_j^{-1} \in K_{\epsilon} \), \( \mathbf{M}_j V_j^{-1} \in K_{\epsilon} \).

We thus find that \( \hat{\mathcal{Z}}(\mu; A_j) \leq \hat{\mathcal{Z}}(\mu; A_j) \leq \hat{\mathcal{Z}}(\mu; A_j) \leq (1 + \delta) \hat{\mathcal{Z}}(\mu; A_j) \). Taking logarithms and dividing by \( V_j \), gives \( \hat{\Psi}(\mu; A_j) \leq \hat{\Psi}(\mu; A_j) \leq (1 + \delta) \hat{\Psi}(\mu; A_j) \). Taking the limit \( j \to \infty \) and then letting \( \epsilon \to 0 \) proves part (i) of the lemma. Part (ii) is proven in the same way.

Combining Lemmas 7.6 and 7.7 proves Theorem 7.1.

Definition. The grand canonical ensemble average particle number vector in the domain \( A_j \), \( \langle \mathbf{M} \rangle = \langle \mathbf{M} \rangle \), is defined as \( \langle \mathbf{M} \rangle = \langle \mathbf{M} \rangle \sum_{\mathbf{M}=0}^{\infty} \cdots \sum_{\mathbf{M}=0}^{\infty} \mathbf{M} ! \exp[\mu \cdot \mathbf{M}] \mathbf{Z}(\mathbf{M}; A_j) \), with similar definitions for \( \langle \mathbf{M} \rangle \), etc. Other averages of interest are \( \langle \mathcal{O} \rangle = \langle \mathcal{O} \rangle \cdot \mathbf{E} \), \( \langle \mathcal{O} \rangle = \langle \mathcal{O} \rangle \cdot \mathbf{E} \), and \( \langle \mathcal{O} \rangle \cdot \mathbf{E} = \langle \mathcal{O} \rangle \cdot \mathbf{E} \). The limit of \( \langle \mathcal{O} \rangle \) as \( j \to \infty \), will be denoted where it exists by \( \hat{\mathcal{O}}(\mu) \).

Lemma 7.8. (i) \( \lim_{j \to \infty} \langle \mathcal{O} \rangle V_j^{-1} = 0 \).

(ii) \( \lim_{j \to \infty} \langle \mathcal{O} \rangle V_j^{-1} = \langle \mathcal{O} \rangle \cdot \mathbf{E} \) if \( \pi(\mu; A_j) \) exists almost everywhere.

Proof. The proof of this lemma is based on the following fact: If \( f(x) \) is a sequence of convex functions which approach a limit \( f(x) \) as \( j \to \infty \), then \( f(x) \) is convex and \( (d/dx) f(x) \to (d/dx) f(x) \) wherever the latter exists, which is almost everywhere.

From its definition \( \langle \mathcal{O} \rangle V_j^{-1} = \langle \mathcal{O} \rangle \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} \). It is readily verified that \( \pi(\mu; A_j) \) is convex in each \( \mu_k \). This proves part (ii) of the lemma. To prove part (i) we write \( \mu = \mu + \lambda \mathbf{E} \), with \( \lambda = \langle \mu \cdot \mathbf{E} \rangle / (\mathbf{E} \cdot \mathbf{E}) \). It is readily seen that \( \langle \mathcal{O} \rangle V_j^{-1} = \langle \mathcal{O} \rangle \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} \). Since the limit \( \pi(\mu + \lambda \mathbf{E}; A_j) \) is independent of \( \lambda \) part (i) follows.

Remarks. (i) Lemma 7.8 shows in a striking way the special nature
of the Coulomb potential. In the absence of the Coulomb potential, but for any tempered potential, one can, by properly choosing the various chemical potentials $\mu_j$, induce essentially any desired values of the densities $\rho_j(\mu)$ of the various components. For Coulomb potentials, on the other hand, only neutral densities appear in the thermodynamic limit.

(ii) If we think of $\rho_j(\mu)$ as a function of the charges of the various species $\{e_j\}$, and consider some limit in which some or all of $e_j$'s vanish then clearly the value $\rho_j(\mu)$ in this limit will be very different from what it would be if we had set these $e_j$'s equal to zero before going to the thermodynamic limit, $j \to \infty$.

An interesting question now arises about the behavior of the charge fluctuations per unit volume,

\[ V_j^{-1}(Q^{(p)} - \langle Q^{(p)} \rangle) = \frac{\partial^2}{\partial \mu_j} \pi(\mu + \lambda E; A_j), \]

when $j \to \infty$. We expect on the basis of convincing but nonrigorous arguments that the left side of (7.39) should vanish as $V_j^{-2/3}$, but we have been unable even to prove that it vanishes.

We note, however, the following: Consider a system in which all the species of particles have hard cores (this is not essential but makes things simple), and let $\exp[\mu_j] = z_j$ be the fugacity of the $j$-th species. Then the grand partition function $Z(z_1, ..., z_S; A_j)$ is a polynomial in the $z_j$'s (Yang and Lee, 1954) whose order is proportional to $V_j$. In the space of the $S$ complex variables $z_1, ..., z_S$, the pressure $\pi(z_1, ..., z_S; A_j)$ will be singular wherever $Z(z_1, ..., z_S; A_j)$ vanishes. This clearly cannot happen, for any finite $j$, in some neighborhood $\epsilon_j$ of the “physical part”, $P^S$, of $C^S$; $P^S = (z: z_i \geq 0, i = 1, ..., S)$, so that $\pi(z; A_j)$ is real analytic in the $z_i$'s on $P^S$. As $j \to \infty$, $\epsilon_j$ may go to zero and we expect that $\pi(z_1, ..., z_S) = \pi(\mu)$ will have singularities on $P^S$ (representing “phase transitions” of the system).

Consider a domain $D \subset C^S$ which is free of zeros of $Z(z_1, ..., z_S; A_j)$, for sufficiently large $j$, and whose intersection with $P^S$ has an $S$-dimensional Lebesgue measure $V(D \cap P^S) > 0$. The pressure $\pi(z; A_j)$ will then be analytic in $D$ and approach a limit as $j \to \infty$ for $z \in D$ and $A$. It can also be verified that there is a bound $|\pi(z; A_j)| \leq A$ for $z \in D$ and $A$ is independent of $j$ (see, for example, Lebowitz and Penrose, 1968, Section IV). It follows then from Vitali's Theorem that the limit function $\pi(z)$ is analytic in $D$ and that all the derivatives of $\pi(z; A_j)$ approach the derivatives of $\pi(z)$.

It follows, for $z \in D$, that since $\pi(\mu) = \pi(\mu + \lambda E) = \pi(\mu')$ is independent of $\lambda$, all derivatives of $\pi(\mu + \lambda E; A_j)$ with respect to $\lambda$ will vanish as $j \to \infty$, and so in particular will the charge fluctuations per unit volume. Unfortunately, the existence of such a domain $D$ for Coulomb systems is not known at present. (For tempered potentials, there is always some $2$-dimensional ball containing the origin $z = 0$ in which $Z(z; A_j)$ is free of zeros, for large $j$. The radius of this ball is, however, inversely proportional to the second virial coefficient and hence vanishes for Coulomb systems.)

VIII. THE MICROCANONICAL ENSEMBLE FOR NEUTRAL SYSTEMS

In the foregoing pages we discussed the existence and properties of the canonical and grand canonical free energies per unit volume. The microcanonical ensemble is an ensemble of even more physical and historical importance. From it the requisite thermodynamic properties of the canonical and grand canonical ensembles may be deduced directly on general grounds, but the converse is not true. The microcanonical partition function $\Omega(E, N; A)$, is a function of energy $E$, the domain $A$, and the particle number vector $N$. There are many ways to define $\Omega$, but in any case one defines an entropy/unit volume $s$ as a function of density $\rho$ and energy/unit volume $e$ by

\[ s(e, \rho; A) = V^{-1} \ln \Omega(eV, \rho V; A), \]

where $V = V(A)$. In addition to showing that $s$ has a thermodynamic limit which is concave in $(e, \rho)$, one also has to show that the various definitions of $\Omega$ yield the same limiting $s$ function (see Ruelle, 1969, and references quoted therein).

It turns out that the proofs of these assertions generally do not deal directly with $s$ but rather with its inverse function $e(s, \rho; A)$. It is the $e$ function that satisfies the desirable inequalities. Instead of following the usual route of first defining $s$ and then $e$ we shall in subsection A define $e$ directly to suit our purposes. We shall show that it has all the requisite thermodynamic properties for neutral systems in general domains as we did in Sections IV and V for the canonical free energy. In subsection B we shall show that our definitions of $e$ and $s$ (which is defined to be the inverse of our $e$ function) agree with the usual definitions in the thermodynamic limit. The “equivalence” of the microcanonical ensemble to the
canonical and grand canonical ensembles in this limit is a consequence of the general arguments already developed for non-Coulomb systems (cf. Ruelle, 1969).

A. The Microcanonical Energy Function $\varepsilon$

We shall carry out the analysis for quantum mechanical systems. Analogous results and definitions hold for classical systems when $H$-stability is satisfied.

**Definition.** Consider a quantum system in a domain $A$ (of volume $V$) with particle density $\rho$. Let $E_1 \leq E_2 \leq \cdots$ be the eigenvalues of the Hamiltonian arranged in increasing order (including multiplicity). Let $\sigma \in \mathbb{R}^1$ and let $l \geq 1$ be the smallest integer $\geq \exp(\sigma V)$. Then the energy function is defined by

$$\varepsilon(\sigma, \rho; A) = (Vl)^{-1} \sum_{i=1}^{l} E_i. \quad (8.2)$$

**Remarks.**

(i) $\varepsilon$ is lower semicontinuous in $\sigma$ and is, in fact, a sum of step functions. It is not defined by linear interpolation insofar as $\sigma$ is concerned. Implicit in the above definitions is that $\varepsilon$ is defined by Eq. (8.2) when the particle numbers are integral, and is defined for other values of $\rho$ by linear interpolation in subsection IV-C. A more refined, but equivalent point of view is to regard each individual energy level (which depends on $\rho$ and $A$) as being defined for all $\rho$ through linear interpolation. This interpolation is to be understood in terms of multiplet numbers as explained in subsection IV-F. We shall need this in Eq. (8.4). Lemma 4.3 will again be required to insure that the inequalities below are satisfied for all $\rho$.

(ii) $H$-stability provides the lower bound

$$\varepsilon(\sigma, \rho; A) \geq -\rho B, \quad (8.3)$$

as given in (2.10).

(iii) The range of $\varepsilon(\sigma, \rho; A)$ is $[\varepsilon_1, \infty)$, since the Hamiltonian is unbounded above, $\varepsilon_1 = E_1/V$.

(iv) It is clear from the definitions that $\varepsilon$ is nondecreasing in $\sigma$. Hence, the energy function has a pseudoinverse called the entropy

function which will be denoted by $\sigma(\varepsilon, \rho; A)$. It is given explicitly by

$$\sigma(\varepsilon, \rho; A) = V^{-1} \ln \left[ \sup \{ \varepsilon : \varepsilon(\sigma, \rho; A) \leq \varepsilon \} \right] \quad (8.4)$$

for $\varepsilon \geq \varepsilon_1$ (which depends upon $A$ and $\rho$). Alternatively,

$$\sigma(\varepsilon, \rho; A) = \sup \{ \varepsilon : \varepsilon(\sigma, \rho; A) \leq \varepsilon \}, \quad (8.5)$$

which is a definition applicable to the classical case as well.

The entropy function is upper semicontinuous in $\varepsilon$. It is also piecewise constant in $\varepsilon$ as is the case for $\varepsilon$ as a function of $\sigma$. It is this latter fact that prevents the energy function from having a true inverse, i.e., $\varepsilon(\varepsilon', \rho; A), \rho; A \neq \varepsilon'$ for all real $\varepsilon'$. What is true is that

$$\sigma(\varepsilon', \rho; A), \rho; A = \sup \{ \sigma : \varepsilon(\sigma, \rho; A) \leq \varepsilon' \}. \quad (8.6)$$

Implicit in Eq. (8.4) is the notion that each $E_i$ is defined for all $\rho$ by linear interpolation as explained before. Thus, the definition (8.4) of $\sigma$ is not the same as one would obtain if one defined $\sigma$ for nointegral particle numbers by linear interpolation of $\varepsilon$. In other words, we have given priority to the energy function. It is also to be noted that while the domain of $\varepsilon$ (in $\sigma$) is $(-\infty, \infty)$, the domain of $\sigma$ (in $\varepsilon$) is $[\varepsilon_1, \infty)$.

We turn now to the minimax principle (Appendix B) which states that if $\{\psi_i\}, i = 1, \ldots, l$ is a set of $l$ orthonormal functions (called variational functions) in the domain of the Hamiltonian $H$ and that if we form the $l$-square Hermitian matrix $A$ whose elements are $A_{ij} = \langle \psi_i, H\psi_j \rangle$, and label the eigenvalues of $A$ as $\lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_l$ then $\lambda_i \geq E_i$ for $i = 1, \ldots, l$. In particular, for integral particle numbers,

$$\varepsilon(\sigma, \rho; A) \leq (Vl)^{-1} \text{Tr} \ A, \quad (8.7)$$

where $\exp(\sigma V) = l$. This formula shows the advantage of our definition of $\varepsilon$ because all we need to know are the diagonal elements of $A$.

To apply this principle, let $A_1 \supset A_1 \cup A_2$, with $A_1$ and $A_2$ disjoint, and let $N = N_1 + N_2$ be the respective particle number in the various domains. If

$$\{\psi_i^1, E_i^1\}, i = 1, \ldots, n_1 \quad \text{(resp. } \{\psi_i^2, E_i^2\}, i = 1, \ldots, n_2 \text{)}$$

are the first $n_1$ (resp. $n_2$) eigenfunctions and eigenvalues in $A_1$ (resp. $A_2$), we can form the set of $n_1n_2$ variational functions in $A$ by $\psi_i = \psi_i^1 \otimes \psi_i^2$. 

To evaluate the right hand side of (8.7) we need consider only $A_{ij,ij}$ and this is given by

$$A_{ij,ij} = E_i^1 + E_j^1 + U_{ij},$$  \hspace{1cm} (8.8)

where $U_{ij}$ is the expectation value of the interdomain part of the potential energy. Obviously, (8.8) generalizes in a trivial way when $A$ contains more than two disjoint subdomains.

The average interaction $U_{ij}$ consists of a non-Coulomb—but tempered—part and a Coulomb part, which we shall denote by $U_{ij}^c$ and $U_{ij}^s$, respectively. The former can be easily bounded; for example, if $A$ is a standard ball packed in the standard manner we can use Lemma 4.2. Bounding $U^c$ is slightly more complicated.

Suppose that $A_1$ in the previous discussion is a ball $B$. Each index $i$ denoting the eigenfunctions and eigenvalues of the Hamiltonian in $B$ can best be written as a pair $(\alpha, m)$ where $\alpha$ denotes the principal quantum numbers, including the angular momentum, $L(\alpha)$ (irreducible representation of the rotation group), and $m$ denotes the magnetic quantum number (row of the representation). The energy $E_i$ depends only on $\alpha$ and not on $m$. Suppose further that $n_1$ is such that for every $\alpha$ all the levels $(\alpha, m)$ with $-L(\alpha) \leq m \leq L(\alpha)$ appear in the list $1, \ldots, n_1$ if any one $(\alpha, m)$ does. In that case we shall say that $n_1$ is perfect. When we do the sum $\sum_{m=-L}^{L} U_{ij}^c(\alpha, m, i, j)$, which is part of the sum in (8.7), we have to evaluate an average charge density in $A_1$ which involves integrals over all but one of the $N_1$ particle coordinates in $B$, such as

$$I_s(r) = \sum_{m=-L}^{L} \int |\psi_{(\alpha, m)}(r_1, \ldots, r_{N_1})|^2 dr_2 \cdots dr_{N_1}.$$  \hspace{1cm} \text{(8.9)}

Clearly $I_s$ depends only on the distance of $r$ from the center of $B$. If, in addition, we postulate that $\mathbf{N}_1 \cdot \mathbf{E} = 0$, i.e., that $A_1$ contains a neutral mixture of particles, then the average Coulomb potential outside of $A_1$ will vanish by Newton's theorem. That is,

$$\sum_{i=1}^{n_1} U_{ij}^c = 0 \quad \text{for all } j,$$

regardless of the shape of $A_2$ and of its constituent particles. If $n_1$ is not perfect, it lies between two perfect numbers $\mu$ and $\nu$, $\mu < n_1 < \nu$, $\nu - \mu = 2L(\alpha) + 1 = t$, where $\nu$ is the last principle quantum number appearing in the first $n_1$ levels. The sum $\sum_{i=1}^{\mu} U_{ij}^c = 0$ and can be ignored.

We are then left with $\mathcal{U} = \sum_{i=1}^{n_1} U_{ij}^c$, where $U_{ij}^c = \sum_{j=1}^{n_1} U_{ij}^c$. The key fact is that we can relabel the last $t$ levels in $\nu$ such that $\mathcal{U} \lesssim 0$. This is so because $\sum_{i=1}^{\mu} U_{ij}^c = 0$.

The following lemma generalizes this idea to the case where $A$ contains a finite number, say $M + 1$, of subdomains, the first $M$ of which are balls with neutral mixtures of particles and the last one is arbitrary.

**Lemma 8.1.** Let $F : (Z^+)^M \rightarrow \mathbb{R}_1$ and let $t$ and $p$ be two elements of $(Z^+)^M$ such that $p_i \leq t_i$, $i = 1, \ldots, M$. Suppose that

$$\sum_{i=1}^{t_1} \cdots \sum_{i_M=1}^{t_M} F(i_1, \ldots, i_M) \leq 0.$$

Then it is possible to relabel the $M$ sets of integers $(1, \ldots, t_1), \ldots, (1, \ldots, t_M)$ such that $\sum_{i_1=1}^{p_1} \cdots \sum_{i_M=1}^{p_M} F(i_1, \ldots, i_M) \leq 0$.

**Proof.** Define $F : Z^+ \rightarrow \mathbb{R}_1$ by

$$F(i) = \sum_{i_1=1}^{t_1} \cdots \sum_{i_M=1}^{t_M} F(i_1, i_2, \ldots, i_M),$$

so that $\sum_{i=1}^{t_1} \cdots \sum_{i_M=1}^{t_M} F(i) \leq 0$.

Relabel the integers $(1, \ldots, t_1)$ so that $F(1) \leq F(2) \leq \cdots$. Then $\sum_{i=1}^{p_1} F(i) \leq 0$.

We can repeat this process inductively, i.e.,

$$(t_1, t_2, \ldots, t_M) \rightarrow (p_1, t_2, \ldots, t_M) \rightarrow (p_1, p_2, \ldots, t_M) \rightarrow \ldots.$$  \hspace{1cm} \text{(8.10)}

To apply this lemma, we identify

$$F(i_1, \ldots, i_M) = \sum_{i_M=1}^{p_M} U_{ij}^c(i_1, i_2, \ldots, i_M).$$

This shows that the interdomain Coulomb interaction in (8.7) is negative when $A$ contains a finite number of subdomains at most one of which is nonspherical and/or nonneutral.

Returning now to the case of two subdomains and under the foregoing condition that $A_1$ is a ball with a neutral mixture of particles, we can write, for $i = 1, 2$, $x_i = V_i^T$ and $\exp(x_i V_i) = n_1$, so that if $\exp(\sigma V) = n_1, n_2$, then $\sigma = x_1^2 \sigma_1 + x_2^2 \sigma_2$. Then, if $\epsilon_i$ denotes the energy function of $A_i$,

$$\epsilon(x_1 \sigma_1 + x_2 \sigma_2, x_3 \phi_1 + x_4 \phi_2; A_1) \leq \epsilon_1 \sigma_1 \phi_1 + \epsilon_2 \phi_2; A_2 \leq \mathcal{U},$$  \hspace{1cm} \text{(8.10)}
where $\bar{U}$ is some bound on $U^\tau$. This is true when $n_1, n_2, N_1$ and $N_2$ are integral, but it is also true when $n_1$ and $n_2$ are arbitrary, precisely because we have defined the energy functions to be lower semicontinuous in $\sigma$. [In an obvious abbreviated notation, if $n_1 = n_1 + n_1$ and $n_2 = n_2 + n_2$ with $n_1$ integral and $0 < n_1 < 1$, then]

$$
\epsilon([n_1 + n_2](n_2 + n_2)) \leq \epsilon(n_1 + 1) + \epsilon(n_2 + 1) + \bar{U}.
$$

Furthermore, the truth of (8.10) for each fixed $\sigma_1$ and $\sigma_2$ and integral particle numbers also implies its truth for all $\rho_1$ and $\rho_2$, as is seen by applying Lemma 4.3 to the function $-\epsilon$.

Thus, we can summarize the situation by saying that (8.10) and its generalization to more than two subdomains is precisely the analog of the inequalities on the $g$ function of Sections IV and V. The differences are three:

(i) The $g$ function is replaced by $-\epsilon$.

(ii) The density $\rho$ is replaced by the pair $(\sigma, \rho)$.

(iii) For each domain $A$ and fixed $\sigma$, $\epsilon(\sigma, \rho; A)$ is continuous in $\rho$ (which, we remind the reader, must be thought of in multiplet space in order to ensure charge neutrality), but it is only lower semicontinuous in $\sigma$ for fixed $\rho$. However, $\epsilon$ is monotone in $\sigma$ for fixed $\rho$.

If we ignore item (iii) for the moment, we see that precisely the same analysis as that given in Sections IV and V will lead to the same conclusions for the energy function, namely, Theorems 4.6 and 5.1. Item (iii) is a cause for concern, however, about the matter of uniform convergence, but we can circumvent the lack of continuity in $(\sigma, \rho)$ in the following manner:

(i) Apart from some inconsequential terms involving the tempered potential, $\epsilon(\sigma, \rho; A)$ converges downward to its limit function $\epsilon(\sigma, \rho)$ (see the proof of Theorem 4.4). This limit function is convex in $(\sigma, \rho)$ because of (8.10) and hence is continuous. It is also monotone in $\sigma$.

(ii) For each $\rho$, the convergence in $\sigma$ is uniform on compacta because a sequence of monotone functions that converges on a compact set to a continuous function does so uniformly. It is then clear that if we introduce $\tilde{\epsilon}(\sigma, \rho; A)$ as the upper semicontinuous analog of $\epsilon$ (which is defined in an obvious way) then $\tilde{\epsilon}$ converges to $\epsilon(\sigma, \rho)$. It is also clear that for each $A$, $\tilde{\epsilon}(\sigma, \rho; A)$ is jointly upper semicontinuous in $(\sigma, \rho)$ because it is piecewise linear; it also has the downward convergence property of (i) above. We can now use Dini’s Theorem to assert that the convergence is uniform on compacta, and since $\epsilon \geq \tilde{\epsilon}$ the same is true for the original $\epsilon$ functions.

We now collect these results in a formal statement:

**Theorem 8.1.** (i) Let $\{A_i; N_i\}$ be a sequence of regular domains and integer valued particle number vectors satisfying the neutrality condition $N_i \cdot E = 0$ and such that $\rho_i = V(A_i)^{-1} N_i$ satisfies $|\rho_i| < \rho_c$. Let a sequence of entropies $\{\epsilon_i\}$ be given and suppose that $\rho_i \to \rho$ with $|\rho| < \rho_c$ and $\sigma_i \to \sigma$. Then, the energy functions $\epsilon(\sigma_i, \rho; A_i)$ converge to a function $\epsilon(\sigma, \rho)$ which is independent of the particular sequence.

(ii) $\epsilon(\sigma, \rho)$ is continuous and convex in $(\sigma, \rho)$ in the domain

$$
D = \{ (\sigma, \rho) : |\rho| < \rho_c, \rho \cdot E = 0, -\infty < \sigma < \infty \}.
$$

It is also non-decreasing in $\sigma$.

(iii) $\epsilon(\sigma, \rho, 0) = 0$.

(iv) Let $K$ be a compact subset of $D$. Suppose that for each $(\sigma, \rho) \in K$ we have a sequence $\{\rho_j(\sigma, \rho), \rho_j(\sigma, \rho)\}$ which converges $(\sigma, \rho)$ uniformly on $K$. Then $\epsilon(\sigma_i, \rho_j; A_i)$ approaches $\epsilon(\sigma, \rho)$ uniformly on $K$.

Using Theorem 8.1 and some real analysis (see Griffiths, 1965) one can also prove

**Theorem 8.2.** The entropy function, $\sigma(\epsilon, \rho; A)$, satisfies Theorem 8.1 except that (ii) must be modified to read:

(ii) $\sigma(\epsilon, \rho)$ is continuous, and concave in $(\epsilon, \rho)$ in the domain

$$
D = \{ (\epsilon, \rho) : |\rho| < \rho_c, \rho \cdot E = 0, \epsilon > \epsilon(\rho) \},
$$

where $\epsilon(\rho) = \lim_{j \to \infty} E_j(\rho_j; A_j)/V_j$ and $E_j(\rho; A)$ is the lowest eigenvalue of the Hamiltonian in $A$. It is also nondecreasing in $\epsilon$ and its range is not bounded above.

We also add:

(v) $\sigma(\epsilon, \rho)$ and $\epsilon(\sigma, \rho)$ are inverse functions.

**B. Equivalence to Other Definitions of the Entropy**

One of the standard definitions of the microcanonical partition function (Griffiths, 1965; Ruelle, 1969) is

$$
\Omega(E, N; A) = Tr \theta(E - H) = \mu(E),
$$

(8.11)
where $H$ is the Hamiltonian, $\theta(x) = 1$ for $x \geq 0$, $\theta(x) = 0$ for $x < 0$ and $\mu(E)$ is the number of eigenvalues of $H$ (counting multiplicity) which do not exceed $E$. By taking logarithms and dividing by $V = V(A)$, we obtain the entropy function
\[
\delta(\varepsilon, \rho; A) = V^{-1} \ln \mu(eV).
\] (8.12)

The energy function inverse to $\delta$ is
\[
\varepsilon(\alpha, \rho; A) = V^{-1}E_1
\] (8.13)
where $l$ is the smallest integer $\geq \exp(\alpha V)$.

We wish to inquire how the $\varepsilon$ function compares with the $\epsilon$ function defined in the previous subsection. As $\rho$ and $A$ are unimportant quantities in this discussion we shall cease to exhibit them explicitly. Clearly, $\varepsilon(\alpha) \geq \epsilon(\alpha)$. On the other hand, if we replace $\alpha$ by $\alpha' = \alpha + V^{-1} \ln 2$, so that $l$ is replaced by $2l$ or $2l - 1$ (this distinction is unimportant when $V$ is large), then $\epsilon(\alpha') = (2V)^{-1} \sum E_l \geq \frac{1}{2} \epsilon(\alpha) + \frac{1}{2} \epsilon(\alpha)$. Thus,
\[
\epsilon(\alpha) + 2[\epsilon(\alpha + V^{-1} \ln 2) - \epsilon(\alpha)] \geq \varepsilon(\alpha) \geq \epsilon(\alpha).
\] (8.14)

This inequality (8.14) together with Theorem 8.1, implies

**Theorem 8.3.** The energy function $\varepsilon(\alpha, \rho; A)$ also satisfies Theorem 8.1 and has the same limit as $\epsilon(\alpha, \rho; A)$. Likewise, the entropy function, $\delta(\varepsilon, \rho; A)$ satisfies Theorem 8.2 and has the same limit as $\sigma(\varepsilon, \rho; A)$.

Our final task is to show the equivalence of $\delta$ to the entropy of greatest physical interest which, for want of a better word, we may term the differential entropy. Actually, this is not a single function but it is a family of functions parametrized by a positive number $\delta$.

**Definition.** With $A$ and $\rho$ fixed and $\delta > 0$ we define the differential entropy to be
\[
\sigma_d(\varepsilon, \rho; A) = V^{-1} \ln \mu_d(eV),
\] (8.15)
where $\mu_d(E)$ is the number of energy levels in the closed interval $[E - \delta V, E]$.

**Theorem 8.4 (Griffiths).** For each $\delta > 0$ the differential entropy $\sigma_d(\varepsilon, \rho; A)$ satisfies Theorem 8.2 and has the same limit as $\sigma(\varepsilon, \rho; A)$.

---

**Proof.** This is proved in Griffiths (1965). One can easily derive the following inequality (in which we suppress explicit mention of $\rho$):
\[
\delta(\varepsilon; A) \geq \sigma_d(\varepsilon; A) \geq \delta(\varepsilon; A) + V^{-1} \ln(1 - \exp V[\delta(\varepsilon - \delta; A) - \delta(\varepsilon; A)]).
\] (8.16)

Now consider the limit function $\sigma(\varepsilon)$, which is concave and non-decreasing in $\varepsilon$. It must, in fact, be strictly increasing, otherwise its range would be bounded above. (It is here that a very important distinction between systems with bounded and unbounded energy levels enters.) Therefore, $\alpha = \sigma(\varepsilon) - \sigma(\varepsilon - \delta) > 0$. Let $A$ be sufficiently large so that $|\delta(\varepsilon; A) - \sigma(\varepsilon)| \leq \alpha/3$ and $|\sigma(\varepsilon - \delta; A) - \sigma(\varepsilon - \delta)| \leq \alpha/3$. Hence, $\delta(\varepsilon - \delta; A) - \delta(\varepsilon; A) \leq -\alpha/3$, and the rest follows.

---

**APPENDIX A**

We show here that condition C implies condition B, as claimed in Section V.

**Proposition.** Let $\{A_j\}$ be a sequence of connected domains in $\mathbb{R}^d$ tending to infinity in the sense of Fisher with shape function $\pi(\varepsilon)$, as defined in (5.2). Then the "ball condition" (defined in (5.1)) is satisfied.

**Proof.** We first remark that if we cover a domain $A$ with closed cubes of side $2y$ having disjoint interiors, the minimal number of cubes required, $N_y$, satisfies
\[
N_y \leq (2y)^{-d} [V(A) + V(-2y \sqrt{d}; A)].
\] (A.1)

This is proved in the same way as Lemma 3.1 and inequality (3.2). Define $L_y = [V(A_j)]^{1/d}$ and, choosing some fixed $\alpha > 0$, set $2y \sqrt{d} = \alpha L_y$ in (A.1). Thus, $N_y$, the number of cubes of this size required to cover $A_j$, is less than $(\sqrt{d}/\alpha)^d[1 + \pi(-\alpha)]$, by the Fisher condition. These $N_y$ closed cubes are connected (since $A_j$ is) and they constitute a set whose diameter is at most $2y \sqrt{d} N_y \leq \alpha L_y (\sqrt{d}/\alpha)^d[1 + \pi(-\alpha)] = \alpha L_y$. These cubes (which cover $A_j$) can then be inscribed in a ball $B_j$ of radius $\alpha L_y$ and $V(A_j)/V(B_j) = \delta$, where $\delta = \alpha^{-d} \sqrt{d}/\alpha^d[1 + \pi(-\alpha)]^{-d}$, with $\alpha$ being the volume of a unit ball in $\mathbb{R}^d$. $\delta$ is independent of $j$ as was to be proved.
Remarks. 1. This proposition is proved in Fisher (1964, Appendix D) by a different method.

2. Only a very weak version of the Fisher condition is used in this proposition. In particular, we do not use the fact that $\pi(\alpha) \to 0$ as $\alpha \to 0$.

**Notation**

$B$ ball in $\mathbb{R}^d$.

$B_k$ standard ball of type $k$.

$-B$ lower bound on energy per particle.

$C(\mathcal{A})$ capacitance of $\mathcal{A}$.

$d$ dimension ($=1, 2, 3, ...$).

$D$ ellipsoidal shell.

$e_i$ charge of species $i$ ($i = 1, ..., S$).

$e^i$ charge of particle $i$ ($i = 1, ..., N$).

$E$ energy.

$E$ $(e_1, ..., e_s)$.

$g(\beta, \varphi; \lambda)$ $V(\mathcal{A})^{-1} \ln Z(\beta, \varphi V(\mathcal{A}); \mathcal{A}) = -\beta \cdot$ (canonical free energy per unit volume).

$g(\varphi; \mathcal{A})$ $g(\beta = 1, \varphi; \mathcal{A})$.

$\tilde{g}(\mathcal{N}; \mathcal{A})$ $g(\mathcal{N}/V(\mathcal{A}); \mathcal{A})$.

$g(\varphi)$ infinite volume limit of $g(\varphi; \mathcal{A})$ for neutral systems.

$G(\mathcal{R}; \mathcal{A})$ $g(\varphi; \mathcal{A})$ expressed in terms of $\mathcal{R}$.

$\tilde{G}(\alpha; \mathcal{A})$ $G(\alpha/V(\mathcal{A}); \mathcal{A})$.

$H(\mathcal{N}; \mathcal{A})$ Hamiltonian of the system.

$m_i$ mass of species $i$ ($i = 1, ..., S$).

$m^i$ mass of particle $i$ ($i = 1, ..., N$).

$n_k$ number of balls of type $k$ used in a packing.

$N^i$ number of particles of species $i$.

$N$ $(N^1, ..., N^S)$.

$N$ total particle number $= \sum_i N^i$ (also used for multiplet number in section IV).

$Q$ net charge.

$\rho$ minimum distance for tempering.

$R_k$ radius of standard ball of type $k$.

$\mathcal{R}$ multiplet density vector.

$S$ number of species of particles.

$S(E, N; \mathcal{A})$ microcanonical entropy.

$T(N; \mathcal{A})$ kinetic energy operator.

$U(N; \mathcal{X})$ configurational potential energy.

$U_C(N; \mathcal{X})$ Coulomb potential.

$U_T(N; \mathcal{X})$ tempered potential.

$V(\mathcal{A})$ or $V$ volume of $\mathcal{A}$.

$V(h; \mathcal{A})$ boundary volume.

$\omega$, $\epsilon$ tempering constants.

$W(N, P_N; \mathcal{X})$ inter-set potential energy.

$x_i$ coordinate of particle $i$ ($i = 1, ..., N$).

$\mathcal{X}$ $(x_1, ..., x_N)$.

$Z(\beta, \mathcal{N}; \mathcal{A})$ canonical partition function.

$Z(\mathcal{N}; \mathcal{A})$ $Z(\beta = 1, \mathcal{N}; \mathcal{A})$.

$\alpha$ multiplet number vector.

$\beta$ reciprocal temperature in units of Boltzmann's constant.

$\gamma$, $\rho$ packing constants, $\gamma = \rho(1 + \rho)^{-1}$.

$\Gamma$ a cubical domain.

$\epsilon(\alpha, \rho; \mathcal{A})$ microcanonical energy per unit volume.

$\theta(\cdot)$ Heaviside step function.

$\mathcal{A}$ domain in $\mathbb{R}^d$ of particle coordinates $x_1, ..., x_N$.

$\mu_i$ chemical potential of species $i$.

$\mathcal{E}(\mu; \mathcal{A})$ grand canonical partition function.

$\mathcal{E}(\mu; \mathcal{A})$ neutral system grand canonical partition function.

$\pi(\mu; \mathcal{A})$ $V(\mathcal{A})^{-1} \ln \mathcal{E}(\mu; \mathcal{A}) = \text{grand canonical pressure}$.

$\pi(\mu; \mathcal{A})$ neutral system grand canonical pressure.

$N^i/V = \text{density of species } i$. 

$\rho^i (\rho^1, ..., \rho^S)$.
\[ \rho \text{ Total density } = N/V \text{ (also used for multiplet density in Section IV).} \]

\[ \rho_c \text{ close packing density (for hard cores).} \]

\[ \sigma_d \text{ volume of unit ball in } \mathbb{R}^d. \]

\[ \sigma(\varepsilon, p; \lambda) \text{ microcanonical entropy per unit volume.} \]

\[ \Omega(E, N; \lambda) \text{ microcanonical partition function.} \]

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References

24. A. Wehrl, Convex and concave traces, Preprint, Institute for Theoretical Physics, University of Vienna.

Appendix B. Operator Theory Needed in Quantum Statistical Mechanics in Boxes

By Barry Simon, Princeton University

In this appendix, we discuss certain technical details concerning operators on a Hilbert space which are needed for discussing the canonical ensemble in bounded regions of \( \mathbb{R}^n \) of arbitrary shape. For a related discussion, see Robinson [6].

A. Quadratic Forms

The natural language in which to discuss the Hamiltonians arising in statistical mechanics is the language of quadratic forms rather than the more familiar language of operators. We thus begin with a brief discussion of quadratic forms, supposing that the reader is already conversant with the notion of self-adjoint operators and the spectral theorem. For additional discussion of quadratic forms, see Kato [3], Nelson [5]; for a
A quadratic form $a$ on a Hilbert space $\mathcal{H}$ is a map $a : D \times D \to \mathbb{C}$ where $D = Q(a)$ is the form domain, a dense subspace of $\mathcal{H}$, and $a (\cdot , \cdot)$ is linear in the second variable, conjugate linear in the first. The canonical example of a form is provided as follows: Let $A$ be a self-adjoint operator with spectral projections $E_\lambda$. Let $Q(a)$ be the set $Q(A)$ of $\psi \in \mathcal{H}$ such that

$$\int_{-\infty}^{\infty} |\lambda| \, d\langle \psi, E_\lambda \psi \rangle < \infty.$$  

If $\psi, \phi \in Q(a)$, let

$$a(\psi, \phi) = \langle \psi, A \phi \rangle = \int_{-\infty}^{\infty} \lambda d\langle \psi, E_\lambda \phi \rangle.$$  

We say $a$ is the form of the self-adjoint operator $A$.

If $a$ is a quadratic form, we say $a$ is semi-bounded if there is some $C > 0$ with $a(\phi, \phi) \geq -C \| \phi \|^2$ for all $\phi \in Q(a)$. But $a$ is called positive, if $a(\phi, \phi) \geq 0$ for all $\phi \in Q(a)$. The form of an operator is semi-bounded (positive) if and only if $A$ is semi-bounded (positive), i.e., if $E_{\{b, \infty \}} = 1$ for some $b < \infty$ (for $b = 0$).

Let $a$ be a semi-bounded quadratic form $a(\phi, \phi) \geq -C \| \phi \|^2$. Define $\langle \phi, \psi \rangle_{+1} = a(\phi, \psi) + (C + 1) \langle \phi, \psi \rangle$. $\langle , \rangle_{+1}$ is an inner product on $Q(a)$. $a$ is called closed if $Q(a)$ with $\langle , \rangle_{+1}$ is a Hilbert space, i.e., if the $\| \cdot \|_{+1}$-norm is complete. It is not hard to see that the form of a semi-bounded self-adjoint operator is closed. The fact that makes quadratic forms so nice is that the converse is true.

**Theorem 1.** Let $a$ be a semi-bounded, closed quadratic form. Then there is a unique self-adjoint operator $A$, so that $a$ is the quadratic form of $A$.

Proof (see Kato [3, pp. 322–331] and/or Nelson [5, pp. 99–100]). Thus, given a semi-bounded quadratic form $a$, it is natural to try to find closed extensions of it. The simplest way of looking for a closed extension is to take the inner product space $Q(a)$, with norm $\| \cdot \|_{+1}$ and complete it to a Hilbert space $\mathcal{H}_{+1}$. There is a natural map $i : Q(a) \to \mathcal{H}$ given by using the fact that $Q(a) \subset \mathcal{H}$ ($i$ is the identity). Since $\| i(\psi) \| = \| \psi \| \leq \| \psi \|_{+1}$, $i$ is continuous and so it has a continuous extension $\bar{i}$ to $\mathcal{H}_{+1}$. If $i$ is one–one we can view $\mathcal{H}_{+1}$ as a subspace of $\mathcal{H}$ and define a form $\bar{a}$ on $\mathcal{H}_{+1}$ by $\bar{a}(\phi, \psi) = \langle \phi, \psi \rangle_{+1} - (C + 1) \langle \phi, \psi \rangle$. $\bar{a}$ is clearly an extension of $a$ and it is closed. If $i$ is one–one, we say $a$ is closable; $a$ is then the smallest closed extension of $a$; $\bar{a}$ is called the closure of $a$. It is not hard to see that $a$ is closable if and only if $a$ has some closed extension. To see that not every form is closable, consider:

**Example.** Let $Q(a) = \{ \psi \in L^2(\mathbb{R}) \mid \psi \text{ is continuous} \}$ and let $a(\psi, \phi) = \phi(0) \bar{\phi}(0)$. Thus $a$ is in some sense the expectation value of $\delta(x)$. Let $\psi_n$ be a sequence in $Q(a)$ with $\psi_n(0) \to 0$ in $L^2$ but $\psi_n'(0) = 1$ for all $n$. Since $\| \phi \|_{+1} = \| \phi \|^2 + \| \phi' \|^2$, we see that $\psi_n$ is Cauchy in $\| \cdot \|_{+1}$. Thus $\psi_n \to \eta$ for some $\eta \in \mathcal{H}_{+1}$. Since $\| \psi_n \|_{+1} \to 1$; $\| \eta \|_{+1} = 1$, which implies $\eta \neq 0$. But $\lim \eta(0) = 0$. Thus $i$ is not one–one; $a$ has no closure. This is as it should be; if $a$ had a closure, Theorem 1 would tell us there was a self-adjoint operator $A$ with $\langle \phi, A \psi \rangle = i(\phi(0))$. Since multiplication by $\delta(x)$ is in no sense an operator, $a$ should not have a closure.

It turns out if $a$ is a semi-bounded form that comes from an operator, it is always closable.

**Theorem 2.** Let $A$ be a Hermitian operator with some domain $D(A)$. Suppose there is a $C$ with $\langle \phi, A \psi \rangle \geq -C \| \phi \|^2$ for all $\psi \in D(A)$. Let $a$ be the quadratic form with $Q(a) = D(A)$ and $a(\psi, \phi) = \langle \psi, A \phi \rangle$. Then $a$ is closable.

**Proof.** See Nelson [5, pp. 101–102].

Thus, if $A$ is a Hermitian operator which is bounded below in the sense of Theorem 2, we can find a self-adjoint extension of $A$ as follows: Let $a$ be the form of Theorem 2; let $a$ be its form closure. By Theorem 1, there is a unique self-adjoint operator $A^\# \bar{a}$ with $\bar{a}$ the form associated to $A^\#$. $A^\#$ is called the Friedrichs extension of $A$. If $A \geq -C$, then $A^\# \geq -C$.

**B. Free Hamiltonian**

Let $Q$ be a bounded open set in $\mathbb{R}^n$. Let $C_0^\infty(\Omega)$ be the $C^\infty$ functions with supports strictly within $\Omega$. Define $A$ on $C_0^\infty(\Omega)$ by

$$A \phi = -A \phi = -\sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2} \psi.$$  

View $A$ as an operator on $L^2(\Omega)$. 
Then
\[ \langle \psi, A\psi \rangle = -\int_\Omega \psi(x)(A\psi)(x) \, dx = \int_\Omega |\nabla\psi(x)|^2 \, dx \geq 0. \]

Thus $A$ is a positive operator. We will call its Friedrichs extension the free Hamiltonian $H_0$ for the region $\Omega$. (This is called $T$ in the rest of the paper).

The operator $A$ is not essentially self-adjoint; so this method of taking the form closure gives us an operator defined on a bigger domain than if we simply took the operator closure. According to the standard folklore associated with the theory of self-adjoint extensions of differential operators (see Wightman [10, pp. 256–267] or Coddington–Levinson [1, pp. 186–207]), $H_0$ should in some sense be $-\Delta$ with some boundary condition added at $\partial \Omega$. We claim $H_0$ is actually $-\Delta$ with $0$ boundary condition on $\partial \Omega$. This is based on the following considerations:

1. In the case $\Omega = (a, b) \subset \mathbb{R}$, any $\psi \in \mathcal{Q}(H_0)$ is a continuous function on $[a, b]$ vanishing at $a$ and $b$.

2. If $\Omega$ is a sufficiently nice region in $\mathbb{R}^n$, say a sphere or a parallelepiped, $H_0$ is essentially self-adjoint on the family of functions $C^2$ on $\Omega$ which vanish on $\partial \Omega$.

3. Most importantly, we have the following theorem:

**Theorem 3.** Let $\Omega \subset \Omega^1$ be bounded regions of $\mathbb{R}^n$ and let $H_0^{(\Omega)}$, $H_0^{(\Omega^1)}$ be the free Hamiltonians for $\Omega$ and $\Omega^1$, respectively. Suppose $\psi \in \mathcal{Q}(\Omega)$ with $\psi \in \mathcal{Q}(H_0^{(\Omega^1)})$. Extend $\psi$ to $\Omega^1$ by setting it equal to $0$ outside $\Omega$. Call this extension $\tilde{\psi}$; then $\tilde{\psi} \in \mathcal{Q}(H_0^{(\Omega^1)})$ also.

**Proof.** Since $\tilde{\psi} \in \mathcal{Q}(H_0^{(\Omega^1)})$, we can find $\psi_n \in C_0^{\infty}(\Omega)$ so that $\psi_n \to \psi$ in $L^2(\Omega)$; $\nabla(\psi_n)$ is Cauchy in $L^2(\Omega)$. But then $\psi_n \to \tilde{\psi}$ in $L^2(\Omega^1)$ and $\nabla(\tilde{\psi})$ is Cauchy in $L^2(\Omega^1)$ so $\tilde{\psi} \in \mathcal{Q}(H_0^{(\Omega^1)})$.

In some cases we have $\Omega \subset \mathbb{R}^n$ and $\Omega^1 \subset \mathbb{R}^n$ so $L^2(\Omega \times \Omega^1) = L^2(\Omega) \otimes L^2(\Omega^1)$ in the sense of Hilbert space tensor products. In this case, it is easy to see $H_0^{(\Omega \times \Omega^1)} = H_0^{(\Omega)} \otimes 1 + 1 \otimes H_0^{(\Omega^1)}$ under this tensor product.

In other cases, we have $\Omega \subset \mathbb{R}^n$ and are interested in $\Omega^1 = \Omega \times \cdots \times \Omega \subset (\mathbb{R}^n)^m$. We note in this case that the space of $\psi \in L^2(\Omega^1)$ transforming according to some representation of the symmetric group on $m$ letters is left invariant by $H_0^{(\Omega^1)}$, i.e., the functions of a given statistics are left invariant by $H_0$. Moreover, $H_0$ restricted to this space is the Friedrichs extension of $-\Delta$ restricted to the $C_0^{\infty}(\Omega^1)$ functions with the correct statistics.

**C. Form Perturbations and Interacting Hamiltonian**

In defining the interacting Hamiltonian, it is useful to think of $V$, the potential, as a perturbation of the free system, an idea going back to a fundamental paper of Kato [4]. That $V$ is a small perturbation of $H_0$ is in some sense a manifestation of the uncertainty principle. We will therefore describe a simple theorem on general form perturbations first and then apply it to potentials which are not too singular. We finally mention what to do with hard cores.

The basic perturbation theorem is the following:

**Theorem 4.** Let $H_0$ be the quadratic form of some positive self-adjoint operator. Let $V$ be another quadratic form with $\mathcal{Q}(V) \supset \mathcal{Q}(H_0)$ and suppose there is an $a < 1$ and a real $b$ such that
\[ \langle \psi, V\psi \rangle < a \langle \psi, H_0\psi \rangle + b \langle \psi, \psi \rangle \]
for all $\psi \in \mathcal{Q}(H_0)$. Then there is a unique self-adjoint operator $H$, with $\mathcal{Q}(H) = \mathcal{Q}(H_0)$, such that
\[ \langle \psi, H\psi \rangle = \langle \psi, H_0\psi \rangle + \langle \psi, V\psi \rangle \]
for all $\psi \in \mathcal{Q}(H_0)$.

**Proof.** The basic idea is to prove that the form $h$ on $\mathcal{Q}(H_0)$ defined by
\[ h(\psi, \phi) = \langle \psi, H_0\phi \rangle + \langle \psi, V\phi \rangle \]
is closed and semibounded and to apply Theorem 1. For details, see Kato [3, pp. 336–343], Simon [7, Section II.2; 8, Appendix 2].

Let $W$ be a function on $\mathbb{R}^n$ such that $W = W_1 + W_2$ with $W_2(x) < c$ for some $c$ independent of $x$ and
\[ \int \frac{|W_2(x)|}{|x|} \frac{|W_2(y)|}{|x-y|} \, dx \, dy < \infty. \]

Following [7], we say $W$ is a **Rollnik potential**. The following are examples of such potentials: (a) Any sum of an $L^2$ and an $L^\infty$ function, in particular, $W(x) = |x|^{-1}$. (b) Any continuous function on $\mathbb{R}^n - \{0\}$ which goes to $0$ at $\infty$ for which $|W(x)| < C|x|^{-2}(1 - \ln |x|)^{-\alpha}$ when $|x| < 1$ for some $C$ and some $\alpha > \frac{1}{2}$. 


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In case $A$ has compact resolvent $\text{Tr}(e^{-\beta A}) < \infty$ if and only if

$$Z = \sum_{n=0}^\infty e^{-\beta E_n} < \infty,$$

in which case $Z = \text{Tr}(e^{-\beta A})$.

Recall that a point $\lambda$ in the spectrum of $A$ is said to be in the discrete spectrum if add only if $\lambda$ is an isolated point of the spectrum and an eigenvalue of finite multiplicity. Otherwise $\lambda$ is said to be in the essential spectrum. It is easy to see that an operator $A$ has compact resolvent if and only if its essential spectrum is empty. The following theorem is thus very useful in proving $H^{(\Omega)}$ has compact resolvent:

**Theorem 6.** Let $A$ be a semibounded self-adjoint operator. Let

$$\mu_n(A) = \max_{\psi \in C_0^\infty(\Omega)} \{ \min_{\psi \in C_0^\infty(\Omega)} \langle \psi, A\psi \rangle \mid \| \psi \| = 1, \langle \psi, |j\rangle = 0, j = 1, \ldots, n-1 \}. \tag{B.2}$$

Then, either

(a) $\mu_n(A)$ is the $n$-th eigenvalue from the bottom of the spectrum (counting multiplicity), or

(b) $\mu_n(A)$ is the bottom of the essential spectrum, and in that case

$$\mu_n(A) = \mu_{n+1}(A) = \cdots = \mu_{n+1}(A) = \cdots.$$

**Proof.** This variant of the Weyl min–max principle is discussed in Simon [9]. It can be shown by combining the spectral theorem with the classical Weyl proof (see Courant–Hilbert [2] for this classical proof).

Thus, $A$ has compact resolvent if and only if $\mu_n(A) \to \infty$ as $n \to \infty$ and $\text{Tr}(e^{-\beta A}) < \infty$ if and only if $\sum_{n=0}^\infty e^{-\beta E_n} < \infty$. We thus have:

**Theorem 7.** Let $\Omega$ be a bounded open region in $\mathbb{R}^n$. Then $H^{(\Omega)}$ has compact resolvent if $Z_0(\Omega) = \text{Tr}(e^{-\beta H^{(\Omega)}}) < \infty$. Moreover for $\beta$ fixed,

$$Z_0(\Omega)$$

is a monotone increasing function of $\Omega$ (i.e., $Z_0(\Omega) \geq Z_0(\Omega')$ if $\Omega \subseteq \Omega'$).

**Proof.** Under the natural imbedding of $L^2(\Omega', d^n x) \hookrightarrow L^2(\Omega, d^n x)$ which occurs when $\Omega' \subset \Omega$, we have seen (Theorem 3) that $Q(H^{(\Omega)})$ is imbedded in $Q(H^{(\Omega')})$. Thus, by the min–max formula (B.2),

$$\mu_n(H^{(\Omega)}) \leq \mu_n(H^{(\Omega')}).$$

To see that $H^{(\Omega)}$ has compact resolvent and $Z_0(\Omega) < \infty$, we merely note that any $\Omega' \subset \mathbb{R}^n$ which is bounded is contained in a cube. For a cube, one can exhibit a complete set of eigenfunctions with $E_n \to \infty$ and $\sum_{n=0}^\infty e^{-\beta E_n} < \infty$. Thus (3) implies $\mu_n(H^{(\Omega)}) \to \infty$ and $\sum_{n=0}^\infty e^{-\beta E_n} < \infty$. The monotonicity of $Z_0(\Omega)$ follows from (3).
The inequality (B.1) is ideal for treating the interaction Hamiltonian as follows:

**Theorem 8.** Let \( \Omega \) be a bounded open region of \( \mathbb{R}^n \). Let \( V \) be a potential obeying the conditions of Theorem 5. Let \( H^{(\Omega)} = H_0^{(\Omega)} + V \) be defined by the method of Theorem 5. Then \( H^{(\Omega)} \) has compact resolvent and \( Z^{(\Omega)} = \text{Tr}(e^{-\beta H^{(\Omega)}}) < \infty \); moreover, for any fixed \( \beta \) and \( V \), \( Z(\Omega) \) is a monotone function of \( \Omega \).

**Proof.** The inequality (B.1) with some fixed \( a < 1 \), implies that
\[
\langle \psi, H^{(\Omega)} \psi \rangle \geq (1 - a)\langle \psi, H_0^{(\Omega)} \psi \rangle - b\langle \psi, \psi \rangle.
\]
It thus follows that
\[
\mu_n(H^{(\Omega)}) \geq (1 - a)\mu_n(H_0^{(\Omega)}) - b.
\]
Thus \( \mu_n(H^{(\Omega)}) \to \infty \) and \( \sum_{n=0}^{\infty} e^{-\beta \mu_n(H^{(\Omega)})} < \infty \). The monotonicity follows from an argument that is identical to the one which implied monotonicity of \( Z_0(\Omega) \).

**E. Correlation Functions**

We should like to discuss the existence of the various correlation functions in the finite box system:

**Lemma.** Suppose \(|V|\) is a perturbation of an operator \( H_0 \) obeying (B.1). Let \( e^{-\beta H_0} \) be trace class for each \( \beta > 0 \). Then \( V e^{-\beta H_0} \) is trace class for all \( \beta > 0 \).

**Proof.** Let \( \mu_1, \ldots, \mu_n \) be the eigenvalues of \( H_0 \). Then
\[
\sum_{n=1}^{\infty} \mu_n e^{-\beta \mu_n} < \infty,
\]
(since \( x e^{-x} < 2e^{-x/2} \) if \( x > 1 \), say). If \( \psi_n \) is an orthonormal basis with \( H_0 \psi_n = \mu_n \psi_n \), then
\[
\sum_{n=1}^{N} \langle \psi_n, V e^{-\beta H_0} \psi_n \rangle = \sum_{n=1}^{N} e^{-\beta \mu_n} \langle \psi_n, V \psi_n \rangle \leq \sum_{n=1}^{N} e^{-\beta \mu_n} (\mu_n + b) < \infty.
\]
Thus \( V e^{-\beta H_0} \) is trace class.

**Theorem 9.** Let \( \Omega \) be a region in \( \mathbb{R}^n \). Let \( H = H^{(\Omega)} \) be a Hamiltonian of the form discussed in Theorem 5. Let \( e^{-\beta H} \) be trace class for all \( \beta > 0 \). Then for any fixed \( \beta > 0 \),

(a) There exist functions \( \rho_1, \ldots, \rho_n \in L^3(\Omega) \) so that for any \( f \in L^3(\Omega) \),
\[
\int \rho_i(r)f(r) dr = \text{Tr}(f e^{-\beta H}),
\]
where \( f_i \) is multiplication by \( f(r_i) \).

(b) For any \( k < n \), there exists functions \( \rho_{i_1}, \ldots, \rho_{i_k} \) on \( \mathbb{R}^3 \) \((i_1 < \cdots < i_k)\) with \( \rho_{i_1}, \ldots, \rho_{i_k} \in L^p(\mathbb{R}^3) \) if \( p < (1 - \frac{k}{3})^{-1} \) so that for any \( f \in L^q(\mathbb{R}^3) \) with \( q > 3k/2 \),
\[
\int \rho_{i_1}, \ldots, \rho_{i_k}(r_{i_1}, \ldots, r_{i_k}) f(r_1, \ldots, r_k) d^{3k}r = \text{Tr}(f_1 \cdots f_k e^{-\beta H})
\]
if \( f_{i_1}, \ldots, f_{i_k} \) is multiplication by \( f(r_{i_1}, \ldots, r_{i_k}) \).

**Proof.** We only prove (a); (b) is proven by using the Hausdorff–Young inequality to establish similar bounds to the basic bound holding for 1-body potentials in \( L^{3/2} \) (which are thus in the Rollnik class). By the lemma (with \( H_0 = H \)), \( \text{Tr}(f e^{-\beta H}) < \infty \) for any \( f \in L^{3/2} \) and by the methods of the lemma it is not hard to prove \( \rho \to \text{Tr}(f e^{-\beta H}) \) is continuous in the topology of \( L^{3/2} \). By the fundamental \( L^p \)-duality theorem, \( \rho_i \in L^3 \).

**Remarks.** 1. The \( \rho_i \)'s have any rotational or point group symmetry that \( H^{(\Omega)} \) has. In particular, if \( \Omega \) and the potentials are invariant under rotation of all the \( \mathbb{R}^3 \) coordinates, so is \( \rho_i \).

2. If \( i \) and \( j \) are coordinates of "identical" particles; \( \rho_i = \rho_j \).

3. Of course, the \( \rho_i \) have support in the projection of \( \Omega \) onto the \( i \)-th \( \mathbb{R}^3 \) coordinate. In particular, if \( \Omega \) is bounded, \( \rho_i \in L^{\infty}(\mathbb{R}^3) \) for any \( p < 3 \).

**F. Some Final Remarks**

1. If \( A \) and \( B \) are closed forms with \( Q(A) \cap Q(B) \) dense and with \( A, B \) bounded below, then \( A + B \) is a closed form on \( Q(A) \cap Q(B) \); so a self-adjoint operator \( C \), whose form is \( A + B \), can be constructed. In particular, if \( H \) is a Hamiltonian of the type constructed in Theorem 5, and \( V \) is bounded below with singularities on a set \( S \), so small that \( C_0^{(\infty)}(\Omega, S) \) is dense in \( L^2(\Omega) \) then \( H + V \) can be defined. Using this idea, we can define Hamiltonians with Lenard–Jones potentials.
2. The relation between the "zero boundary condition" $H_0$ we have defined, and the Neumann (vanishing boundary normal derivative) condition extension of $-\Delta$ is best seen in the formalism used by Robinson [6]. If $A$ is defined to be the operator closure of $-i\nabla$ on $C_0^\infty(\Omega)$, the Friedrichs $H_0$ is just $A^*A$ defined on $\{\psi \mid A\psi \in D(A^*)\}$ while the Neumann extension is $AA^*$ defined on $\{\psi \mid A^*\psi \in D(A)\}$. As forms, $AA^*$ is an extension of $A^*A$.

REFERENCES FOR APPENDIX B