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The Thermodynamic Limit for Jellium

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The thermodynamic limit of the free energy, energy, pressure, and entropy is established for a neutral system of charged particles interacting with a fixed, uniformly charged background (jellium).

KEY WORDS: Thermodynamic limit; jellium; charged particles; uniform background; neutral system; free energy density; quantum mechanics; equilibrium statistical mechanics.

1. INTRODUCTION

In 1938 Wigner[(1)] introduced a model for matter which is now called jellium. One supposes that the electrons in a solid provide a uniform, constant charge background in which the heavier nuclei move. The Hamiltonian for the system consisting of N particles with coordinates $\mathbf{X} = \{\mathbf{x}_1,..., \mathbf{x}_N\}$ in a three-dimensional domain Λ is

$$H = (2m)^{-1} \sum_{i=1}^{N} p_i^2 + e^2 U(\mathbf{X})$$

$$U(\mathbf{X}) = \sum_{i<j}^{N} |\mathbf{x}_i - \mathbf{x}_j|^{-1} - \rho \sum_{i=1}^{N} \varphi(\mathbf{x}_i) + \tfrac{1}{2}\rho^2 \int_\Lambda \varphi(\mathbf{x})\, d\mathbf{x} \qquad (1)$$

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and where

$$\rho\varphi(\mathbf{x}) = \rho \int_{\Lambda} |\mathbf{x} - \mathbf{y}|^{-1}\, d\mathbf{y}$$

is the Coulomb potential produced by the background of charge density ρ.

Throughout the following we shall set $m = e^2 = 1$, and $\hbar = 1$ in the quantum case. Thus the Bohr radius is equal to unity and the energy unit, the Rydberg (Ry), is equal to one-half. The dimensionless length r_s is equal to $[3/(4\pi\rho)]^{1/3}$. Whenever the distinction is necessary, we shall assume $\rho > 0$ and that the particles are negative.

We shall show that for neutral systems, i.e., $\rho|\Lambda| = N$, the thermodynamic functions per unit volume (free energy, energy, entropy, pressure) exist as $\Lambda \to \infty$.

It is also possible to consider the one- and two-dimensional versions of this problem, where the Coulomb potential $|\mathbf{x}|^{-1}$ is replaced by $-|x|$ and $-\ln|\mathbf{x}|$, respectively. In the one-dimensional, classical case, Baxter[(2)] calculated the partition function exactly. For that case, Kunz[(3)] showed that the one-particle distribution function exists and that it has crystalline ordering, i.e., the Wigner lattice exists for all temperatures. Brascamp and Lieb[(4)] showed the same to be true in the quantum mechanical case for one-component fermions when β is large enough. Although we do not deal with the one-dimensional problem here, our methods would apply in that case. In two dimensions there are difficulties connected with the long-range nature of the $-\ln|\mathbf{x}|$ potential, and we shall not discuss this here.

The problem of jellium is closely related to the same problem for real matter treated by Lebowitz and Lieb[(5,6),5] and their methods will be employed here. The difficulty with jellium is that the background is held rigid by definition and one cannot freely constrain the particles to lie in balls without at the same time imparting an enormous electrostatic energy to the system. On the other hand, the fixed background considerably simplifies the H-stability question. (Cf. Dyson and Lenard.[(8)]) The connection between the jellium and the real matter problems is discussed by Narnhofer and Thirring.[(9)]

In Section 2 we use H-stability to get an upper bound on the partition function Z. The H-stability itself is proved in the appendix.

Section 3 deals with the classical case. We first treat a distinguished sequence of domains, which are balls, and then we treat general domains. The usual results are obtained, except that since the free energy is not a convex function of the density for jellium, the compressibility can be negative and the grand canonical ensemble is not equivalent to the canonical ensemble.

[5] See also Penrose and Smith.[(7)]

As in Ref. 5, we show that a system with an excess charge $Q \sim |\Lambda|^{2/3}$ has an excess free energy $-(2\beta)^{-1}Q^2/C$, where C is the capacity of Λ.

In Section 4 we outline the proof when weakly tempered potentials are also present. Although the thermodynamic limit exists in this case, we lose continuity in ρ—at least by our methods. This is an open question. The inclusion of hard cores is also not covered by our method and this, too, is an open question.

In Section 5 we explain the additional techniques needed for the quantum case. An open question here is to show the equivalence of different boundary conditions; we use Dirichlet conditions. A related problem is to show that the particle density and the electrostatic potential stay suitably bounded as $N \to \infty$.

2. *H*-STABILITY

The condition of H-stability is that the Hamiltonian is bounded below by a constant times N. It is sufficient to require that the potential energy alone has this property, since the kinetic energy operator is positive. For real matter one is obliged to consider the total Hamiltonian because the interaction energy of a positive and a negative particle has no lower bound. The proof of H-stability in this latter case is very difficult and was given by Dyson and Lenard[8,10] and recently a new proof was given by Federbush.[11] It is essential here that the electrons be fermions, thereby excluding classical particles.

For jellium, on the other hand, one can easily find a lower bound on U, by using an idea due to Onsager.[12] This is given in the appendix. A different proof and a different bound are also given in Ref. 10. Our bound is

$$U > -0.9N/r_s \tag{2}$$

and we emphasize that this result holds for all N and all domains, connected or not, and requires only that the background have charge density $(3/4\pi)r_s^{-3}$ or zero everywhere. This lower bound is surprisingly accurate. In Ref. 13 a numerical evaluation for the body-centered cubic lattice of particles in a uniform background gives

$$U_{\min} \leqslant -0.896N/r_s \tag{3}$$

when the system is neutral.

The significance of the lower bound, and the only place it will be used here, is to establish an upper bound for the partition function Z, i.e.,

$$Z \leqslant Z_{\text{ideal}}e^{\xi N} \tag{4}$$

where ξ is some constant and Z_{ideal} is the partition function of ideal, non-interacting particles. Thus, defining

$$g = V^{-1} \ln Z \tag{5}$$

for a domain of volume V, one has that g is bounded above.

3. CLASSICAL PARTICLES WITH PURELY COULOMB FORCES

3.1. Canonical Ensemble (Spherical Domains)

Fix the density ρ. Let $\{B_k\}_{k=0}^{\infty}$ be a sequence of balls of radii $R_k = R_0(1+p)^k$, where $p = 26$ and the volume of $B_0 \equiv |B_0|$ is ρ^{-1}. Let $N_k = (1+p)^{3k}$ be the number of particles in B_k, whence $\rho_k = N_k/|B_k| = \rho$. Let $n_j = p^{j-1}(1+p)^{2j}$. According to Ref. 5, Section III, one can pack B_K with $\cup_{j=0}^{K-1}$ (n_{K-j} balls B_j) so that they do not overlap, and

$$\lim_{K\to\infty} |B_K|^{-1} \sum_{j=0}^{K-1} n_{K-j}|B_j| = 1 \tag{6}$$

The part of B_K not covered by the above packing will be called D_K.

At this point the principal difference between the proof for the jellium model and the proof for a system of positive and negative particles appears. In the latter, the N_K particles are constrained to be in the balls B_j, $j < K$, and the domain D_K is left empty. For jellium this cannot be done because the domain D_K would then not be neutral and the electrostatic energy of the system would be too large. Even though $|D_K|/|B_K| \to 0$ as $K \to \infty$, N_K^{-1} (the electrostatic energy of D_K) would go to infinity.

We proceed as follows: Let Z_k, $k = 0, 1, 2, \ldots$, be the configurational partition function of the ball B_k with N_k particles and with a uniform background of density ρ:

$$Z_k = (N_k!)^{-1} \int_{(B_k)^{N_k}} \exp[-\beta U(\mathbf{x}_1, \ldots, \mathbf{x}_{N_k})]\, d\mathbf{x}_1 \ldots d\mathbf{x}_{N_k} \tag{7}$$

Let $Z_K{}^D$ be the configurational partition function of D_K with M_K particles, where

$$M_K = N_K - \sum_{j=0}^{K=1} n_{K-j}N_j = N_K p^K(1+p)^{-K} \tag{8}$$

D_K is understood to have a uniform background of density ρ. Clearly, $\rho D_k = M_k$ and $M_k/N_k \to 0$ exponentially fast.

The fundamental inequality, to be found in Ref. 5, Section IIE, is that

$$\ln Z_K \geqslant \sum_{j=0}^{K=1} n_{K-j} \ln Z_j + \ln Z_K{}^D \tag{9}$$

This inequality exploits Newton's electrostatic theorem and the fact that all the subdomains, except D_K, are both spherical and neutral; therefore the average interdomain interaction is zero.

The next step is to estimate $Z_K{}^D$. Using Jensen's inequality,

$$\ln Z_K{}^D \geqslant M_K \ln|D_K| - \ln(M_K!) - \beta\langle U\rangle_{D_K}$$

where

$$\begin{aligned}\langle U\rangle_{D_K} = {} & \tfrac{1}{2}M_K(M_K - 1)|D_K|^{-2}\int\int_{D_K} |\mathbf{x} - \mathbf{y}|^{-1}\, d\mathbf{x}\, d\mathbf{y} \\ & + \tfrac{1}{2}\rho^2\int\int_{D_K} |\mathbf{x} - \mathbf{y}|^{-1}\, d\mathbf{x}\, d\mathbf{y} \\ & - \rho M_K|D_K|^{-1}\int\int_{D_K} |\mathbf{x} - \mathbf{y}|^{-1}\, d\mathbf{x}\, d\mathbf{y} \end{aligned} \tag{10}$$

Since $M_K = \rho \int_{D_K} d\mathbf{x}$,

$$\langle U\rangle_{D_K} = -\tfrac{1}{2}\rho|D_K|^{-1}\int\int_{D_K} |\mathbf{x} - \mathbf{y}|^{-1}\, d\mathbf{x}\, d\mathbf{y} < 0 \tag{11}$$

Thus, defining

$$g_K = |B_K|^{-1}\ln Z_K \tag{12}$$

and

$$\gamma = p(1 + p)^{-1} < 1 \tag{13}$$

we have, for large K,

$$g_K \geqslant p^{-1}\sum_{j=0}^{K-1} \gamma^{K-j}g_j + \gamma^K\rho(1 - \ln\rho) \tag{14}$$

where Stirling's formula for $M_K!$ has been used. As shown in Ref. 5, Section IVD, this inequality implies that g_K *has a limit*, $g(\beta, \rho)$, *for this special, ρ-dependent sequence of domains B_K.*

3.2. Canonical Ensemble (General Domains)

Let ρ be fixed. We take a regular sequence of domains $\{\Lambda_j\}_{j=1}^{\infty}$ tending to infinity which satisfies conditions A (Van Hove limit) and B (ball condition) given in Ref. 5, Section V, and which *also* satisfies the condition that $\rho|\Lambda_j| = j$. To get a lower bound on $Z(\Lambda_j)$, we pack Λ_j with balls B_k of the standard sequence appropriate to ρ given above and distribute the j particles with constant density in the balls and in D_j, which is the complement of the B_k in Λ_j. As above, we have

$$|\Lambda_j|g_j \equiv \ln Z(\Lambda_j) \geqslant \sum_k m_{jk}\ln Z_k + \ln Z_j{}^D \tag{15}$$

where m_{jk} is the number of balls B_k in the packing of Λ_j. Met M_j be the number of particles in D_j, i.e.,

$$M_j = j - \sum_k m_{jk}(1 + p)^{3k}$$

Then, as before,

$$\ln Z_j^D \geqslant M_j \ln|D_j| - \ln(M_j!) - \beta\langle U\rangle_{D_j} \tag{16}$$

and $\langle U\rangle_{D_j} \leqslant 0$. Following the proof in Ref. 5, Section V,

$$\liminf_{j\to\infty} g_j \geqslant g(\beta, \rho) \tag{17}$$

where $g(\beta, \rho)$ is the limit for the standard balls.

An upper bound to $Z(\Lambda_j)$ can be found by embedding Λ_j in a minimum standard ball $B_{K(j)}$ and packing $B_{K(j)}\backslash\Lambda_j$ with balls B_k. Let D_j be as before, i.e., $B_{K(j)}\backslash(\Lambda_j \cup B_k)$ and $M_j = \rho|D_j|$. Then

$$\begin{aligned}\ln Z_{K(j)} \geqslant \ln Z(\Lambda_j) + \sum m'_{jk} \ln Z_k + M_j \ln|D_j| - \ln(M_j!) \\ - \beta\langle U(D_j, D_j)\rangle - \beta\langle U(D_j, \Lambda_j)\rangle\end{aligned} \tag{18}$$

In the last four terms we use Jensen's inequality for the integration over the coordinates of the particles in D_j: $\langle U(D_j, D_j)\rangle$ is the average Coulomb energy in D_j in an ensemble in which the particles are free; $\langle U(D_j, \Lambda_j)\rangle$ is the average interdomain interaction between D_j and Λ_j when the particles in D_j are free and the particles in Λ_j are fully interacting. The last term is zero because the average total charge distribution in D_j is zero. The term $\langle U(D_j, D_j)\rangle$ is negative as before. Thus we can use the argument of Ref. 5, Section V, to conclude that

$$\limsup_{j\to\infty} g_j \leqslant g(\beta, \rho) \tag{19}$$

The result of these inequalities is that for any regular sequence of domains $\{\Lambda_j\}$ and particle numbers $N_j = j$ such that $N_j = \rho|\Lambda_j|$,

$$\lim_{j\to\infty} g_j = g(\beta, \rho) \tag{20}$$

While this establishes the existence and shape independence of the thermodynamic limit for each fixed ρ, we do not yet know anything about the dependence of $g(\beta, \rho)$ on ρ or whether the limit is uniform in ρ. We next discuss how such a relationship can be obtained.

3.3. Scaling Relations

Let $\{\Lambda_j\}_{j=1}^{\infty}$ be a regular sequence of domains for a given ρ, i.e., $\rho|\Lambda_j| = j$. Let $\eta > 0$ be fixed and define the following:

$$\rho' = \rho\eta^3, \qquad \beta' = \beta\eta^{-1}, \qquad \Lambda_j' = \eta^{-1}\Lambda_j = \{\eta^{-1}\mathbf{x}|\mathbf{x}\in\Lambda_j\} \tag{21}$$

Thus $\rho'|\Lambda_j'| = j$.

If one considers the integral defining $Z(\beta, \rho; \Lambda_j)$ and changes integration variables $\mathbf{x}$ to $\mathbf{y} = \eta^{-1}\mathbf{x}$, then one derives

$$|\Lambda_j|g(\beta, \rho; \Lambda_j) = |\Lambda_j'|g(\beta\eta^{-1}, \rho\eta^3; \Lambda_j') + 3j \ln \eta \tag{22}$$

Since the thermodynamic limit is independent of the sequence of domains, one has that

$$g(\beta, \rho) = \eta^{-3}g(\beta\eta^{-1}, \rho\eta^3) + 3\rho \ln \eta \tag{23}$$

for all $\eta > 0$. Now let $\eta = \rho^{-1/3}$, whence

$$g(\beta, \rho) = \rho g(\beta\rho^{1/3}, 1) - \rho \ln \rho = \rho\bar{g}(\beta\rho^{1/3}) + \rho(1 - \ln \rho) \tag{24}$$

where $\bar{g}(\cdot) \equiv g(\cdot, 1) - 1$.

From the basic definition of $g(\beta, \rho; \Lambda_j)$ one has that these functions, and hence their limits also, are convex functions of β. Therefore the function $t \to \bar{g}(t)$ is convex in t.

For finite j, let $\{\Lambda_j'\}$ be a regular sequence of domains with $|\Lambda_j'| = j$, and define

$$\bar{g}(\beta) = g(\beta, 1; \Lambda_j') - 1 \tag{25}$$

Then

$$\lim_{j \to \infty} \bar{g}_j(\beta) = \bar{g}(\beta) \tag{26}$$

3.4. Properties of the Thermodynamic Limit

3.4.1. Uniformity of the Limit. Since $\bar{g}(t)$ is bounded on finite t intervals, its convexity implies that it is continuous. Furthermore, each $\bar{g}_j(\cdot)$ has the same properties from (25). Thus the sequence of functions $\bar{g}_j(\beta\rho^{1/3})$ is continuous in ρ and has a continuous limit $\bar{g}(\beta\rho^{1/3})$ and the limit is essentially monotone as one sees from (14). Hence Dini's theorem tells us that the limit is uniform on compact ρ intervals.

3.4.2. Pressure and Compressibility. For a normal thermodynamic system, $g(\beta, \rho)$ is *concave* in ρ. This implies positive compressibility and, since the pressure is zero at zero density, it implies positive pressure. For jellium this is unfortunately not true. Using (24), and assuming differentiability, we obtain

$$\beta P/\rho = 1 - \tfrac{1}{3}\beta\rho^{1/3}\dot{\bar{g}}(\beta\rho^{1/3}) \tag{27}$$

where the dot denotes derivative, and

$$\beta\kappa^{-1} = \beta\frac{dP}{d\rho} = 1 - \frac{4}{9}\beta\rho^{1/3}\dot{\bar{g}}(\beta\rho^{1/3}) - \frac{\beta^2}{9}\rho^{2/3}\ddot{\bar{g}}(\beta\rho^{1/3}) \tag{28}$$

Note that $\ddot{g} > 0$. This implies that for $t > 0, \dot{g}(t) \geqslant \dot{g}(0) = 0$. These formulas show that P and κ can have either sign. In fact, for fixed β, they are both negative for sufficiently high density since, from (3), one sees that the potential energy will go as $\rho^{4/3}$ for large ρ, i.e., $g(t) \sim t$ for large t. Since $\dot{g}(t)$ is monotone, $t\dot{g}(t)$ is also monotone. This implies that there is always exactly one value, $(\beta\rho^{1/3})_c$, of $\beta\rho^{1/3}$ at which the pressure is zero. Without any constraint on the volume, classical jellium would collapse to a density $\rho^{1/3} = (\beta\rho^{1/3})_c\beta^{-1}$. This fact is not unrelated to the absence of H-stability for real matter without Fermi statistics.

3.5. Systems That Are Not Neutral

We wish to consider a sequence of systems with fixed background density ρ, but where $N \neq \rho|\Lambda|$. Define $Q_j \equiv -N_j + \rho|\Lambda_j|$ to be the net charge in Λ_j, and consider a sequence of domains Λ_j of *fixed shape* of capacitance $C_j = c|\Lambda_j|^{1/3}$. If $Q_j|\Lambda_j|^{-2/3} \to \sigma$, the result to be proved is that

$$g_j(\beta, \rho) \to g(\beta, \rho) - \tfrac{1}{2}\sigma^2 c \tag{29}$$

Note that σ can have either sign. If $|\sigma| = \infty$, then $g_j(\beta, \rho) \to -\infty$. This last statement is easily proved by noting that $|\Lambda_j|^{-1}\min\{U(\mathbf{x})|\mathbf{x}_i \in \Lambda_j\} \to +\infty$ when $|Q_j|\,|\Lambda_j|^{-2/3} \to +\infty$.

In order to simplify matters we shall prove the theorem only for balls, in which case $c = (4\pi/3)^{-1/3}$.

Let B be a ball of radius R and let B' be a concentric ball of radius $R' > R$. Note that a uniform charge density τ placed in $\Sigma \equiv B'\backslash B$ produces a constant potential $\tau\Phi(\Sigma)$ inside B. This same charge density in Σ has a self-energy $\tau^2 S(\Sigma)$. If $R \to \infty$ and $R'/R \to 1$, then

$$\Phi(\Sigma)|\Sigma|/S(\Sigma) \to 2 \tag{30}$$

Let $Z(N, B')$ be the partition function for N particles in B' with background density ρ. A lower bound to $Z(N, B')$ can be obtained as follows:

1. Restrict the configurations to N_1 particles in B and $N_2 = N - N_1$ particles in Σ.

2. Let $U_1(\mathbf{X}_1)$ [resp. $U_2(\mathbf{X}_2)$] be the potential energy of the particles and background in B [resp. Σ] and let $U_{12}(\mathbf{X}_1, \mathbf{X}_2)$ be the interdomain energy, where $\mathbf{X}_1$ and $\mathbf{X}_2$ are the particle coordinates. Then

$$Z(N, B') \geqslant (N_1!\,N_2!)^{-1} \int_{B^{N_1}} \exp[-\beta U_1(\mathbf{X}_1)] \times \int_{\Sigma^{N_2}} \exp\{-\beta[U_2(X_2) + U_{12}(\mathbf{X}_1, \mathbf{X}_2)]\} \tag{31}$$

3. Use Jensen's inequality on the second integral together with the aforementioned constancy of the potential $\Phi(\Sigma)$. Thus,

$$\begin{aligned}\ln Z(N, B') \geqslant \ln Z(N_1, B) &+ \ln\{|\Sigma|^{N_2}/N_2!\} \\ &- \beta S(\Sigma)\left[\tfrac{1}{2}\rho^2 + \binom{N_2}{2}|\Sigma|^{-2} - N_2\rho|\Sigma|^{-1}\right] \\ &- \beta\Phi(\Sigma)[\rho - N_2|\Sigma|^{-1}][\rho|B'| - N_1] \qquad (32)\end{aligned}$$

Now we consider a sequence of balls B_j of radii R_j with background density ρ and particle numbers $N_j = j$, $j = 1, 2, \ldots$. For $Q_j \equiv -j + \rho|B_j|$ negative we first use (32) with $N = j$, $B' = B_j$, $R = R_j - 1$, and $N_1 = \rho|B|$. Then we use (32) with $N = N_1 = j$, $B = B_j$, and $|B'| = j/\rho$. When $Q_j > 0$, we first use (32) with $N = N_1 = j$, $B' = B_j$, and $|B| = j/\rho$. Then we use (32) with $N_1 = j$, $B = B_j$, $R' = R_j + 1$, and $N = |B'|\rho$. Using the fact that $Q_j|B_j|^{-2/3} \to \sigma$ and (30), we obtain the desired result (29).

3.6. Microcanonical Ensemble

The existence of the thermodynamic limit for the microcanonical ensemble can be demonstrated using the methods of Ref. 5, Section VIII. There, the energy as a function of entropy was given for the quantum case. The corresponding classical equation is as follows: Let $\Gamma(N, \Lambda) = (\Lambda \times \mathbf{R}^3)^N$ be the phase space (including momentum). For σ real, let

$$\Delta(\sigma, N, \Lambda) = \{A \subset \Gamma(N, \Lambda) | \mu(A) = e^{\sigma|\Lambda|}\} \qquad (33)$$

where μ is Lebesgue measure. Let

$$\epsilon(A, N, \Lambda) = |\Lambda|^{-1} \int_A H(\mathbf{X}, \mathbf{P}) e^{-\sigma|\Lambda|} \qquad (34)$$

where

$$H(\mathbf{X}, \mathbf{P}) = U(\mathbf{X}) + \sum \mathbf{p}_i^2/2m$$

Then we define

$$\epsilon(\sigma, N, \Lambda) = \inf\{\epsilon(A, N, \Lambda) | A \in \Delta(\sigma, N, \Lambda)\} \qquad (35)$$

to be the energy per unit volume as a function of the entropy per unit volume, σ.

Obviously, when Λ_1 and Λ_2 are disjoint,

$$\Delta(\sigma_1 + \sigma_2, N_1 + N_2, \Lambda_1 \cup \Lambda_2) \supset \Delta(\sigma_1, N_1, \Lambda_1) \times \Delta(\sigma_2, N_2, \Lambda_2) \qquad (36)$$

Hence

$$\begin{aligned}&|\Lambda|\epsilon(\sigma_1 + \sigma_2, N_1 + N_2, \Lambda_1 \cup \Lambda_2) \\ &\qquad \leqslant |\Lambda_1|\epsilon(\sigma_1, N_1, \Lambda_1) + |\Lambda_2|\epsilon(\sigma_2, N_2, \Lambda_2) + \langle U(\Lambda_1, \Lambda_2)\rangle \qquad (37)\end{aligned}$$

where $\langle U \rangle$ is the average over A_1 and A_2 of the interaction energy between Λ_1 and Λ_2. [This may require passing to a subsequence in (35) for Λ_1 and Λ_2.]

Now we are in the same position as in (16); the existence and appropriate convexity properties of $\epsilon(\sigma)$ and $\sigma(\epsilon)$ follow. See Ref. 5, Section VIII for details.

The one essential difference from the systems studied in Ref. 5, Section VIII is that for jellium we do not obtain convexity of ϵ as a function of ρ, but only as a function of σ. This lack does not alter the equivalence of the canonical and microcanonical ensembles.

3.7. The Grand Canonical Ensemble

If one considers the grand canonical ensemble (GCE) for fixed Λ, fixed background density ρ, and fixed chemical potential μ, then the GCE partition function Ξ will exist. From the results of Section 3.5 the thermodynamic limit of $\pi = |\Lambda|^{-1} \ln \Xi$ will exist and $\pi = \rho\mu + g(\rho)$ as in Theorem 7.1 of Ref. 5, Section VII. If, on the other hand, one defines Ξ for neutral jellium by requiring that $\rho = N/|\Lambda|$ for each N, then Ξ will diverge, even for finite Λ. This is a consequence of (3) that $g(N, \Lambda) \sim N^{4/3}$ for large N. In the quantum case with fermions, this divergence will not occur since the kinetic energy is proportional to $N^{5/3}$. Although the thermodynamic limit of π for neutral jellium would then exist, it would not be equivalent to the canonical partition ensemble because of the lack of convexity of the free energy in ρ.

4. ADDITIONAL POTENTIALS

As was shown in Ref. 5, additional short-range forces among the particles can be included without any conceptual difficulty, but with a great deal of technical difficulty, provided they are tempered and provided that these forces are integrable. This means that hard cores are excluded. We do not say that the thermodynamic limit does not exist when hard cores are present—it probably does—but only that our method is not adequate. The difficulty arises in (11), where $\ln Z_K{}^D$ is estimated by Jensen's inequality in terms of $\langle U \rangle$. We made this estimate in order to show that the energy of the particles in D_K was not too large. If some other method could be found to show this, then perhaps hard cores could be included, but in our estimate, $\langle U \rangle = +\infty$ and $\ln Z_K{}^D \geqslant -\infty$ when hard cores are present.

There is another serious difficulty when additional potentials, even nice ones, are present. The scaling relation of Section 3.3 does not hold, and hence the continuity with respect to ρ that was used in Section 3.4.1 cannot be established that way.

5. QUANTUM MECHANICAL PARTICLES

We first remark that it is immaterial for our purposes whether the particles are bosons or fermions. In contrast to the situation for real particles, H-stability (2) holds in the classical sense and therefore Fermi statistics is not required. We shall construct the proof for fermions and it will obviously be valid for bosons as well. Dirichlet boundary conditions will be employed, i.e., $\psi = 0$ on the boundary of Λ.

5.1. Canonical Ensemble (Spherical Domains)

By well-known arguments (see Ref. 5, Section II), a lower bound to Z_K can be obtained by constraining the particles to lie in various subdomains. In this way we arrive at precisely the same inequality (9) as for the classical case. The problem is to show that $\ln Z_K{}^D$ is not too small. For this purpose it would be sufficient to find one wave function ψ for the M_K particles in D_K such that $\langle H_K \rangle \equiv \langle \psi, H_K \psi \rangle <$ (positive constant)M_K, where H_K is the total Hamiltonian of the M_K particles in D_K, including the background self-energy. Then, by the Peierls–Bogoliubov inequality,

$$\ln Z_K{}^D \geqslant -\beta \langle H_K \rangle \tag{38}$$

A natural suggestion would be to take a determinantal wave function that vanishes on the boundary of D_K, but this will not work for the reason that the single-particle density will not be a constant and consequently the estimate $\langle U \rangle_{D_K} < 0$ [Eq. (11)] will not hold. On the other hand, suppose one could find M_K points $\mathbf{Y} = \{\mathbf{y}_1, \ldots, \mathbf{y}_{M_K}\}$ in D_K such that:

(a) $U(\mathbf{Y}) <$ (positive constant)M_K.
(b) $|\mathbf{y}_i - \mathbf{y}_j| > 2h$ for some fixed $h > 0$.
(c) The distance of $\mathbf{y}_i$ to the boundary of D_K is $> h$ for all i.

Then one could construct a product wave function in which the single-particle wave functions have support in balls of radius h centered at the $\mathbf{y}_i$ and which are spherically symmetric about the $\mathbf{y}_i$. The kinetic energy would be proportional to h^{-2}. Due to the peculiar shape of D_K, we are unable to find such a $\mathbf{Y}$. What Eq. (11) shows is that there certainly exists a $\mathbf{Y}$ satisfying condition (a) but we do not know if it satisfies (b) and (c).

It is in fact possible to find a $\mathbf{Y}$ such that condition (a) is satisfied and condition (b) is *effectively* satisfied. To do this, define

$$U'(\mathbf{Y}) = U(\mathbf{Y}) + \sum_{i<j}^{M_K} L(\mathbf{y}_i - \mathbf{y}_j) \tag{39}$$

where $U(\mathbf{Y})$ is the Coulomb potential as before and

$$\begin{aligned} L(\mathbf{y}) &= 2(\pi/|\mathbf{y}|)^2 \qquad \text{for} \quad |\mathbf{y}| \leqslant 1 \\ &= 0 \qquad\qquad\quad \text{for} \quad |\mathbf{y}| > 1 \end{aligned} \tag{40}$$

Using (11), we obtain

$$\langle U'\rangle_{D_K} = \langle U\rangle_{D_K} + \binom{M_K}{2}|D_K|^{-2}\int_{D_K}\int L(\mathbf{x}-\mathbf{y})\,d\mathbf{x}\,d\mathbf{y}$$
$$\leqslant \binom{M_K}{2}|D_K|^{-1}8\pi^3 \leqslant 4\pi^3 M_K\rho \tag{41}$$

Therefore there exists a $\mathbf{Y}$ such that

$$U'(\mathbf{Y}) \leqslant 4\pi^3 M_K\rho \tag{42}$$

Let $d_i = \frac{1}{2}\min\{1, \min_{j\neq i}|\mathbf{y}_i - \mathbf{y}_j|\}$. Construct a product trial function ψ using single-particle functions $\{\varphi_i\}_{i=1}^{M_K}$ centered at $\mathbf{y}_i$ and having support in a ball of radius d_i of the form

$$\varphi_i(\mathbf{x}) = (2\pi d_i)^{-1/2}|\mathbf{x}-\mathbf{y}_i|^{-1}\sin[\pi|\mathbf{x}-\mathbf{y}_i|/d_i] \tag{43}$$

The kinetic energy of φ_i is $(\pi/d_i)^2/2$. The potential energy of ψ can be evaluated as follows: The particle–particle energy is the same as if the particles were located at $\mathbf{y}_i$, by Newton's theorem. The interaction of a smeared-out particle with the background is changed by the amount

$$\rho\int_{|\mathbf{x}|<d_i} d\mathbf{x}\int_{|\mathbf{y}|<d_i} d\mathbf{y}\,|\mathbf{x}-\mathbf{y}|^{-1}[\varphi_i(\mathbf{x}+\mathbf{y}_i)^2 - \delta(\mathbf{x})]$$
$$= \xi\rho\, d_i^2 \leqslant \xi\rho \tag{44}$$

where ξ is a constant, assuming that the ball of radius d_i lies entirely in D_K. Thus the total energy $\langle\psi, H_K\psi\rangle$ is less than

$$U'(Y) + \xi\rho M_K + 2\pi^2 M_K \leqslant (2\pi^2)M_K[1 + 2\pi\rho + \xi\rho(2\pi^2)^{-1}] \tag{45}$$

This result is exactly what conditions (a) and (b) would give.

Condition (c) is more difficult, for it requires that the coordinates in $\mathbf{Y}$ are not too close to the boundary. If one tries to introduce

$$U''(\mathbf{Y}) = U'(\mathbf{Y}) + \sum_i d(\mathbf{y}_i)^{-2}$$

where $d(\mathbf{y}_i)$ is the distance to the boundary, one will find that $\langle U''\rangle_{D_K} = \infty$ since $d(\mathbf{x})^{-2}$ is not integrable.

Since we are unable to deal with this problem directly, we shall modify our basic construction for the ball packing in such a way that the balls have a minimum spacing of some length independent of K.

Let $\{B_k\}_{k=0}^{\infty}$ be a sequence of balls of radii $R_k = R_0'(1+p)^k(1-\frac{1}{2}\theta^k)$ with $\theta = (1+p)^{-1}$, $p = 26$, and R_0' chosen so that $\rho|B_0| = 1$. Let $N_k = \rho|B_k|$, whence N_k is an integer. As shown in Ref. 5, Section IV, it is possible to pack B_K with n_{K-j} balls B_j so that the distance of every ball to the boundary is not less than $4h$ and the distance between balls is not less than $8h$, where

$h = R_0'(1 - \theta)/8$. As in Section 3.1, the part of B_K not covered by the packing will be called D_K.

Let us label the individual balls in the packing of B_K by a superscript i, namely B^i, and let R^i be its radius. Around B^i we construct two concentric, spherical shells S^i and T^i of radii $(R^i, R^i + h)$ and $(R^i + h, R^i + 2h)$, respectively. *Inside* B_K we also construct two concentric, spherical shells S_K and T_K of radii $(R_K - h, R_K)$ and $(R_K - 2h, R_K - h)$, respectively. All these shells are disjoint and lie in D_K and we denote by $D_K' \subset D_K$ the complement of the shells in D_K, and define $D_K'' = D_K' \cup T^i \cup T_K$.

We wish to find a $\mathbf{Y} = \{\mathbf{y}_1,\ldots, \mathbf{y}_{M_K}\}$ with $\mathbf{y}_i \in D_K''$, and a corresponding product wave function ψ such that $\langle H_K\rangle$ is not too large. To this end, let

$$\begin{aligned} f(\mathbf{y}) &= 1, && \mathbf{y} \in D_K' \\ &= 0, && \mathbf{y} \notin D_K'' \\ &= f^i, && \mathbf{y} \in T^i \\ &= f_K, && \mathbf{y} \in T_K \end{aligned} \tag{46}$$

where

$$\begin{aligned} f^i &= 1 + [(R^i + h)^3 - (R^i)^3][(R^i + 2h)^3 - (R^i + h)^3]^{-1} < 2 \\ f_K &= 1 + [(R_K - h)^3 - (R_K - 2h)^3]^{-1}[R_K{}^3 - (R_K - h)^3] < 3 \end{aligned} \tag{47}$$

whence

$$\int_{T^i} (f - 1) = \int_{S^i} 1$$

and similarly for T_K, S_K, and $\int f = |D_K|$.

Let

$$F(\mathbf{Y}) = \prod_{i=1}^{M_K} f(\mathbf{y}_i)$$

and let

$$\langle U'\rangle_F = \int F(\mathbf{Y})U'(\mathbf{Y}) \Big/ \int F(\mathbf{Y}) \tag{48}$$

The part involving L is [using (41)]

$$\binom{M_K}{2} |D_K|^{-2} \int\int f(\mathbf{x})f(\mathbf{y})L(\mathbf{x} - \mathbf{y}) \leqslant 9\cdot 4\pi^3 M_K\rho$$

since $f(\mathbf{x}) \leqslant 3$. The part involving $U(\mathbf{Y})$ is

$$\begin{aligned} &\tfrac{1}{2}\rho^2 \int_{D_K} d\mathbf{x} \int_{D_K} d\mathbf{y} |\mathbf{x} - \mathbf{y}|^{-1}[1 - f(\mathbf{x})][1 - f(\mathbf{y})] \\ &\quad - \tfrac{1}{2}\rho|D_K|^{-1} \int_{D_K} d\mathbf{x} \int_{D_K} d\mathbf{y}\, |\mathbf{x} - \mathbf{y}|^{-1} f(\mathbf{x})f(\mathbf{y}) \end{aligned} \tag{49}$$

The second term is negative. The first is the Coulomb energy of double shells, each pair of which is neutral and spherically symmetric. By Newton's theorem, this is just the sum of the self-energies of each pair. Let E_k be the self-energy of the two shells S and T surrounding a ball B_k in the packing and let W_K be the self-energy of the shells S_K and T_K. Then

$$\langle U'\rangle_F \leqslant 36\pi^3 M_K \rho + \sum_{j=0}^{K-1} n_{K-j} E_j + W_K \leqslant \text{const} \times M_K \tag{50}$$

The latter inequality comes from an elementary calculation of E_k and W_K.

The conclusion is that there exists a $\mathbf{Y}$ with $\mathbf{y}_i \in D_K''$ such that $U'(\mathbf{Y})$ is bounded by a constant times $|D_K|$. Now we construct a trial function ψ as before with φ_i given by (43) except that

$$d_i = \tfrac{1}{2}\min\{2h, 1, \min_{j\neq i}|\mathbf{y}_i - \mathbf{y}_j|\}$$

Then

$$\begin{aligned} |B_K|^{-1}\ln Z_K^D &\geqslant -\beta |B_K|^{-1}\langle\psi, H_K\psi\rangle \\ &\geqslant -\beta \times \text{const} \times |D_K|\,|B_K|^{-1} \end{aligned} \tag{51}$$

and this goes to zero as $K \to \infty$ like γ^K [Eq. (13)]. Thus the thermodynamic limit is established as in the classical case.

5.2. Canonical Ensemble (General Domains)

Let ρ be fixed. We take a regular sequence of domains $\{\Lambda_j\}_{j=1}^{\infty}$ tending to infinity which satisfies conditions A and B of Ref. 5, Section V. Also, $|\Lambda_j|\rho = j$. In addition, we require some conditions on the sequence which are not required in the classical case. These are the following:

(i) Let $h > 0$ and let Λ_j^h and Λ_j^{2h} be the domains

$$\begin{aligned} \Lambda_j^h &= \{\mathbf{x} \in R^3 | \mathbf{x} \notin \Lambda_j, d(\mathbf{x}; \partial\Lambda_j) \leqslant h\} \\ \Lambda_j^{2h} &= \{\mathbf{x} \in R^3 | \mathbf{x} \notin \Lambda_j^h \cup \Lambda_j, d(\mathbf{x}; \partial\Lambda_j^h) \leqslant h\} \end{aligned} \tag{52}$$

where $d(\cdot\,;\,\cdot)$ is the Euclidean distance. We require that $|\Lambda_j^h|/|\Lambda_j^{2h}|$ be bounded in j for each fixed h.

(ii) Consider the charge density

$$\begin{aligned} \sigma_j^h(\mathbf{x}) &= 1, & \mathbf{x} \in \Lambda_j^h \\ &= -|\Lambda_j^h|/|\Lambda_j^{2h}|, & \mathbf{x} \in \Lambda_j^{2h} \end{aligned} \tag{53}$$

Thus σ_j^h is neutral. Let $\varphi_j^h(\mathbf{x})$ be the Coulomb potential of σ_j. We require that there exists a function $C(h) < \infty$ such that for all $\mathbf{x} \in \Lambda_j^{2h} \cup \Lambda_j^h \cup \Lambda_j$

$$|\varphi_j^h(\mathbf{x})| < C(h) \tag{54}$$

and that

$$\lim_{h\to 0} C(h) = 0$$

(iii) Let E_j^h be the Coulomb self-energy of the double layer σ_j^h. We require that

$$\lim_{j=\infty} |\Lambda_j|^{-1} E_j^h = 0 \tag{55}$$

Conditions (i) and (ii) obviously imply (iii) since

$$E_j^h \leqslant \tfrac{1}{2}[\sup_{\mathbf{x}}|\sigma_j^h(\mathbf{x})|\,|\varphi_j^h(\mathbf{x})|][|\Lambda_j^{2h}| + |\Lambda_j^h|]$$

and

$$[|\Lambda_j^{2h}| + |\Lambda_j^h|]/|\Lambda_j| \to 0$$

by the Van Hove limit.

(iv) Define $\tilde{\Lambda}_j^h$, $\tilde{\Lambda}_j^{2h}$, $\tilde{\sigma}_j^h(x)$, and $\tilde{E}_j^h$ similarly to the above except $\mathbf{x} \notin \Lambda_j$ (resp. $\mathbf{x} \notin \Lambda_j^h \cup \Lambda_j$) is replaced by $\mathbf{x} \in \Lambda_j$ (resp. $\mathbf{x} \in \Lambda_j \backslash \Lambda_j^h$). That is, the double layer $\tilde{\sigma}_j^h$ is now inside Λ_j. We require that

$$\lim_{j\to\infty} |\Lambda_j|^{-1} \tilde{E}_j^h \to 0 \tag{56}$$

We do not require that the analogs of (i) and (ii) hold.

It is clear that for any reasonable sequence of domains, such as cubes or ellipsoids, these conditions will be satisfied. We shall not attempt to determine geometric conditions on the Λ_j so that (i)–(iv) hold.

Let Λ_j contain j particles. As in the classical case, we derive a lower bound for $Z(\Lambda_j)$. The kinetic energy for D_j can be handled as in Section 5.1. The only essential difference from inequality (15) is that we have to add the self-energy of the double layer $\tilde{\sigma}_j^h$ inside Λ_j and that of the double layers of the balls in the packing of Λ_j. Call this latter quantity $W(j)$. Thus, on the right side of the inequality we must add $-\beta\tilde{E}_j^h - \beta W(j)$. Using condition (iv), we have that

$$\liminf g_j \geqslant g(\beta, \rho) \tag{57}$$

An upper bound for $Z(\Lambda_j)$ is also obtained as in the classical case (18). For the domain D_j we choose a vector state ψ and have to compute

$$E(\psi) = \langle H_K \rangle + \langle U(D_j, \Lambda_j) \rangle \tag{58}$$

The kinetic energy part of $\langle H_K \rangle$ can be handled as in Section 5.1. If M_j is the number of particles in D_j, we have to find M_j points in $D_j'' = D_j -$

$\{\bigcup S^i \cup \Lambda_j{}^h\}$ in such a way that $E(\psi)$ is not too large. The novel feature is that $U(D_j, \Lambda_j)$ involves the additional term

$$\sum_{i=1}^{M_j} w(\mathbf{x}_i) \qquad \text{where} \qquad w(\mathbf{x}) = \int_{\Lambda_j} \rho_j(\mathbf{y})|\mathbf{x} - \mathbf{y}|^{-1}\, d\mathbf{y}$$

and $\rho_j(\mathbf{y})$ is the average charge distribution (including the background) in Λ_j in the canonical distribution. Although Λ_j is neutral, $w \neq 0$ because Λ_j is not spherical. To find these M_j points we again average over all allowed configuration in D_j''.

The self-energy of the double layers S^i and T^i is small for the same reason as in Section 5.1. The problem then reduces to computing $E_j{}^h$ as defined in condition (iii), together with the energy of the charge distribution $\sigma_j{}^h$ in the potential w. Condition (iii) states that $|\Lambda_j|^{-1}E_j{}^h \to 0$, so we can ignore it. The latter contribution, Δ_j, can be bounded as follows:

$$\begin{aligned} |\Delta_j| &= \left|\int w(\mathbf{x})\rho\sigma_j{}^h(\mathbf{x})\right| \\ &= \left|\int_{\Lambda_j} d\mathbf{x} \int d\mathbf{y}\ \rho_j(x)|\mathbf{x} - \mathbf{y}|^{-1}\rho\sigma_j{}^h(\mathbf{x})\right| \\ &= \rho\left|\int_{\Lambda_j} d\mathbf{x}\ \rho_j(\mathbf{x})\varphi_j{}^h(\mathbf{x})\right| \leqslant \rho C(h)\int_{\Lambda_j} d\mathbf{x}\ |\rho_j(\mathbf{x})| \\ &\leqslant \rho C(h)\int_{\Lambda_j} |\rho_+(\mathbf{x})| + |\rho_-(\mathbf{x})| \leqslant 2j\rho C(h) \end{aligned} \tag{59}$$

where $\rho_+ = \rho$ is the background charge and $\rho_-(\mathbf{x})$ is the average particle charge distribution.

Now we divide by $|\Lambda_j| = j$ and let $j \to \infty$. For each fixed h we obtain

$$\limsup_{j\to\infty} g_j \leqslant g(\beta, \rho) + \beta\rho C(h) \tag{60}$$

Since h is arbitrary, we can now let $h \to 0$ and, recalling condition (ii), obtain

$$\lim_{j\to\infty} g_j = g(\beta, \rho) \tag{61}$$

which is the desired result.

5.3. Scaling Relations

In Section 3.3 we showed that $g(\beta, \rho) = \rho(1 - \ln \rho) + \rho\bar{g}(\beta\rho^{1/3})$. Such a simple relation will not hold quantum mechanically. To obtain a similar result quantum mechanically, we have to add another parameter; the simplest is α, the square of the electric charge. Thus $H = K + U \rightarrow K + \alpha U$, where K is the kinetic energy operator.

We make a scale change which now involves α:

$$\rho' = \rho\eta^3, \qquad \beta' = \beta\eta^{-2}, \qquad \alpha' = \alpha\eta, \qquad \Lambda_j' = \eta^{-1}\Lambda_j \tag{62}$$

Then, as in Section 3.3 [Eq. (22)],

$$|\Lambda_j| g(\beta, \rho, \alpha; \Lambda_j) = |\Lambda_j'| g(\beta\eta^{-2}, \rho\eta^3, \alpha\eta; \Lambda_j') \tag{63}$$

Again, choosing $\eta = \rho^{-1/3}$, and taking the limit $j \rightarrow \infty$, we obtain

$$g(\beta, \rho, \alpha) = \rho g(\beta\rho^{2/3}, 1, \alpha\rho^{-1/3}) \tag{64}$$

This equation tells us nothing that we did not know before, i.e., α is an inessential parameter. But it does tell us something important about the continuity with respect to ρ. Define $\gamma = \beta\alpha$. Then

$$\ln Z = \ln \operatorname{Tr} \exp(-\beta K - \gamma U) \tag{65}$$

is a *jointly* convex function of (β, γ) for $\beta > 0$. Thus, when $\gamma > 0$, the thermodynamic limit $g(\beta, \rho, \gamma\beta^{-1})$ is convex, and hence continuous, in (β, γ). Hence the function $g(x, 1, y)$ is continuous in (x, y) when $x, y > 0$. Therefore $g(\beta, \rho, \alpha)$ is continuous in ρ for $\rho > 0$.

5.4. Properties of the Thermodynamic Limit and Related Questions

The results given for the classical case in Sections 3.4–3.6 and 4 hold for the quantum case. The conclusions of Section 3.7 have to be modified. In summary one has:

(i) Uniformity and continuity of the limit.

(ii) Unusual behavior of the pressure and compressibility.

(iii) Equivalence of canonical and microcanonical ensembles. The existence of the thermodynamic limit of the microcanonical ensemble includes as a special case the existence of the limiting ground state energy per unit volume. This is also true classically.

(iv) Existence of the grand canonical pressure even for strictly neutral systems because for large ρ, the quantum kinetic energy, which behaves like $\rho^{5/3}$, will dominate the electrostatic $-\rho^{4/3}$ term. We shall not prove this statement since the lack of convexity in ρ prevents the grand canonical ensemble from being equivalent to the canonical ensemble.

(v) The possibility of adding tempered potentials, with the same caveat as in Section 4.

APPENDIX. A LOWER BOUND FOR THE CLASSICAL AND QUANTUM MECHANICAL GROUND-STATE ENERGY

Consider a bounded, measurable set Λ with a uniform charge density ρ and N point particles of charge -1. We do not assume that Λ is spherical, that the points are constrained to lie in Λ, or that the total charge is zero.

To find a lower bound for the total electrostatic energy we use an idea of Onsager[12] to replace point charge distributions by charges smeared around the initial points. In fact one can show, by taking functional derivatives, that the best smearing is a uniform charge distribution inside a ball of radius a.

We define

U_{BB} the self-energy of the background;
U_i the interaction energy of the particle i at position $\mathbf{x}_i$ with the background;
U_{ij} the interaction of two particles at positions $\mathbf{x}_i$ and $\mathbf{x}_j$;
$\hat{U}_{ij}(a)$ the interaction (or twice the self-energy when $i = j$) of balls of total charge -1 with centers $\mathbf{x}_i$ and $\mathbf{x}_j$;
$\hat{U}_i(a)$ the interaction of such a ball with the background.

Then, with $\mathbf{X} = \{\mathbf{x}_1, \ldots, \mathbf{x}_N\}$

$$U(\mathbf{X}) = U_{BB} + \sum_{i=1}^{N} U_i + \sum_{i<j} U_{ij}$$

$$\begin{aligned} U(X) = U_{BB} + \sum_{i=1}^{N} \hat{U}_i + \frac{1}{2}\sum_{i,j}^{N} \hat{U}_{ij} \qquad & (\alpha) \\ + \sum_i (U_i - \hat{U}_i) \qquad & (\beta) \\ - \frac{1}{2}\sum_i \hat{U}_{ii} \qquad & (\gamma) \\ + \sum_{i<j} (U_{ij} - \hat{U}_{ij}) \qquad & (\delta) \end{aligned}$$

Let us consider these terms individually:

The (α) terms are evidently positive, being the total electrostatic energy of the background charge and the charged balls.

In (δ), a term $U_{ij} - \hat{U}_{ij}$ is zero if the two balls do not overlap by Newton's theorem. For overlapping balls, a simple calculation shows that $U_{ij} - \hat{U}_{ij} > 0$. Thus ($\delta$) is positive.

For (β) we calculate

$$U_i - \hat{U}_i \geqslant -(2\pi/5)\rho\alpha^2 \qquad \text{(A.1)}$$

The above is an equality whenever the ball lies completely in Λ.

For (γ)

$$\hat{U}_{ii} = 6/(5a) \tag{A.2}$$

Our lower bound is (β) + (γ), and the best bound is obtained when a is

$$a_{\max} = \rho^{-1/3}(3/4\pi)^{1/3} = r_s \tag{A.3}$$

With this value we obtain

$$U(\mathbf{X}) \geqslant -0.9Nr_s^{-1} = -0.9N\rho^{1/3}(4\pi/3)^{1/3} \tag{A.4}$$

for all $\mathbf{X}$.

For the quantum mechanical case, when the particles are spin-$\frac{1}{2}$ fermions, we consider a sequence of domains $\{\Lambda_j\}$ which tend to infinity in the sense of Van Hove and we constrain the particles to lie in Λ_j. We also suppose that $\rho|\Lambda_j| = j$, the number of particles, although this neutrality restriction is not essential in what follows.

Let

$$E_j = \inf_\psi \langle\psi|H|\psi\rangle|\Lambda_j|^{-1} \geqslant \inf_\psi |\Lambda_j|^{-1}\langle\psi|K|\psi\rangle + \inf_\psi |\Lambda_j|^{-1}\langle\psi|U|\psi\rangle$$

For $m = 1$ and j large

$$\begin{aligned}\inf\langle\psi, K\psi\rangle \approx j\rho^{2/3}(6/5)(3\pi^2)^{2/3} &= jr_s^{-2}(6/5)(9\pi/4)^{2/3} \\ &= 2.21jr_s^{-2}\ \mathrm{Ry}\end{aligned} \tag{A.5}$$

Therefore, to leading order in j,

$$j^{-1}H \geqslant r_s^{-2}(2.21 - 0.45r_s)\ \mathrm{Ry} \tag{A.6}$$

It makes sense here, unlike the situation for the classical or the Bose problem, to ask for the r_s that gives the lowest ground-state energy per particle. We obtain

$$r_s = 9.82 \tag{A.7}$$

and

$$j^{-1}H \geqslant -0.0229\ \mathrm{Ry} \tag{A.8}$$

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