Journal of Statistical Physics, Vol. 41, Nos. 5/6, 1985

Thermodynamics for Coulomb Systems: A Problem at Vanishing Particle Densities

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Received March 19, 1985; final July 11, 1985

In this paper I combine techniques recently developed by Charles Fefferman with the well-known methods of Joel Lebowitz and Elliott Lieb to resolve some technical problems left unsettled by Lebowitz and Lieb's fundamental 1972 paper "The constitution of matter: Existence of thermodynamics for systems composed of electrons and nuclei."

KEY WORDS: Coulomb; thermodynamics; quantum statistical mechanics; partition function.

1. INTRODUCTION

In their important papers[1] Joel Lebowitz and Elliott Lieb proved the existence of the infinite-volume Helmholtz free energy density limit for a neutral system of electrons and nuclei interacting via Coulomb forces. They showed that the limit is a convex function of the particle density vectors. This means that the free energy limit is continuous everywhere except possibly at the boundary of its domain of definition, i.e., at vanishing particle densities. As Lebowitz pointed out in Ref. 2, he and Lieb overlooked this possible discontinuity at vanishing particle densities when they applied their analysis of the neutral system free energy limit to other problems in their paper. In particular, it leaves a gap in their proof of the free energy limit for systems with a net charge and causes technical difficulties in their analysis of the grand canonical ensemble. Continuity at vanishing particle densities is actually necessary for their net charge result to hold. The major problem with their analysis of the grand canonical ensemble can be circumvented using ideas implicit in other parts of their paper.

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0022-4715/85/1200-0975$04.50/0

In addition to what might be called its technical interest, this possible discontinuity at vanishing particle densities poses the physically meaningful question of whether a vanishingly small density of some particle species can render a nonvanishing catalytic effect on the thermodynamics of the system. Lebowitz discusses this in (2) and expresses interest in seeing the problem resolved. I will do that in this paper by combining Charles Fefferman's recent analysis[3] of the infinite-volume pressure limit with the work of Lebowitz and Lieb. These approaches complement each other and provide the apparatus for dealing with many interesting questions is quantum statistical physics. This will be evident in a forthcoming article by Fefferman in which he shows that quantized electrons and protons at suitable temperature and density form an ideal gas of hydrogen atoms or molecules. To present the results in this paper in an understandable way, I need to describe and relate the essential ideas of the Lebowitz–Lieb and the Fefferman approaches. I hope that researchers interested in applying these techniques will find this exposition useful. This paper also contains an explicit calculation of the low-density asymptotic form of the free energy.

As the free energy limit is the central object in their approach, Lebowitz and Lieb focus on the canonical ensemble. Fefferman analyzes the grand canonical ensemble. The problem of continuity of the free energy at the boundary of the particle density vector domain amounts to the question of whether the infinite-volume limit and the vanishing particle density limit can be interchanged. Lebowitz and Lieb's method does not give the uniform convergence necessary to interchange these limits. On the other hand, it is not hard to deduce some quantitative control on the rate of convergence of Fefferman's grand canonical pressure limit as a component of the chemical potential approaches $-\infty$. In particular, the convergence is uniform there. Once the equivalence of the canonical and grand canonical ensembles has been established (the possible discontinuity caused problems with Lebowitz and Lieb's proof of this), we can equate particle density tending to zero and chemical potential tending to $-\infty$ and conclude that the same uniformity holds for the free energy limit. I thank both Elliot Lieb and, of course, my thesis advisor Charles Fefferman for suggesting this problem and for many helpful discussions.

2. NOTATION

This paper deals with systems of s species of positively and negatively charged particles with charges $(e_1,..., e_s) = E \in \mathbb{Z}^s$. The negatively charged particles are assumed to be fermions. For finite-volume systems the particles are contained in some region $\Omega \subset \mathbb{R}^3$ whose volume is denoted $|\Omega|$. The number of species j particles is denoted N_j; $N = (N_1,..., N_s)$ is the particle number vector and $\rho = N/|\Omega|$, the particle density vector. In this paper the regions Ω will always be balls B_R. The results here extend to the same more general domains that are considered in (1) and (3). The Hamiltonian governing a system of N particles in a ball B_R is $H_{N,B_R} = -\Delta_N + V_N$, where

$$-\Delta_N = -(m_1 \Delta_{N_1} + \cdots + m_s \Delta_{N_s})$$
$$= -\sum_{i=1}^{s} m_i \sum_{k=1}^{N_i} \Delta_{X_i^k}$$

$$\text{and} \quad V_N = \frac{1}{2} \sum_{i=1}^{s} \sum_{j=1}^{s} \sum_{k=1}^{N_i} \sum_{l=1}^{N_j} \frac{e_i e_j}{|X_i^k - X_j^l|}, \qquad l \neq k \quad \text{if} \quad i = j$$

with m_i the mass of a species i particle and X_i^k the kth species i particle. H_{N,B_R} acts on $L^2_{N,B_R} = \{$square integrable $\psi(...X_i^k...)$ on $\sum_{B_R}^{s}{}_{i=1} N_i$ and satisfying the correct statistics$\}$ with Dirichlet boundary conditions. In our problem the negatively charged particles are fermions. So, if $e_i < 0$ ψ is assumed antisymmetric in the species i variables. The positively charged species may be either fermions or bosons (depending on which species) and therefore require that ψ be either antisymmetric or symmetric in the corresponding variables. This is what is meant by "satisfying the correct statistics." Let β^{-1} = temperature. The canonical partition function for N particles in a ball B_R is $\operatorname{Tr}[\exp(-\beta H_{N,B_R})]$. Define this trace to be 1 if $N = 0$. This defines the free energy per unit volume by

$$F_R(\beta, N/|B_R|) = -(\beta\,|B_R|)^{-1} \ln \operatorname{Tr}[\exp(-\beta H_{N,B_R})] \tag{2.1}$$

For ρ not of the form $N/|B_R|$, $F_R(\beta, \rho)$ is defined by linear interpolation. The grand canonical partition function depends on another variable $\mu \in \mathbb{R}^s$, the chemical potential. It is given by $\sum_{N \in \mathbb{Z}^s_{\geq 0}} e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R})]$ and defines the pressure by

$$\Pi_R(\beta, \mu) = (\beta\,|B_R|)^{-1} \ln \sum_{N \in \mathbb{Z}^s_{\geq 0}} e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R})] \tag{2.2}$$

In this paper, we are interested in the infinite-volume (or "thermodynamic") limits $F(\beta, \rho) = \lim_{R \to \infty} F_R(\beta, \rho)$ and $\Pi(\beta, \mu) = \lim_{R \to \infty} \Pi_R(\beta, \mu)$. The dependence of these function on β will not be important here and will usually be suppressed. That is, we will write $F_R(\rho)$, etc.

3. LEBOWITZ AND LIEB'S ANALYSIS

3.1. The neutral free energy limit

Consider a system of N particles in a ball B_R. Let B_{R_1} and B_{R_2} be disjoint subdomains of B_R and let $N^1 + N^2 = N$. The key step is a comparison between the system with N particles in B_R and the system with N^1 particles in B_{R_1} and N^2 in B_{R_2}. Under the assumption that one of N^1 and N^2 is neutral, we will prove that the free energy is increased if the particles are contrained to lie in the smaller domains. This fact lies at the heart of thermodynamic stability and manifests itself in the convexity of the free energy limit $F(\rho)$. Let us record and prove it in the following form.

L.L. Inequality. Let $B_{R_1} \cup B_{R_2} \subset B_R$ with $B_{R_1} \cap B_{R_2} = \varnothing$. And $N^1 + N^2 = N$ with $N^1 \cdot E = 0$. Then,

$$\operatorname{Tr}[\exp(-\beta H_{N,B_R})] \geqslant \operatorname{Tr}[\exp(-\beta H_{N^1,B_{R_1}})] \cdot \operatorname{Tr}[\exp(-\beta H_{N^2,B_{R_2}})] \tag{3.1}$$

Proof. Notice that

$$\operatorname{Tr}[\exp(-\beta H_{N,B_R})] = \sup_{\{\psi_n\}} \sum_{n=1}^{\infty} \exp - \beta(H_{N,B_R}\psi_n, \psi_n) \tag{3.2}$$

where the supremum is taken over all orthonormal sequences $\{\psi_n\}$ of $L^2_N(B_R)$ functions. This quantity is only decreased if the supremum is taken over a restricted class of functions, namely, those which correspond to having N^i particles in B_{R_i}, $i = 1, 2$. This idea is behind the proof.

Consider the disjoint union of the

$$K = \prod_{i=1}^{s} \binom{N_i}{N_i^1}$$

permutation copies $\{D_i\}$ of $D_1 = X_{i=1}^s (B_{R_1}^{N_i^1} \times B_{R_2}^{N_i^2})$. Notice that $L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$ is isomorphic to the subset of $L^2(D_1)$ functions which are statistically correct in the N^1 and N^2 variables *separately*. Let H_{D_1} be the old Hamiltonian H_{N,B_R} acting on $L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$. Any $\Phi \in L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$ can be extended in the unique and obvious way to a function $\tilde{\Phi}$ which is statistically correct in all N variables, i.e., which is $L^2_N(B_R)$. Notice that $(\tilde{\Phi}_i, \tilde{\Phi}_j) = K(\Phi_i, H_{D_1}\Phi_j)$ for $\Phi_i, \Phi_j \in L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$. Hence, if $\{\Phi_i\} \in L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$ is an orthonormal sequence then $\{(1/\sqrt{K})\, \tilde{\Phi}_i\} \subset L^2_N(B_R)$ is a candidate for the supremum on the right side of (3.2) and $\sum_i \exp\{-\beta(H_{N,B_R}(1/\sqrt{K})\, \tilde{\Phi}_i, (1/\sqrt{K})\, \tilde{\Phi}_i]\} = \sum_i \exp[-\beta(H_{D_1}\Phi_i, \Phi_i))$. If the supremum of this quantity is taken over all orthonormal sequences in $L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$ we obtain $\operatorname{Tr}[\exp(-\beta H_{D_1})]$ and, by the comments about restricting the class of functions in (2.2), find that $\operatorname{Tr}[\exp(-\beta H_{N,B_R})] \geqslant \operatorname{Tr}[\exp(-\beta H_{D_1})]$.

Claim.

$$\operatorname{Tr}[\exp(-\beta H_{D_1})] \geqslant \operatorname{Tr}[\exp(-\beta H_{N^1,B_{R_2}})] \cdot \operatorname{Tr}[\exp(-\beta H_{N^2,B_{R_2}})].$$

Proof of Claim. Observe that $H_{D_1} = H_{N^1,B_{R_1}} + H_{N^2,B_{R_2}} - W$ where

$$W(\cdots X_i^k \cdots, \cdots Y_j^l \cdots) = \sum_{i=1}^{s} \sum_{k=1}^{N_i^1} \sum_{j=1}^{s} \sum_{l=1}^{N_j^2} \frac{eiej}{|X_i^k - Y_j^l|} \quad \text{for} \quad X_i^k \in B_{R_1} \quad \text{and} \quad Y_j^l \in B_{R_2}$$

is the Coulomb interaction between the disjoint balls. The eigenfunctions for $H_{N^1,B_{R_1}} + H_{N^2,B_{R_2}}$ on $L^2_{N^1}(B_{R_1}) \otimes L^2_{N^2}(B_{R_2})$ are $\{\psi_{1i}(\cdots X_i^k \cdots)\, \psi_{2j}(\cdots Y_j^l \cdots)\}_{i,j=1}^{\infty}$ where $\{\psi_{1i}\}$ and $\{\psi_{2j}\}$ are those for $H_{N^1,B_{R_1}}$, and $H_{N^2 B_{R_2}}$, respectively. This decomposition results in $\mathrm{Tr}\{\exp[-\beta(H_{N^1,B_{R_1}} + H_{N^2,B_{R_2}})]\} = \mathrm{Tr}[\exp(-\beta H_{N^1,B_{R_1}})] \cdot \mathrm{Tr}[\exp(-\beta H_{N^2,B_{R_2}})]$. The assumption $N_1 \cdot E = 0$ will allow us to conclude that the expected value taken over the above trace of the Coulomb interaction between the disjoint balls is zero. This is the screening that keeps the world from collapsing and consequently insures the existence of the thermodynamic limit.

Let $\langle W \rangle$ denote this expected value. That is,

$$\langle W \rangle = \frac{\sum_{i,j=1}^{\infty} (W\psi_{1i}\psi_{2j}, \overline{\psi_{1i}\psi_{2j}}) \exp\{-\beta((H_{N^1,B_{R_1}} + H_{N^2,B_{R_2}})\, \psi_{1i} \cdot \psi_{2j}, \overline{\psi_{1i}\psi_{2j}})\}}{\sum_{i,j} \exp[-\beta(\cdots)_{ij}]}$$

$$= \frac{\sum_{i,j=1}^{\infty} \int_{B_{R_1}} \int_{B_{R_2}} \Phi_{1i}(x)\, \Phi_{2j}(y)/(|x-y|)\, dxdy \exp[-\beta(\cdots)_{ij}]}{\sum_{i,j} \exp[-\beta(\cdots)_{ij}]}$$

where Φ_{1i}, Φ_{2j} are the charge densities associated with ψ_{1i}, ψ_{2j}, respectively. Pulling the sum inside the integral gives

$$\langle W \rangle = \int_{B_{R_1}} \int_{B_{R_2}} \frac{\Phi_1(x)\, \Phi_2(y)}{|x-y|}\, dxdy, \qquad \text{where}$$

$$\Phi_1(x) = \frac{\sum_{i=1}^{\infty} \Phi_{1i}(x) \exp[-\beta(H_{N^1,B_{R_1}}\psi_{1i}, \bar{\psi}_{1i})]}{\sum_{i=1}^{\infty} \exp[-\beta(H_{N^1,B_{R_1}}\psi_{1i}, \bar{\psi}_{1i})]}$$

with the analogous definition of Φ_2. As $N_1 \cdot E = 0$, $\int_{B_{R_1}} \Phi_{i1}(x)\, dx = 0$ for all $i = 1,..., \infty$ and so $\int_{B_{R_1}} \Phi_1(x)\, dx = 0$. As simple arguments show [see Appendix of Ref. (1) if necessary], the rotational symmetry of $H_{N^i,B_{R_i}}$ implies that $\Phi_i(x)$ is radial, $i = 1, 2$. Since $B_{R_1} \cap B_{R_2} = 0$, Newton's famous electrostatic theorem shows that

$$\int_{B_{R_1}} \int_{B_{R_2}} \frac{\Phi_1(x)\, \Phi_2(y)}{|x-y|}\, dxdy = \left[\int_{B_{R_1}} \Phi_1(x)\, dx\right] \times \left[\int_{B_{R_2}} \Phi_2(y)\, dy\right] \frac{1}{|\text{distance of centers}|} = 0$$

proving that $\langle W \rangle = 0$.

The claim now follows from the following theorem by substituting

$$A = H_{N^1, B_{R_1}} + H_{N^2, B_{R_2}},\ B = W,\ \{f_i\} = \{\psi_{1i} \cdot \psi_{2j}\}$$

Theorem (Peierls). Let A and B be self-adjoint operators on a Hilbert space with domains $D(A)$ and $D(B)$ and let $F = \{f_i\}$ be a countable set of orthogonal vectors in $D(A) \cap D(B)$. Then,

$$\begin{aligned} \mathrm{Tr}[\exp(A+B)] &\geqslant \sum_i [f_i, \exp(A+B) f_i] \\ &\geqslant \sum_i \exp[f_i, (A+B) f_i] \\ &\geqslant \exp\langle B \rangle_{A,F} \cdot \sum_i \exp(f_i, Af_i) \end{aligned}$$

where

$$\langle B \rangle_{A,F} = \frac{\sum_i (Bf_i, f_i) \exp(f_i, Af_i)}{\sum_i \exp(f_i, Af_i)}$$

Proof. The first inequality follows from our alternative definition of trace as a supremum. The second and third follow from the convexity of exp as a function on the measure space that a function f_i induces on the spectrum of $A+B$ and on the space $\{f_i, Bf_i\}$ with measure $\exp(f_i, Af_i)/\sum_i \exp(f_i, Af_i)$, respectively. ∎

Therefore, the L.L. Inequality is proved. Taking the logarithm of both sides better reflects its fundamental physical significance as a statement about free energies:

$$|B_R|\, F_R(N/|B_R|) \leqslant |B_{R_1}|\, F_{R_1}(N^1/|B_{R_1}|) + |B_{R_2}|\, F_{R_2}(N^2/|B_{R_2}|) \qquad (3.3)$$

Divide both sides by $|B_R|$ and notice that it closely resembles a convexity condition.

The L.L. Inequality generalizes in the obvious way to the cas of any finite number of disjoint subdomains $B_{R_i} \subset B_R$ with neutral particle vectors N^i. (It still works if just one N^i is not neutral.) Using its free energy density form, the statement is that

$$F_R(N/|B_R|) \leqslant \sum_i |B_{R_i}|/|B_R|\, F_{R_i}(N_i/|B_{R_i}|) \qquad (3.4)$$

This results in a kind of montonicity in R for F_R as $R \to \infty$. To prove the existence of the limit, Lebowitz and Lieb pack subdomains $\{B_{R_i}\}$ in a ball

B_R in a special way, make precise what monotonicity exists, and then demonstrate a lower bound.

For imagistic reasons, Lebowitz and Lieb refer to their packing as a "swiss cheese" (see Ref. 4). The construction is based on the simple idea that disjoint open cubes of side length d can be placed inside of a domain Ω in such a way that they cover at least $|\Omega\setminus\Omega_{\sqrt{3}d}|/|\Omega|$ proportion of the volume, where $\Omega_{\sqrt{3}d}=\{x\in\Omega \mid |x-\Omega^c|<\sqrt{3}\,d\}$. To see that this is true, simply cover Ω by disjoint cubes and then remove all those that touch Ω^c. Now, if a ball B_R is packed with specified finite numbers of balls of known radii $\{R_i\}_{i=1}^M$, then for $\Omega=B_R\setminus UB_{R_i}$ we can get a lower bound on $|\Omega\setminus\Omega_{\sqrt{3}d}|/|\Omega|$. By placing a ball of sufficiently small radius R_0 at the center of each cube, we can increase our packing in such a way that a definite additional proportion of B_R is covered. As Lebowitz and Lieb calculate, it is possible to pick $R_i=(1/28)\,R_{i+1}$ and to have the B_{R_i} cover 1/28 of the volume $B_R\setminus\bigcup_{k=i+1}^M B_{R_k}$ (where $R_m=(1/28)\,R$). If we start with an arbitrary R_0 and define $R_i=28R_{i-1}$ then we have a method for packing exponentially larger domains B_{R_k} with the smaller domains $\{B_{R_i}\}_{i<k}$ in such a way that the proportion not covered goes exponentially to zero.

Suppose now that R_0 has been picked so that $28(4\pi/3)\,R_0^3\rho=N^0\in\mathbb{Z}_{\geq 0}^s$ where $\rho\in\mathbb{R}^s$ is our particle density vector. Define $N^j=28^{3j}(4\pi/3)\,R_0^3\,\rho$ for $j\geq 1$. If N^j particles are in B_{R_j} then their density is ρ if $j\geq 1$ and 28ρ if $j=0$. Hence, the N^K particles in a large ball B_{R_k} can be divided among the smaller balls B_{R_i}, $i<k$, by putting N^i particles in each ball of radius R_i. The reason that the density in the smallest ball must be 28ρ rather than ρ is that by construction only 1/28 of the volume of $B_{R_k}\setminus\bigcup_{i=1}^{k-1} B_{R_i}$ is covered by B_{R_0}.

Assuming $\rho\cdot E=0$, the L.L. Inequality in the form (3.4) applies to give a recursion relation between the F_{R_k}:

$$F_{R_k}(\rho)=\frac{|\bigcup B_{R_0}|}{|B_{R_k}|}\,F_{R_0}(28\rho)+\sum_{j=1}^{k-1}\frac{|\bigcup B_{R_j}|}{|B_{R_k}|}\,F_{R_j}(\rho)-d_k(\rho) \tag{3.5}$$

for some $d_k(\rho)\geq 0$. Here, $\bigcup B_{R_j}$ denotes the union of all balls of radius R_j. One can explicitly calculate the volume ratios and use the implicit recursion to obtain

$$F_{R_k}(\rho)=(1/28)\,F_{R_0}(28\rho)-\sum_{j=1}^{k-1}\frac{d_j(\rho)}{28}-d_k(\rho) \tag{3.6}$$

Since each $d_j(\rho)\geq 0$ the quantity $F_{R_k}(\rho)+d_k(\rho)$ is decreasing. This should not be surprising since $F_{R_k}+d_k$ is the free energy per unit volume for the system obtained by restricting the particles to the balls in the covering; as

$R_k \to \infty$ a smaller proportion must be constrained to the smaller balls (in particular to the B_{R_0} at much higher density 28ρ). Note that we do not know that $F_{R_k}(\rho)$ is decreasing as $R_k \to \infty$.

To show that $F_{R_k}(\rho)$ converges, Lebowitz and Lieb demonstrate a lower bound $h(\rho)$ for $F_{R_k}(\rho)$ which is independent of R. For if $F_{R_k}(\rho) > h(\rho)\, \forall R_k$ then by (3.6) $\sum_{j=1}^{\infty} [d_j(\rho)/28] < \infty$ and $d_k \to 0$. Thus $F_{R_k}(\rho) + d_k(\rho)$ is also bounded. By its monotonicity it converges to a limit $\lim_{k\to\infty} F_{R_k}(\rho) + d_k(\rho) = F(\rho)$. Because $\lim_{k\to\infty} d_k(\rho) = 0$, this limit equals $\lim_{k\to\infty} F_{R_k}(\rho)$. If we take a different sequence of balls with radii $R'_j \to \infty$ then, by on one hand packing the $B_{R'_j}$ with balls of our original radii R_i and on the other picking our B_{R_j} with balls of radii $B_{R'_j}$, we can see that both sequences give the same limiting free energy $F(\rho)$. We can thus write $F(\rho) = \lim_{R\to\infty} F_R(\rho)$. Finally, let me indicate the lower bound that Lebowitz and Lieb use.

Lemma. There exists a finite function $h(\beta, \rho)$ such that for any B_R and N with $\rho = N/|B_R|$. We have

$$F_R(\rho, \beta) \geqslant h(\beta, \rho) \tag{3.7}$$

Proof. Recall the familiar Lieb–Thirring "stability of matter" inequality:

$$H_{N,B_R} \geqslant -C\left(\sum_{i=1}^{s} N_i\right)$$

for class of ψ that we have been considering. The same holds with a different constant C if we replace $H_{N,B_R} = -\Delta_N + V_N$ by $-1/2\Delta_N + V_N$. Inserting this into the partition function gives

$$\mathrm{Tr}[\exp(-\beta H_{N,B_R})] \geqslant \exp\left(\beta C \sum_{i=1}^{\infty} N_i\right) \mathrm{Tr}[\exp(\beta/2\Delta_{N,B_R})]$$

The result now follows from the free particle free energy bound (see Fisher (1964)).

3.2. Additional Properities and the Problem at $\partial E^{\perp}$

Notice that the convergence proof presented above offers no means of determining the rate at which F_{R_k} converges to F. The quantity $|F - F_{R_k}|$ is related to the convergence of the d_j to zero. The d_j arise as errors in the inequality (3.4) and are related to ratios of supremums taken over complicated sets of functions. They appear quantitatively unmanageable. However, Lebowitz and Lieb were able to deduce several qualitative features about the convergence of F_{R_k} and about the resulting limit. These rely primarily on the convexity inherent in (3.3). In particular, they prove the following theorem.

Theorem. The limit $F(\rho)$ is a convex function on the set $E^\perp = \{p \in \mathbb{R}^s_{\geqslant 0} \mid \rho \cdot E = 0\}$.

Proof. Let $\rho = \lambda\rho_1 + (1-\lambda)\rho_2$ where $\rho_i \in E^\perp$ and λ is a rational number between 0 and 1. As I pointed out above, the limit F is independent of the sequence of balls converging to infinity. In particular, we can pick a sequence $\{R_i\}_{i=0}^\infty$ and an associated packing of B_{R_k} by $\{B_{R_i}\}_{i<k}$ in such a way that λ proportion of balls of each radius R_i, $i \geqslant 1$, can contain density ρ_1 of particles and $(1-\lambda)$ density ρ_2 and the smallest balls B_{R_0} contain the necessary larger ratio. If we divide the $\rho \cdot |B_{R_k}|$ particles of B_{R_k} in this way and apply (3.4) we obtain

$$F_{R_k}(\rho) \leqslant \lambda \left[\sum_{l=1}^{k-1} |\bigcup B_{Rl}|/|B_{R_k}|\, F_{R_l}(\rho_1) + |\bigcup B_{R_0}|/|B_{R_k}|\, F_{R_0}(c\rho_1) \right]$$

$$+ (1-\lambda) \left[\sum_{l=1}^{k-1} |\bigcup B_{R_l}|/|B_{R_k}|\, F_{R_k}(\rho_2) + |\bigcup B_{R_0}|/|B_{R_k}|\, F_{R_0}(c\rho_2) \right]$$

In analogy with (3.5) this is

$$= \lambda[F_{R_k}(\rho_1) + d_k(\rho_1)) + (1-\lambda)(F_{R_k}(\rho_2) + d_k(\rho_2)]$$

which converges to $\lambda F(\rho_1) + (1-\lambda) F(\rho_2)$. ∎

Since $F(\rho)$ is convex on $E^\perp$ it is continuous everywhere except possibly at the boundary $\{\rho_i = 0 \text{ some } i\}$ of $E^\perp$. Furthermore, F is a monotone limit of continuous functions. To see this, notice that defining F_R for all $\rho \in \mathbb{R}^s$ by linear interpolation preserves inequalities (3.3) and (3.4). If $\{R_j\}_{j=0}^\infty$ is a sequence of radii corresponding to a particular ρ via the construction in the proof of the limit, then the errors $d_k(\rho)$ in (3.5) are likewise defined by linear interpolation. The same recursion exists and the convexity of the lower bound h insures that it still holds. Hence, $F_{R_k}(\rho) + d_k(\rho)$ decreases to $F(\rho)$ for all ρ. Since $F_{R_k} + d_k$ is defined by linear interpolation it is continuous.

A simple advanced calculus argument shows that a monotone limit of continuous functions converges *uniformly* to its limit on every compact set on which the limit is continuous. The converse of course also holds. As $F_{R_k}(\rho) + d_k(\rho) = 1/28 F_{R_0}(28\rho) - \sum_{j=1}^{k-1} d_j(\rho)/28$, we see that $d_k(\rho)$ converges uniformly to zero and $F_{R_k}(\rho)$ converges uniformly to $F(\rho)$ *only* where F is continuous. The convexity of F on $E^\perp$ does not guarantee this at $\partial E^\perp$.

Notice that if F_R converges uniformly to F in a neighborhood of a point ρ then we do not have to specify the particle density exactly when taking the infinite-volume limit. That is, if $N_R/|B_R| \to \rho$ then $F_R(N_R/|B_R|) \to F(\rho)$. As Lieb points out in (4), this is important for the practical reason that particle density can never be exactly pinpointed in the laboratory. Lack of uniform convergence at $\{\text{some } \rho_i = 0\}$ would mean that our theory predicts that a few stray atoms whose nuclei are supposed to have density zero could change the laboratory results. In the same vein, notice that *any* density $\rho \in \mathbb{R}^s_{\geqslant 0}$ is at "vanishing particle density" if we decide to consider move species of particles in our analysis.

In the next two sections, I will indicate the problems that this difficulty at $\partial E^\perp$ caused in Lebowitz and Lieb's paper.

3.3. Systems with Excess Charge

To apply the L.L. Inequality to the balls $\{B_{R_i}\}_{i<k}$ packed in B_{R_k} it was necessary that $\rho \cdot E = 0$. Lebowitz and Lieb used the analysis implicit in the proof of the L.L. Inequality to extend their result to the case $\rho \cdot E = Q \neq 0$.

Basic electrostatics tells us that any excess charge Q in a domain Ω concentrates itself on the boundary where it has energy $Q^2/2C\,|\Omega|^{1/3}$, C being the shape dependent capacity of Ω. For a ball B_R, the charge concentrates itself uniformly on $S_R = \partial B_R$ with density $Q/4\pi R^2$. The electrostatic energy is thus

$$\frac{1}{2} \frac{Q^2}{(4\pi R^2)^2} \iint_{S_R \times S_R} \frac{1}{|x-y|}\, d_{\text{Б}R}(x)\, d_{\text{Б}R}(y)$$

$d_{\text{Б}R}$ = Lebesque measure on S_R. By dilation this equals

$$\frac{1}{2} \frac{Q^2}{(4\pi R^2)^2} (4\pi R^2)^2 \frac{1}{R} \iint_{S_1 \times S_1} \frac{1}{|x-y|}\, d_{\text{Б}}(x)\, d_{\text{Б}}(g)$$

where now $d_{\text{Б}}$ is normalized measure on the unit sphere S_1. Since

$$\iint_{S_1 \times S_1} \frac{1}{|x-y|}\, d_{\text{Б}}(x)\, d_{\text{Б}}(y) = \int_{S_1} \frac{1}{|x|}\, d(x) = 1$$

the surface energy for B_R is $Q^2/2R$ and $C = 1/(4\pi/3)^{1/3}$. This leads to the expectation that adding some excess charge Q_R to our otherwise neutral system of $N_R = \rho\,|B_R|$ particles in B_R results in a free energy per unit volume that is approximately $F_R(p) + Q_R^2/2C\,|B_R|^{4/3}$. If $Q_R/|B_R|^{2/3}$ converges to a "surface charge" Б then we expect that the limiting free energy density should be $F(p) + \text{Б}^2/2C$. Except for the possible discontinuity problem at $\partial E^\perp$, Lebowitz and Lieb prove this.

To be precise, assume $N_R \cdot E = 0$ and $N_R/|B_R| = \rho$. (Fixing this density precisely avoids undue complication arising from the problem discussed at the end of Section 3.2.) Let $n_R \cdot E = Q_R$ with $n_R/|B_R| \to 0$ and $Q_R/|B_R|^{2/3} \to Б$. The desired result is that $F_R((N_R + n_R)/|B_R|) \to F(\rho) + Б^2/2C$. The method of attack incorporates the idea used in proving the L. L. Inequality that the partition function is only decreased if we restrict the class of functions over which the trace defining it is taken. To get a lower bound on $\mathrm{Tr}[\exp(-\beta H_{N+n,B_R})]$ we will restrict to functions ψ for which the excess charge particles n are contained in a spherical shell bounding, but disjoint from, the ball containing N. For an upper bound we will add particles m to neutralize the system and then restrict to functions ψ for which the m particles are in a spherical shell about the $N+n$ particles.

Since $n_R/|B_R| \to 0$ there is α_R with $\alpha_R/R \to 0$ such that $n_R/\alpha_R R^2 \to 0$. Let $S_R = B_R \setminus B_{R-\alpha_R}$. The analysis implicit in the proof of the L. L. Inequality shows that

$$\begin{aligned} &\mathrm{Tr}[\exp(-\beta H_{N+n,B_R})] \\ &\qquad \geqslant \mathrm{Tr}[\exp(-\beta H_{N,B_{R-\alpha_R}})] \cdot \mathrm{Tr}[\exp(-\beta H_{n,S_R})] \exp\langle W \rangle \end{aligned} \tag{3.8}$$

where $\langle W \rangle$ is the expected Coulomb interaction taken over the above traces. However, as $N \cdot E = 0$ and $H_{N,B_{R-\alpha_R}}$ is spherically symmetric, the earlier arguments show that $\langle W \rangle = 0$. Furthermore, if ψ is any $L_n^2(S_R)$ wave function then $\mathrm{Tr}[\exp(-\beta H_{n,S_R})] \geqslant \exp(-\beta H_{n,S_R}\psi, \psi))$. ψ can be picked so that it approximates a uniform charge distribution in S_R as $R \to \infty$. Simply let ψ correspond to charge clouds about the n particles placed uniformly around S_R. Since $n_R/|S_R| \to 0$ this can be done so that total kinetic energy $\langle -\Delta_{n_R}\psi, \psi \rangle$ is $o(R^3)$. Thus, $\langle H_{n_R,S_R}\psi, \psi \rangle = 2C(Q_R^2/|B_R|^{2/3}) + o(R^3)$, the electrostatic energy of uniform charge distribution on a sphere of radius R. [For more details see (1).] This, (3.8), and the fact that $\langle W \rangle = 0$ show

$$F_R\left(\frac{N+n}{|B_R|}\right) \leqslant \frac{|B_{R-\alpha_R}|}{|B_R|} F_{R-\alpha_R}\left(\frac{N}{|B_{R-\alpha_R}|}\right) + \frac{1}{2C}\left(\frac{Q_R}{|B_R|^{2/3}}\right)^2 + o(1) \tag{3.9}$$

Since

$$\frac{|B_{R-\alpha_R}|}{|B_R|} \to 1, \qquad \lim_{R\to\infty} F_R\left(\frac{N+n}{|B_R|}\right) \leqslant F(\rho) + \frac{1}{2C} Б^2$$

For the lower bound, add some particles m_R to neutralize the system. That is, suppose $(N_R + n_R + m_R) \cdot E = 0$. Also, make sure that $m_R/|B_R| \to 0$.

Pick α_R such that $\alpha_R/R \to 0$ and $m_R/\alpha_R R^2 \to 0$ and let $S_R = B_{R+\alpha_R} \setminus B_R$. By our restriction technique

$$\operatorname{Tr}[\exp(-\beta H_{N+n+m,B_{R+\alpha_R}})] \geqslant \sup_{\{\psi_j\}} \sum_{j=1}^{\infty} \exp -\beta \langle H_{N+n+m} \psi_j \cdot \psi, \overline{\psi_j \cdot \psi} \rangle \tag{3.10}$$

where the supremum is taken over orthonormal sequences in $L^2_{N+n}(B_R)$ and $\psi \in L^2_m(S_R)$ is an arbitrary wave function. As with the upper bound, pick ψ to represent a uniform distribution of the m_R particler in S_R. The operator on $L^2_{N+n}(B_R)$ taking $\Phi(x)$ to $\int \cdots \int_{S_R^M} [H_{N+n+m} \Phi(x) \cdot \psi(y)] \overline{\psi(y)}\, dy$ (see terms in the exponentials on right side of 3.10) becomes $H_{N+n} + W_\psi + Q_R^2/2C\,|B_R|^{1/3} + o(R^3)$, where W_ψ is multiplication by $\int_{S_R} [\Phi_\psi(y)/|x-y|]\, dy$ and Φ_ψ is the charge density corresponding to ψ. The right side of 3.10 is the trace of this operator over $L^2_{N+n}(B_R)$. By our now familiar application of Peierl's theorem, we see that

$$\begin{aligned} \operatorname{Tr}[\exp(-\beta H_{N+n+m,B_{R+\alpha_R}})] &\geqslant \operatorname{Tr}[\exp(-\beta H_{N+n,B_R})] \\ &\quad \times \exp\langle W_\psi \rangle + \left[\frac{Q_R^2}{2C\,|B_R|^{1/3}} + o(R^3) \right] \end{aligned} \tag{3.11}$$

In this situation,

$$\langle W_\psi \rangle = \int_{B_R} \int_{S_R} \frac{\Phi_R(x)\, \Phi_\psi(y)}{|x-y|}\, dy dx = \int_{S_R} \Phi_\psi(y) \left[\int_{B_R} \frac{\Phi_R(x)}{|x-y|}\, dx \right] dy$$

where Φ_R is the expected charge density taken over $\operatorname{Tr}[\exp(-\beta H_{N+n,B_R})]$. By our earlier analysis Φ_R is radial with $\int_{B_R} \Phi_R(x)\, dx = Q_R$. By Newton's theorem, $\int_{B_R} [\Phi_R(x)/|x-y|]\, dx = Q_R/|y|$ for all $y \in S_R$. Hence, $\langle W_\psi \rangle = Q_R \int_{S_R} [\Phi_\psi(y)/|y|\, dy$. Since, Φ_ψ approaches a uniform charge density as $R \to \infty$, the explicit calculations at the beginning of this section show that $\int_{S_R} [\Phi_\psi(y)/|y|\, dy \to -Q_R/C\,|B_R|^{1/3}$ and $\langle W_\psi \rangle \to -Q_R^2/C\,|B_R|^{1/3}$. The minus sign appears because $m_R \cdot E = -n_R \cdot E = -Q_R$. (3.11) now becomes

$$\begin{aligned} &\operatorname{Tr}[\exp(-\beta H_{N+n+m,B_{R+\alpha_R}})] \\ &\qquad \geqslant \operatorname{Tr}[\exp(-\beta H_{N+n,B_R})] \cdot \exp\left[-\frac{Q_R^2}{2C\,|B_R|^{1/3}} + o(R^3) \right] \end{aligned}$$

which has free energy form

$$\begin{aligned} F_R(N_R + n_R/|B_R|) &\geqslant |B_{R+\alpha_R}|/|B_R|\; F_{R+\alpha_R}(N_R + n_R + m_R/|B_{R+\alpha_R}|) \\ &\quad + Q_R^2/2C\,|B_R|^{4/3} + o(R) \end{aligned} \tag{3.12}$$

As $(N_R + n_R + m_R) \cdot E = 0$ and $N_R + n_R + m_R/|B_{R+\alpha_R}| \to \rho$, it is tempting to conclude that the right side of this inequality converges to the desired limit $F(\rho) + Б^2/2C$. However, we may be faced with the technical difficulty that for some i $\rho_i = 0$ but $n_i^R + m_i^R \neq 0$. Then $F_R(N^R + n^R + m^R/|B_R|)$ is the free energy density as we approach the point $\rho \in \partial E^\perp$. A discontinuity in F there would mean that we could not interchange these limits and derive the desired conclusion. The situation $\rho_i = 0$, $m_i^R + n_i^R \neq 0$ occurs if the excess charge comes from the introduction of a new species of particles. The discontinuity would mean that our theory predicts that these particles render some additional thermodynamic effect. Technically, it means that we do not have the lower bound necessary to establish the thermodynamic limit.

3.4. The Grand Canonical Ensemble

The grand canonical ensemble defines the pressure $\Pi_R(\mu)$ by (2.2). Basic thermodynamics requires that this be related to the free energy density by the Legendre transform:

$$\Pi(\mu) = \sup_\rho \{\mu \cdot \rho - F(\rho)\} \tag{3.13}$$

This is what is meant in statistical mechanics by the "equivalence of the canonical and grand canonical ensemble." Notice that grand canonical partition function $\sum_N e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R})]$ is a weighted average over the various particle number vectors of the canonical partition function. The special character of the logarithm and properties of the free energy insure that the logarithm of this sum is close (in comparison to the volume) to the logarithm of the largest term. That is,

$$\begin{aligned}
&(\beta\,|B_R|)^{-1} \log \sum_N e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R})] \\
&\quad\approx (\beta\,|B_R|)^{-1} \log \max_N e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R})] \\
&\quad= (\beta\,|B_R|)^{-1} \max_N \{\beta\mu \cdot N + \log \operatorname{Tr}[\exp(-\beta H_{N,B_R})\} \\
&\quad= \max_N \{\mu \cdot N/|B_R| - F_R(N/|B_R|\}
\end{aligned}$$

This is the mechanism behind the proof that the pressure limit exists and equals the theoretically necessary value given by (3.13).

The key step in this approach is contained in Lemmas 7.3, 7.4, 7.5 of

(1). The upshot is the existence of a constant $M(\mu)$, monotonic increasing in μ, for which

$$\sum_{|N|<M(\mu)|B_R|} e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})] \geqslant 2^{-1}\sum_N e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})$$

That is, densities in a bounded set contribute a fixed proportion of the grand canonical partition function. Hence

$$\begin{aligned}\sum_{|N|<M(\mu)|B_R|} & e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})]\\ &\leqslant \sum_N e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})]\\ &\leqslant 2\sum_{|N|<M(\mu)|B_R|} e^{\beta\mu\cdot M}\operatorname{Tr}[\exp(-\beta H_{N,B_R})]\end{aligned} \tag{3.14}$$

The maximum of all the terms in the sum obviously is attained in the set $|N|<M(\mu)\,|B_R|$. Combining this with (3.14) gives

$$\begin{aligned}\max_N &\{e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})]\}\\ &\leqslant \sum_N e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})]\\ &\leqslant 2[M(\mu)\,|B_R|]^s \max_N \{e^{\beta\mu\cdot N}\operatorname{Tr}[\exp(-\beta H_{N,B_R})]\}\end{aligned} \tag{3.15}$$

On taking logarithms and dividing by volume this gives

$$\pi_R(\mu) = \sup_\rho \{\mu\cdot\rho - F_R(\rho)\} + \varepsilon_R(\mu) \tag{3.16}$$

where $\varepsilon_R(\mu) = S\log M(\mu)\,|B_R|/|B_R|$, which $\to 0$ as $R\to\infty$. [The maximum in the brackets in (3.15) is always attained at a lattice point $N/|B_R|$. So, there is no problem in going from (3.15) to (3.16).]

Since $F_R(\rho)\to F(\rho)$, the obvious tactic is to deduce from (3.16) the analogous limiting relationship as $R\to\infty$. This would simultaneously prove the existence of the pressure limit and the equivalence of ensembles. Lebowitz and Lieb used their analysis of nonneutral systems to show that the supremum on the right side of (3.16) only needs to be taken over neutral ρ, i.e., over $\rho\in E^\perp$. The *neutrality lemma* proved in Section 5 of this paper rigorously establishes this. That is,

$$\pi_R(\mu) = \sup_{\rho\cdot E=0} \{\mu\cdot\rho - F_R(\rho)\} + \varepsilon_R(\mu) \tag{3.17}$$

Operating under the assumption that the neutral free energy F_R converges uniformly to F on every compact subset of $E^{\perp}$ (in particular, on the set $|\rho| < M(\mu)$ where this supremum is attained), Lebowitz and Lieb concluded from (3.17) the desired limiting behavior.

A proof of the continuity of $F(\rho)$ at $\partial E^{\perp}$ would make this argument fly. However, as I mentioned in the Introduction, the proof of the continuity of F presented in this paper depends on two things. First, Fefferman's independent analysis of the infinite-volume limit for the pressure π is uniform as some $\mu i \to -\infty$; second, the equivalence of ensembles (3.13) converts this into a statement about F as $\rho_i \to 0$. That is, to relate Fefferman's analysis and Lebowitz and Lieb's analysis for the resolution of the continuity problem, we must know that (3.13) holds. Fortunately, (3.13) can be proved without the relying on the boundary continuity of $F(\rho)$. Initially, I did this by showing that terms corresponding to N around the mean particle number $\bar{N}$ contribute a dominating portion of the sum. However, as a conversation with Lieb revealed, the fact that (3.17) implies (3.13) can be proved using only ideas implicit in Lebowitz and Lieb's paper. I will present this argument here.

The reason that the problem at $\partial E^{\perp}$ might prevent the convergence of $\sup_{\rho \cdot E=0} \{\mu \cdot \rho - F_R(\rho)\}$ to $\sup_{\rho \cdot E=0} \{\mu \cdot \rho - F(\rho)\}$ is illustrated graphically in Fig. 1. It represents F_R and F along a curve in $E^{\perp}$ parametrized by ρ_i as $\rho_i \to 0$. Even though the limit $F(\rho)$ is convex, the

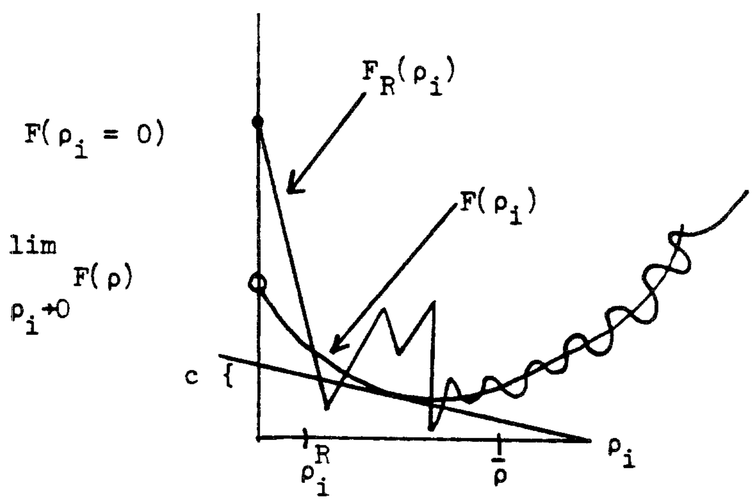

Figure 1

finite volume F_R may not be. If F_R were "very nonconvex" then a sequence of "spikes" at points $\rho_i^R \to 0$ could make

$$\sup_\rho \{\mu\cdot\rho - F_R(\rho)\} = \mu\cdot\rho^R - F_R(\rho^R) > C + \mu\cdot\bar\rho - F(\bar\rho)$$
$$= C + \sup_\rho \{\mu\cdot\rho - F(\rho)\}$$

When I presented Lieb with this possibility, he argued that the convexity implicit in (3.3) prevents such an anomoly. In terms of the picture, he reasoned that (3.3) should imply that some point on the graph of F would lie below the line joining $\lim_{R\to\infty} [\rho_i^R, F_R(\rho_i^R)]$ and $[\bar\rho, F(\bar\rho)]$. This is the essential idea in the proof presented below.

Proof of (3.13). First assume that $\sup_\rho \{\mu\cdot\rho - F(\rho)\}$ is attained at some $\bar\rho \in \operatorname{int}(E^\perp)$. Since $F_R(\bar\rho)$ converges to $F(\bar\rho)$

$$\sup_\rho \{\mu\cdot\rho - F_R(\rho)\} \geqslant \mu\cdot\bar\rho - F_R(\bar\rho)$$
$$= \mu\cdot\bar\rho - F(\bar\rho) + \varepsilon_R(\bar\rho)$$
$$= \sup_\rho \{\mu\cdot\rho - F(\rho)\} + \varepsilon_R(\bar\rho)$$

with $\varepsilon_R(\bar\rho) \to 0$ as $R\to\infty$. Hence, $\underline{\lim}_{R\to\infty} \sup_\rho\{\mu\cdot\rho - F_R(\rho)\} \geqslant \sup_\rho\{\mu\cdot\rho - F(\rho)\}$. The corresponding bound for the $\overline{\lim}$ is more complicated. Assume to the contrary that there is a constant $C>0$, a sequence $R_k\to\infty$, and a sequence $\rho_k \to \rho_\infty \in \partial E^\perp$ with $\mu\cdot\rho_k - F_k(\rho_k) > C + \sup_\rho\{\mu\cdot\rho - F(\rho)\} = C + \mu\cdot\bar\rho - F(\bar\rho)$, There is ε_k with $|\varepsilon_k| \to 0$ as $k\to\infty$ for which $F_k(\bar\rho) + \varepsilon_k(\bar\rho) = F(\bar\rho)$. Hence, the negative assumption implies that $\mu\cdot\rho_k - F_k(\rho_k) > C + \mu\cdot\bar\rho - F_k(\bar\rho) + \varepsilon_k$. Pick k large enough that $|\varepsilon_k| < c/2$. The above inequality now gives

$$F_k(\bar\rho) - F_k(\bar\rho_k) > c/2 + \mu\cdot(\bar\rho - \rho_k)\ \forall k \tag{3.18}$$

Given k, there is large enough $R_*(k)$ so that any ball B_R with $R > R_*$ can be packed with disjoint balls with radii contained in $\{R_i\}_{i=k}^\infty$ in such a way that all but $1/k$ proportion of B_R is covered. Assume that this is done with an even number of balls of each radius. Place density $\bar\rho$ in half the balls of each radius and density ρ_i in the other half of the balls of radius R_i for each i. Let $\rho_{k,R} = \sum_{i=k}^\infty |\bigcup B_{R_i}|/|B_R|\ \rho_i$ (Only finitely many terms will be non-zero.) By the L. L. Inequality

$$F_R\left(\frac{1}{2}\rho_{k,R} + \frac{1}{2}\bar\rho\right) \leqslant \sum_{i=k}^\infty \frac{|\bigcup B_{R_i}|}{|B_R|}\cdot\frac{1}{2}\,[F_{R_i}(\rho_i) + F_{R_i}(\bar\rho)] \tag{3.19}$$

As k and $R > R_*(k) \to \infty$, $\rho_{k,R} \to \rho_\infty$ and so $\frac{1}{2}\rho_{k,R} + \frac{1}{2}\bar{\rho} \to \frac{1}{2}(\rho_\infty + \bar{\rho}) \in \operatorname{int}(E^\perp)$. As F_R converges uniformly on compact sets of $E^\perp$ away from $\partial E^\perp$, the left side of (3.19) converges to $F(\frac{1}{2}(\rho_\infty + \bar{\rho}))$. Examine the right side. For each i,

$$\tfrac{1}{2}[F_{R_i}(\rho_i) + F_{R_i}(\bar{\rho})] = \tfrac{1}{2}[F_{R_i}(\rho_i) - F_{R_i}(\bar{\rho})] + F_{R_i}(\bar{\rho})$$

By (3.18) this is

$$\leqslant -\frac{c}{4} + \frac{1}{2}\mu \cdot (\rho_i - \bar{\rho}) + F_{R_i}(\bar{\rho})$$

$$= -\frac{c}{4} + \frac{1}{2}\mu \cdot (\rho_i + \bar{\rho}) - \mu \cdot \bar{\rho} + F_{R_i}(\bar{\rho})$$

If we now average over $\sum_{i=k}^{\infty} |\bigcup B_{R_i}|/|B_R|$ and let k and $R > R_*(k) \to \infty$, we see that the limiting right side of (3.19) is

$$\leqslant -\frac{c}{4} + \mu\left(\frac{\rho_\infty + \bar{\rho}}{2}\right) - [\mu \cdot \bar{\rho} - F(\bar{\rho})]$$

Putting this together with the limiting value of the left side gives

$$\mu \cdot \bar{\rho} - F(\bar{\rho}) \leqslant -\frac{c}{4} + \mu\left(\frac{\rho_\infty + \bar{\rho}}{2}\right) - F\left(\frac{\rho_\infty + \bar{\rho}}{2}\right)$$

a contradiction to the choice of $\bar{\rho}$ as maximizer.

If $\sup_\rho\{\mu \cdot \rho - F(\rho)\}$ is not actually attained, but equals $\lim_{\rho_k \to \bar{\rho} \in \partial E^\perp}\{\mu \cdot \rho_k - F(\rho_k)\}$ then the same arguments work by picking $\bar{\rho} \in \operatorname{int}(E^\perp)$ which gives a value $\mu \cdot \bar{\rho} - F(\bar{\rho})$ arbitrarily close to the Supremum. ∎

3.5. Explicit Low-Density Calculation of the Free Energy

A corollary of this section is that F is continuous at $\rho = 0$. This *a priori* knowledge will simplify the proof given in Section 5 of continuity at arbitrary other points $\rho \in \partial E^\perp$.

Standard calculations of the free energy per unit volume of a completely ionized ideal gas of electrons and nuclei give the low-density asymptotic form $\beta^{-1} \sum_{i=1}^{s} \rho_i \ln \rho_i$. For the neutral systems that we have been considering, Lebowitz and Lieb's methods can be used to prove

$$F(\rho, \beta) = \beta^{-1} \sum_{i=1}^{s} \rho_i \ln \rho_i + O\left(\sum_{i=1}^{s} \rho_i\right) \tag{3.20}$$

[where $O(\sum_{i=1}^{s} \rho_i)$ depends on β].

Lebowitz and Pena dealt with this in Ref. 4. Owing to a technical oversight, they actually only proved

$$\begin{aligned}
&\beta^{-1} \sum_{i=1}^{s} \rho_i \ln \rho_i + O\left(\sum_{i=1}^{s} \rho_i\right) \\
&\quad \leqslant F(\beta, \rho) \\
&\quad \leqslant \beta^{-1} \sum_{i=1}^{s} \rho_i \ln\left(\sum_{i=1}^{s} \rho_i\right) + O\left(\sum_{i=1}^{s} \rho_i\right) \qquad (3.21)
\end{aligned}$$

Notice, however, that even the weaker (3.21) is enough to establish continuity of F at $\rho = 0$.

The lower bound in (3.20) is easily derived from the stability of matter inequality mentioned at the end of Section 3.1 and bounds on the ideal Fermi or Bose gas partition functions (Fisher (1964)). I will modify Lebowitz and Pena's method to establish the necessary upper bound.

Lemma. There is $k(e_1,..., e_s)$ so that if $\sum_{i=1}^{s} N_i \cdot e_i = 0$ and $\sum_{i=1}^{s} N_i > k(e_1,..., e_s)$, then $N = N^1 + N^2$ with $N^1 \cdot E = N^2 \cdot E = 0$ and $N^1 \neq 0$, $N^2 \neq 0$.

Proof. Given $e_i < 0$, $e_j > 0$ let $k_{ij} = \min\{k_i + k_j > 0 \mid k_i e_i + k_j e_j = 0\}$. Let $k = \max_{e_i < 0, e_j > 0}\{k_{ij}\}$. Notice that each k_{ij} can be written $k_{ij} = k_i + k_j$ and so k can be written $k = k_{\text{neg}} + k_{\text{pos}}$. Let $e = \max_{e_i < 0, e_j > 0}\{|e_i|/e_j + e_j/|e_i|\}$. Suppose $\sum_{i=1}^{s} N_i > s \cdot e \cdot k$ with $\sum_{i=1}^{s} N_i \cdot e_i = 0$. Then, $N_i > k_{\text{neg}}$ for at least one i with $e_i < 0$ and $N_j > k_{\text{pos}}$ for at least one j with $e_j > 0$. Let N^1 consist of k_i species i particles and k_j species j particles and let $N^2 = N - N^1$.

Corollary. The N particles can be divided into at least $M = (\sum_{i=1}^{s} N_i)/k(e_1,..., e_s)$ neutral "atoms" $A^1,..., A^M$, each with $\leqslant k(e_1,..., e_s)$ particles. In general, many of the atoms will be identical.

Pack Ω with M balls $B_1,..., B_M$ of equal volume $\approx |\Omega|/M = C|\Omega|/(\sum_{i=1}^{s} N_i)$. The L. L. Inequality applies to give

$$\operatorname{Tr}[\exp(-\beta H_{N,\Omega})] \geqslant \prod_{j=1}^{M} \operatorname{Tr}[\exp(-\beta H_{A^j,B_j})] \qquad (3.22)$$

This inequality can be strengthened to

$$\operatorname{Tr}[\exp(-\beta H_{N,\Omega})] \geqslant \prod_{i=1}^{s} \left(\frac{CM}{N_i}\right)^{N_i} \prod_{j=1}^{M} \operatorname{Tr}[\exp(-\beta H_{A^j,B_j})] \qquad (3.23)$$

for the following reason. Recall that the L. L. Inequality in the form (3.22) is obtained by restricting the wave functions over which the trace is taken to have their supports in the union of the statistically dependent permutation copies of $\mathsf{X}_{j=1}^{M} \mathsf{X}_{i=1}^{s} B_j^{A_i^j} \equiv S \subset \Omega^{\sum N_i}$. If two atom A^j, A^k with $A^j \neq A^k$ interchange balls then this gives rise to another subset S' of $\Omega^{\sum N_i}$ disjoint from S. Denote those $L_N^2(\Omega)$ functions with supports in S and S' by $L^2(S)$ and $L^2(S')$, respectively. The disjointness of S and S' implies orthogonality of $L^2(S)$ and $L^2(S')$. The number of mutually disjoint sets S clearly dominates $M!/N_1! \cdots N_s!$, which dominates $\prod_{i=1}^{s} (CM/N_i)^{N_i}$. (3.23) is obtained by adding the traces taken over the associated mutually orthogonal $L^2(S)$.

Now deal with a given $\mathrm{Tr}[\exp(-\beta H_{A^j,B_j})]$. Here I mimic Lebowitz and Pena's paper.[4] First, divide the individual particles of the atom A^j into disjoint subballs of B_j^k, $k=1,..., \sum_{i=1}^{s} A_i^j$, with equal volume $\approx C\,|\Omega|/M$ (i.e., one particle per subball). The L. L. Inequality applies again to give

$$\mathrm{Tr}[\exp(-\beta H_{A^j,B_j})] \geqslant \prod_k \mathrm{Tr}[\exp(C\beta \Delta_{1,B_j^k})] \cdot \exp\langle W\rangle \tag{3.24}$$

It is easily calculated that after taking logarithms and dividing by volume the Coulomb term $\langle W\rangle$ gives rise to an additional quantity of size $O((\sum \rho_i)^{4/3})$, which from the point of view of (3.21) is negligible. By elementary eigenvalue asymptotics for Δ_1 we see that

$$\mathrm{Tr}[\exp(C\beta \Delta_{1,B_j^k})] \geqslant C\beta^{-3/2}\,|B_j^k| \approx C\beta^{-3/2}\,|\Omega|/M \tag{3.25}$$

Modulo the negligible Coulomb term this gives

$$\mathrm{Tr}[\exp(-\beta H_{A^j,B_j})] \geqslant \prod_{i=1}^{s} (C\,|\Omega|/M)^{A_i^j}$$

and hence from (3.23)

$$\mathrm{Tr}[\exp(-\beta H_{N,\Omega})] \geqslant \prod_{i=1}^{s} (C\,|\Omega|/N_i)^{N_i}$$

Take logarithms and divide by $\beta \cdot |\Omega|$ to obtain (3.21).

4. FEFFERMAN'S ANALYSIS OF THE PRESSURE LIMIT

In Ref. 3 Fefferman proves that the infinite-volume pressure limit exists for a quantum mechanical system in which the nuclei are fixed on a lattice. Because the lattice system lacks the rotational symmetry to discount the Coulomb interaction between disjoint neutral balls, the method of Lebowitz and Lieb does not work for this system. Fefferman develops powerful and general techniques for comparing the real Hamiltonian to one in which we *neglect* the interdomain interaction. This analysis carries over to the case of quantised nuclei, where it simplifies considerably. Except for minor modifications convenient for the resolution of the discontinuity problem, the following is a straightforward application of Ref. 3 to the case of quantized nuclei.

4.1. Qualitative Preview

The essential ingredient in Fefferman's analysis is the following.

Fefferman's Inequality. There is a constant $k(\mu, \beta)$ with the following property. If $1 \leqslant R_1 < R_2 \cdots < R_M$ is any sequence of radii with $R_{i+1} > 2\sqrt{3}\, R_i$, there is $R_*(M, R_M)(\approx CM^{4/3}R_M^4)$ such that if $R > R_*(1/M, R_M)$ then

$$\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})] \leqslant \exp\left[\frac{k(\mu,\beta)}{M}\right] |B_R| \prod_{i=1}^{M} \times \left\{\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})]^{C_i}\right\} \tag{4.1}$$

where $C_i \approx (1/M)(|B_R|/|B_{R_i}|)$ is the number of balls of radius R_i used in a special covering of B_R.

Notice that if the sums are restricted to neutral N then the L. L. Inequality applies to give (4.1) in the opposite direction and without $\exp[k(\mu, \beta)/M]\ |B_R|$). The two approaches complement each other in this way. If the logarithm of both sides of (4.1) is divided by $\beta\,|B_R|$ an inequality relating the pressure results:

$$\Pi_R(\mu, \beta) \leqslant \frac{k(\mu, \beta)}{\beta M} + \frac{1}{M} \sum_{i=1}^{M} \Pi_{R_i}(\mu, \beta) \tag{4.2}$$

As $\Pi_R(\mu, \beta) > 0$ for all μ, β, R, $\underline{\lim}_{R\to\infty} \Pi_R(\mu)$ exists. When applied to a sequence R_i for which $\Pi_{R_i}(\mu)$ approaches $\underline{\lim}_{R\to\infty} \Pi_R(\mu)$, (4.2) allows us to conclude that $\overline{\lim}_{R\to\infty} \Pi_R(\mu) = \underline{\lim}_{R\to\infty} \Pi_R(\mu)$.

The special covering needed for Fefferman's Inequality is given by the Covering Lemma in the next section. We will deal with a family of coverings $\{\mu_{\gamma,\tau}\}$ depending on a parameter τ corresponding to uniform translations of the sets in a particular covering $\{u_\gamma\}$. Fefferman defines a "phony" system in which these sets $\{u_\gamma\}$ are treated as disjoint independent subsystems. The phony Hamiltonian H^{ph}_{N,B_R} does not include any Coulomb interaction between different u_γ. Because of the independence of these subsystems, the grand canonical partition function for H^{ph}_{N,B_R} factors as a product of those for the u_γ. (4.1) is an approximation to this factoring for the real system. To get it, Fefferman relates H_{N,B_R} to an average over translations τ of the $H^{\text{ph},\tau}_{N,B_R}$ corresponding to different coverings $\{u^\tau_\gamma\}$.

4.2. Details

The number (C_i) of balls of each radius R_i used in the special covering of B_R is approximately $(1/M)(|B_R|/|B_{R_i}|)$, where M is the number of different radii. This means that the proportion of volume of B_R covered by the balls of a given radius R_i is approximately $1/M$. This requirement is important for the comparision of H_{N,B_R} and $\text{avg}_\tau\, H^{\text{ph},\tau}_{N,B_R}$ mentioned above. I will postpone the proof of the following until its technical importance can be better appreciated.

Covering Lemma. Let $\{R_i\}^M_{|i=1|}$ be real numbers with $R_i > 2\sqrt{3}\, R_{i-1}$. Disjoint balls of radii $\{R_i\}^M_{i=1}$ can be packed into $\mathbb{R}^3$ in such a way that if B_R has sufficiently large radius R then $1/(M+6) \leqslant |\bigcup B_{R_i} \cap B_R|/|B_R| \leqslant 1/(M+5)\ \forall_i$. As usual, $\bigcup B_{R_i}$ denotes the union of the balls in the packing with radius R_i.

Apply the Covering Lemma with $R_1 > 1$. We can complete a covering of $\mathbb{R}^3$ by including slightly overlapping cubes. First, decompose $\mathbb{R}^3$ into a grid of disjoint unit cubes. Then, enter into the covering the double of any unit cube which intersects the complement of the balls already in the covering. Call the sets in this covering of $\mathbb{R}^3 \{u_\gamma\}$. That is, a given u_γ may be either a ball or a cube. Notice that $\sum_{\text{cubes } u_\gamma} |u_\gamma \cap B_R|/|B_R| \leqslant C/M$. There is a partition of unity

$$\sum_\gamma \Phi^2_\gamma = 1 \tag{4.3}$$

for which each function Φ_γ has its support contained in its corresponding u_γ. Assume that it is constructed in the following way:

1. For each radius R_i, there is a smooth radial function Φ_i supported in $B_{R_i}(0)$, indentically 1 on $B_{R_i-1}(0)$, and $|\partial^\alpha_x \Phi_i| \leqslant C$ for $|\alpha| \leqslant 3$, so that if $u_\gamma = B_{R_i}(y)$ then $\Phi_\gamma(x) = \Phi_i(x-y)$.

2. If u_γ is a cube then assume that $|\partial^\alpha_x \Phi_\gamma| \leqslant C$ for $|\alpha| \leqslant 3$.

We are now in a position to define the phony system.

Let B_R be a large ball on which our system is defined. Consider only those u_γ which intersect B_R. As mentioned earlier, we treat the u_γ as disjoint. This is accomplished by taking an "exploded" view: to each u_γ which intersects B_R correspond a vector $\xi_\gamma \in \mathbb{R}^3$ in such a way that the $u_\gamma + \xi_\gamma \equiv u_\gamma^\uparrow$ are all disjoint. The Hilbert space for our phony system is $L_N^2(\bigcup u_\gamma^\uparrow)$. The phony Hamiltonian acting on $L_N^2(\bigcup u_\gamma^\uparrow)$ is defined by

$$H_{N,B_R}^{\mathrm{ph}} = -\Delta_{N,\bigcup u_\gamma^\uparrow} + \sum\nolimits_\gamma^R \frac{1}{2} \sum_{i,j,k,l} \chi_{u_\gamma^\uparrow}(x_i^k)\, \chi_{u_\gamma^\uparrow}(x_j^l) \frac{e_i e_j}{|x_i^k - x_j^l|} \tag{4.4}$$

where $\sum_\gamma^R$ denotes the sum over all those u_γ *which are balls* and which intersect B_R and where $\chi_{u_\gamma^\uparrow}$ is the characteristic function of the set $u_\gamma^\uparrow$. It takes into account the Coulomb interaction only between particles in the same *ball* $u_\gamma^\uparrow$.

Because the $u_\gamma^\uparrow$ are all independent in the phony system, the partition function decomposes as a product of the partition functions for the $u_\gamma^\uparrow$:

$$\begin{aligned}
&\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R}^{\mathrm{ph}})] \\
&\quad = \Bigg\{ \sum_{\substack{\text{cubes } u_\gamma \\ \text{s.t. } u_\gamma \cap B_R \neq \varnothing}} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta\Delta_{N,u_\gamma})] \Bigg\} \\
&\qquad \times \Bigg\{ \cdot \prod\nolimits_\gamma^R \Big(\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,u_\gamma})] \Big) \Bigg\} \\
&\quad \leqslant \exp\left[\frac{c_1(\beta,\mu)}{M} |B_R| \right] \times \Bigg\{ \cdot \prod\nolimits_\gamma^R \Big(\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,u_\gamma})] \Big) \Bigg\}
\end{aligned} \tag{4.5}$$

where $\prod_\gamma^R$ has meaning analogous to $\sum_\gamma^R$. We have used (3.7) with $c_1(\beta, \mu) = ch(\beta, \mu)$ and the fact that $\sum_{\text{cubes } u_\gamma} |u_\gamma \cap B_R|/|B_R| \leqslant C/M$.

Fefferman's Inequality results from a comparison between the left side of (4.5) and the same quantity with H_{N,B_R}^{ph} replaced by H_{N,B_R}. The first step is to pull H_{N,B_R}^{ph} back to an operator on $L_N^2(B_R)$. The partition of unity gives rise to an injection i: $L_N^2(B_R) \to L_N^2(\bigcup u_\gamma^\uparrow)$ that accomplishes this. Any $y \in \bigcup u_\gamma^\uparrow$ is uniquely expressible as $y = X + \xi_\gamma(y)$ for some $X \in u_\gamma$. Extend any $\psi \in L_N^2(B_R)$ to be zero outside B_R^N and define $i\psi \in L_N^2(\bigcup u_\gamma^\uparrow)$ to be

$$i\psi(y_1^1,..., y_s^{N_s}) = \psi(X_1^1,..., X_s^{N_s}) \prod_{i=1}^{s} \prod_{k=1}^{N_i} \Phi_\gamma(y_i^k)(X_i^k) \tag{4.6}$$

where $y_i^k = X_i^k + \xi_\gamma(y_i^k)$. $i\psi$ clearly satisfies the correct symmetry requirements if ψ does. Check that the inner product is preserved:

$$\int_{(\bigcup u_\gamma^\uparrow)} \cdots \int_N i\psi(\dots y_i^k \dots)\, \overline{i\Phi}(\dots y_i^k \dots)\, d\bar{y}$$

$$= \sum_{\gamma_1^1, \dots, \gamma_s^{N_s}} \int_{u_{\gamma_1^1}^\uparrow x \dots x u_{\gamma_s^{N_s}}^\uparrow} \cdots \int i\psi(\dots y_i^k \dots)\, \overline{i\Phi}(\dots y_i^k \dots)\, d\bar{y}$$

where the sum is over all $\sum_{i=1}^s N_i$-tuples of the γ in the indexing set of the $u_\gamma^\uparrow$ (i.e., of the u_γ which intersect B_R). The above equals

$$= \sum_{\gamma_1^1, \dots, \gamma_s^{N_s}} \int_{u_{\gamma_1^1}^\uparrow x \dots x u_{\gamma_s^{N_s}}^\uparrow} \cdots \int \psi(\dots X_i^k \dots)\, \bar{\Phi}(\dots X_i^k \dots) \prod_{i=1}^{s} \prod_{k=1}^{N_i} \Phi_{\gamma_i^k}^2(X_i^k)\, d\bar{y}$$

Because $\operatorname{supp}(\Phi_\gamma) = \mu_\gamma$, this equals

$$= \int_{B_R^N} \cdots \int \psi(\dots X_i^k \dots)\, \bar{\Phi}(\dots X_i^k \dots) \prod_{i=1}^{s} \prod_{k=1}^{N_i} \left[\sum_\gamma \Phi_\gamma^2(X_i^k) \right] d\bar{x}$$

As $\sum_\gamma \Phi_\gamma^2(X_i^k) = 1$, this equals $\langle \psi, \Phi \rangle_{L_N^2(B_R)}$. Note that i is definitely not onto. This is because each $i\psi$ satisfies a compatibility condition due to the fact that one point $x \in B_R$ can correspond to more than one point in $\bigcup u_\gamma^\uparrow$.

This injection pulls H_{N,B_R}^{ph} back to an operator $H_{N,B_R}^i = i^* \circ H_{N,B_R}^{\mathrm{ph}} \circ i$ acting on $L_N^2(B_R)$. Since i maps orthonormal sequences $\{\psi_k\} \subset L_N^2(B_R)$ to orthonormal sequences $\{i\psi_k\} \subset L_N^2(\bigcup u_\gamma^\uparrow)$ and $\langle H_{N,B_R}^i \psi, \psi \rangle = \langle H_{N,B_R}^{\mathrm{ph}} \psi, \psi \rangle$, the definition of trace as a supremum gives

$$\operatorname{Tr}[\exp(-\beta H_{N,B_R}^i)] \leqslant \operatorname{Tr}[\exp(-\beta H_{N,B_R}^{\mathrm{ph}})]$$

Summing over N and using (4.5), we obtain

$$\sum_N e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R}^i)]$$

$$\leqslant \exp\left[\frac{C_1(\beta, \mu)}{M} |B_R| \right] \prod_\gamma^R \left\{ \sum_{N \geqslant 0} e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,u_\gamma})] \right\} \tag{4.7}$$

Suppose that we now translate each set in our covering $\{u_\gamma\}$ of $\mathbb{R}^3$ by a fixed vector $\tau \in \mathbb{R}^3$. Call this translated covering $\{u_{\gamma,\tau}\}$. It gives rise to a different collection of sets which intersect B_R and a different partition of unity

$\sum_\gamma \Phi^2_{\gamma,\tau}(x) = \sum_\gamma \Phi^2_\gamma(X-\tau) = 1$. Hence we obtain a different Hilbert space $L^2_N(Uu^\dagger_{\gamma,\tau})$, a different injection $i_\tau : L^2_N(B_R) \to L^2_N(Uu^\dagger_{\gamma,\tau})$, and a different operator $H^\tau_{N,B_R} \equiv i^*_\tau \circ H^{\mathrm{ph},\tau}_{N,B_R} \circ i_\tau$. (4.7) still holds with H^τ_{N,B_R} and $\{u_{\gamma,\tau}\}$ replacing H^i_{N,B_R} and $\{u_\gamma\}$, respectively. Notice that for any $\tau \in \mathbb{R}^3$ the quantity on the right side of (4.7) depends only on the numbers of balls of each radius R_i in the covering $\{u_{\gamma,\tau}\}$ that intersect B_R. By the covering lemma this differs from the c_i in the statement of Fefferman's Inequality by $O(1/M^2)(|B_R|/|B_{R_i}|)$. We absorb this in $[c_1(\beta,\mu)/M]\,|B_R|$. Therefore, independently of τ, the quantity on the right side of (4.7) is

$$\leqslant \exp\left[\frac{c_1(\beta,\mu)}{M}|B_R|\right] \cdot \prod_{i=1}^{M} \left\{\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_{R_i}})]\right\}^{c_i}$$

Now, for some large ball B_d define the operator $H^{\#}_{N,B_R} = \mathrm{avg}_{\tau\in B_d} H^\tau_{N,B_R}$. That is, for $\psi \in L^2_N(B_R)$ $H^{\#}_{N,B_R}\psi(\ldots X^k_i \ldots) = (1/|B_d|)\int_{B_d} H^\tau_{N,B_R}\psi(\ldots X^k_i\ldots)\,d\tau$. An elementary calculation (using $2ab \leqslant a^2 + b^2$) shows that for operators A, B acting on the same Hilbert space, $\mathrm{Tr}\{\exp[\frac{1}{2}(A+B)]\} \leqslant \frac{1}{2}(\mathrm{Tr}[\exp A] + \mathrm{Tr}[\exp B])$ as long as both sides are well defined. This inequality generalizes to continuous averages. When applied to operators H^τ_{N,B_R}, it gives

$$\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H^{\#}_{N,B_R})]$$
$$\leqslant \exp\left[\frac{c_1(\beta,\mu)}{M}|B_R|\right] \prod_{i=1}^{M} \left\{\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_{R_i}})]\right\}^{c_i} \tag{4.8}$$

The major effort in Fefferman's analysis goes into proving the following theorem.

Main Theorem. In the above setting, if the smallest balls in the covering have radius $R_1 > R_{\min}$ and if the ball B_d over which translations τ are averaged is large enough, then $H^{\#}_{N,B_R} \leqslant (1 + C/M)\,H_{N,B_R} + (C/M)\sum_{i=1}^{s} N_i$, with C independent of R and N.

Let $\varepsilon = C/M$ and let $\bar\varepsilon$ be the s-tuple $\bar\varepsilon = (\varepsilon,\ldots,\varepsilon)$. Plugging the Main Theorem into (4.8) gives

$$\sum_N e^{\beta(\mu-\bar\varepsilon)\cdot N}\,\mathrm{Tr}\{\exp[-\beta(1+\varepsilon)\,H_{N,B_R}]\}$$
$$\leqslant \exp[c_1(\beta,\mu)\varepsilon|B_R|] \prod_{i=1}^{M} \left\{\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_{R_i}})]\right\}^{c_i} \tag{4.9}$$

Claim:

$$\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})]$$
$$\leqslant \exp[c_2(\beta,\mu)\varepsilon|B_R|]\sum_N e^{\beta(\mu-\bar{\varepsilon})\cdot N}\,\mathrm{Tr}\{\exp[-\beta(1+\varepsilon)\,H_{N,B_R}]\}$$

Once this claim is proved, (4.9) gives

$$\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})]$$
$$\leqslant \exp\{[c_1(\beta,\mu)+c_2(\beta,\mu)]\cdot\varepsilon\cdot|B_R|\}\cdot\prod_{i=1}^{M}$$
$$\times\left\{\sum_{N\geqslant 0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_{R_i}})]\right\}^{c_i} \tag{4.10}$$

(4.10) is Fefferman's Inequality with $\varepsilon = C/M$ and $k(\beta,\mu) = c_1(\beta,\mu)+c_2(\beta,\mu)$. When we discuss uniformity of the convergence of $\Pi_R(\mu,\beta)$ to $\Pi(\mu,\beta)$ in Section 5 we will consider c_1 and c_2 more closely.

Proof of Claim. Notice that

$$\frac{1}{\beta|B_R|}\log\sum_N e^{\beta(\mu-\bar{\varepsilon})\cdot N}\,\mathrm{Tr}\{\exp[-\beta(1+\varepsilon)\,H_{N,B_R}]\}$$
$$=\Pi_R(\mu-\bar{\varepsilon},\beta(1+\varepsilon))$$

As is easily checked by examining its derivatives, $\Pi_R(\mu,\beta)$ is convex in both μ and β for each R. Estimate (3.7) shows that Π_R is bounded above by the free particle pressure. Like the free energy density lower bound $h(\mu,\beta)$, this bound can be calculated and shown independent of R. As $\Pi_R(\mu,\beta)>0$ for all μ,β,R also, the convexity implies that $\Pi_R(\mu,\beta)$ is uniformly (in R) Lipshitz on bounded μ,β sets. Hence $|\Pi_R(\mu-\bar{\varepsilon},\beta(1+\varepsilon))-\Pi_R(\mu,\beta)|\leqslant c_2(\mu,\beta)\,\varepsilon$. Multiplying by $\beta|B_R|$ and exponentiating gives the claim. ▌

Since $(\partial/\partial\mu_i)\,\Pi_R(\mu,\beta)>0$ everywhere and $\lim_{\mu_i\to-\infty}(\partial/\partial\mu_i)\,\Pi_R(\mu,\beta)=0$, convexity implies that the $c_2(\mu,\beta)$ is uniform for the μ_i bounded above and β in bounded sets. This will be important in Section 5.

4.3. Proof of Main Theorem

Recall what needs to be proved. For each $\tau\in\mathbb{R}^3$ we have a covering $\{\mu_{\gamma,\tau}\}$ of B_R defined by the Covering Lemma, an associated partition of unity $\sum_\gamma \Phi^2_{\gamma,\tau}=1$ given by (4.3), an injection $i_\tau\colon L^2_N(B_R)\to L^2_N(\bigcup u^\dagger_{\gamma,\tau})$ defined by (4.4), and the pullback of $H^{\mathrm{ph},\tau}_{N,B_R}$ to an operator $H^\tau_{N,B_R}\equiv i^*_\tau\circ H^{\mathrm{ph},\tau}_{N,B_R}\circ i_\tau$ on $L^2_N(B_R)$. For some as yet unspecified large d, we defined the operator $H^\#_{N,B_R}=\mathrm{avg}_{\tau\in B_d} H^\tau_{N,B_R}$. For d large enough we want to prove

$$\langle H^\#_{N,B_R}\psi,\psi\rangle\leqslant\left(1+\frac{C}{M}\right)\langle H_{N,B_R}\psi,\psi\rangle+\frac{C}{M}\left(\sum_{i=1}^s N_i\right)\langle\psi,\psi\rangle \quad (4.11)$$

for all $\psi\in L^2_N(B_R)$.

Temporarily fix a τ and suppress the framework's dependence on it. We have

$$\langle H^\tau_{N,B_R}\psi,\psi\rangle=\langle H^{\mathrm{ph}}_{N,B_R}i\psi,i\psi\rangle,\qquad \psi\in L^2_N(B_R)$$

H^{ph}_{N,B_R} has a kinetic energy term and a potential energy term. First handle the kinetic energy term:

$$\langle -\Delta_{N,\bigcup u^\dagger_\gamma}(i\psi),(i\psi)\rangle=\sum_{\gamma^1_1,\dots,\gamma^{N_s}_s}\|\nabla_N(i\psi)\|^2_{L^2(u^\dagger_{\gamma^1_1}\dots u^\dagger_{\gamma^{N_s}_s})} \quad (4.12)$$

Recall that $i\psi(\dots,X^k_i+\xi_{\gamma^k_i},\dots)=\psi(\dots,X^k_i,\dots)\prod_{i=1}^s\prod_{k=1}^{N_i}\Phi_{\gamma^k_i}(X^k_i)$. Use the trivial equality (proved by integration by parts) $\|\nabla(\Phi(x)\,\psi(x)\|^2_{L^2}=\int|\Phi|^2-\int\Phi\Delta\Phi\cdot|\psi|^2$ to see that (4.12) equals

$$\begin{aligned}&\sum_{\gamma^1_1,\dots,\gamma^{N_s}_s}\int\cdots\int_{B^N_R}\prod_{i=1}^s\prod_{k=1}^{N_s}\Phi^2_{\gamma^k_i}(X^k_i)\,|\nabla_N\psi(\dots,X^k_i,\dots)|^2\,dX_i\dots dX^{N_s}_s\\&\quad-\sum_{i=1}\sum_{k=1}\sum_{\gamma^1_1,\dots,\gamma^{N_s}_s}\int\cdots\int_{B^N_R}\left[\left(\sum_{(j,l)\neq(i,k)}\Phi^2_{\gamma^l_j}(X^l_j)\right)\Phi_{\gamma^k_i}(X^k_i)\,\Delta_1\Phi\gamma^k_i(X^k_i)\right]\\&\quad\times|\psi(\dots X^k_i\dots)|^2\,dx^{N_1}_1\dots dx^{N_s}_s\end{aligned}$$

If we take the sums inside the integrals and use the fact that $\sum_\gamma\Phi^2_\gamma=1$, we see that this equals

$$\begin{aligned}&=\|\nabla_N\psi\|^2_{L^2_N(B_R)}-\sum_{i=1}^s\sum_{k=1}^{N_i}\sum_\gamma\int\cdots\int_{B^N_R}[\Phi_\gamma(X^k_i)\,\Delta\Phi_\gamma(X^k_i)]\\&\qquad\times|\psi(\dots,X^k_i,\dots)|^2\,dx^{N_1}_1\dots dX^{N_s}_s\end{aligned}$$

By the antisymmetry or symmetry of ψ in each variable, this equals

$$\|\nabla_N \psi\|^2_{L^2_N(B_R)} - \sum_{i=1}^{s} N_i \int \cdots \int_{B_R^N} \left[\sum_\gamma \Phi_\gamma(y)\, \Delta\Phi_\gamma(y)\right] |\psi(..., X_{i-1}^{N_{i-1}}, y, X_i^2, ...)|^2$$
$$\times\ dx_1^1 ... \widehat{dx_i^1} ... dx_s^{N_s}\, dy \tag{4.13}$$

Hence, we see that the kinetic energy for the phony system equals that for the real system except for an error corresponding to the expected particle density in the support of $\sum_\gamma \Phi_\gamma \Delta\Phi_\gamma$, i.e., where multiplication by Φ_γ changes the derivative of ψ.

Now, average (4.13) over translations τ in some ball $B_d(0)$. The only change is that $\sum_\gamma \Phi_\gamma(y)\, \Delta\Phi_\gamma(y)$ becomes $|B_d|^{-1} \int_{B_d} \sum_\gamma \Phi_\gamma(y+\tau)\, \Delta\Phi_\gamma(y+\tau)\, d\tau$. Except for an error $O(1/d)$ coming from u_γ at a distance d from y this equals

$$|B_d|^{-1} \sum_{\substack{\gamma \text{ s.t.} \\ u_\gamma \cap B_d \neq \varnothing}} \int \Phi_\gamma \Delta\Phi_\gamma\, dx \tag{4.14}$$

The properties (4.3) of the Φ_γ allow us to estimate (4.14). If u_γ is a ball of radius R_i then

$$\int \Phi_\gamma \Delta\Phi_\gamma\, dx = \int_{B_{R_i}} \Phi_i(x)\, \Delta\Phi_i(x)\, dx$$

Since $\Phi_i \equiv 1$ on B_{R_i-1} and $|\Delta\Phi_i| < C$ by assumption, this quantity is $\leqslant CR_i^2$. The number of balls of radius R_i which intersect $B_d(y)$ is $\leqslant |B_d|\ |B_{R_i}|^{-1}\, [1/(M+5)]$. Therefore, the part of (4.14) corresponding to balls has total contribution

$$\leqslant |B_d|^{-1} \sum_{i=1}^{M} |B_d|\ |B_{R_i}|^{-1} \left(\frac{1}{M+5}\right) CR_i^2 = \left(\frac{1}{M+5}\right) \sum_{i=1}^{M} CR_i^{-1}$$

Since $R_{i+1} > 2R_i$, $R_1 > 1$, this is $\leqslant C/M$. (The constant C has of course changed in each line of the inequality. It can be taken as 10.) As the first three derivatives of the Φ_γ for cubes u_γ are bounded, they contribute something bounded by their proportion of the volume, i.e., by C/M. Hence, $|B_d|^{-1} \int_{B_d} \sum_\gamma \Phi_\gamma(y+\tau)\, \Delta\Phi_\gamma(y+\tau)\, d\tau \leqslant C/M$. As long as d is large enough to make the error $O(1/d)$ at $\partial B_d(y)$ negligible, we can plug this into (4.13) to get the kinetic energy part of $\langle H^{\#}_{N,B_R}\psi, \psi\rangle$ equal to $\|\nabla\psi\|^2_{L^2_N(B_R)}$ modulo an error $C/M(\sum_{i=1}^{s} N_i) < \psi, \psi >$.

The potential energy term in $\langle H^{\#}_{N,B_R}\psi, \psi\rangle$ is more complicated. For a given $\langle H^{\tau}_{N,B_R}\psi, \psi\rangle$ it is

$$\left\langle\left(\sum_{\gamma}^{R}\frac{1}{2}\sum_{\substack{X_i^k, X_j^l\in u_\gamma^\tau\\(i,k)\neq(j,l)}}\frac{eiej}{|X_i^k-X_j^l|}\right)i_\tau\psi, i_\tau\psi\right\rangle$$

$$=\int\cdots\int_{B_R^N}\left[\sum_{\gamma}^{R}\frac{1}{2}\sum_{\substack{X_i^k, X_j^l\in u_{\gamma,\tau}\\(i,k)\neq(j,l)}}\frac{eiej}{|X_i^k-X_j^l|}\prod_{i=1}^{s}\prod_{k=1}^{N_i}\Phi^2_{\gamma(X_i^k)}(X_i^k+\tau)\right]$$

$$\times|\psi(\ldots, X_i^k, \ldots)|^2\, dx_1^1\ldots dX_s^{N_s}$$

$$=\int\cdots\int_{B_R^N}\left\{\frac{1}{2}\sum_{(i,k)\neq(j,l)}\left[\frac{eiej}{|X_i^k-X_j^l|}\sum_{\gamma}^{R,\tau}\Phi^2_\gamma(X_i^k+\tau)\,\Phi^2_\gamma(X_j^l+\tau)\right]\right\}$$

$$\times|\psi(\ldots X_i^k\ldots)|^2\, dx_1^1\ldots dX_s^{N_s}$$

where $\sum_{\gamma}^{R,\tau}$ is the sum over all those γ for which u_γ is ball with $\{u_\gamma+\tau\}\cap B_R\neq\varnothing$. For k^τ defined on $\mathbb{R}^3\times\mathbb{R}^3$ by $k^\tau(x, y)=|x-y|^{-1}\sum_{\gamma}^{R,\tau}\Phi^2_\gamma(x+\tau)\,\Phi^2_\gamma(y+\tau)$, this quantity can be written $\langle\frac{1}{2}\sum_{i,j,k,l}k^\tau(X_i^k, X_j^l)\,\psi, \psi\rangle$. Now average k^τ over a huge ball $B_d(0)$. This yields a potential

$$k^{\#}(x, y)=|B_d|^{-1}\int_{B_d}k^\tau(x, y)\,d\tau$$

$$=|x-y|^{-1}\,|B_d|^{-1}\int_{B_d}\sum_{\gamma}^{R,\tau}\Phi^2_\gamma(x+\tau)\,\Phi^2_\gamma(y+\tau)\,d\tau$$

If $|x-y|>2R_M$ this quantity is zero. If $|x-y|<2R_M$, then, except for the error $O(1/d)$ as with the kinetic energy term,

$$k^{\#}(x, y)=|x-y|^{-1}\,|B_d|^{-1}\sum_{i=1}^{M}\left\{|B_d|\;|B_{R_i}|^{-1}\left[\frac{1}{M+6}+O\left(\frac{1}{M^2}\right)\right]\right.$$

$$\left.\times\int_{\mathbb{R}^3}\Phi^2_{R_i}(x+\tau)\,\Phi^2_{R_i}(y+\tau)\,d\tau\right\}$$

$$=\left[\frac{1}{M+6}+O\left(\frac{1}{M_2}\right)\right]\sum_{i=1}^{M}|x-y|^{-1}\frac{\Phi^2_{R_i}*\Phi^2_{R_i}}{|B_{R_i}|}(x-y)$$

A potential $k(x, y)=k(x-y)$ gives rise to an operator $V[k]$ on $L^2_N(B_R)$ analogous to the Coulomb interaction operator:

$V[k]\,\psi(..., X_i^k,...) = \frac{1}{2}\sum_{(i,k)\neq(j,l)} eiejk(X_i^k - X_j^l)\,\psi(..., X_i^k,...)$. In Ref. 3, Fefferman analyzes in detail the operators $V[k]$ associated with certain "Coulomb-type" potentials k. The simplest examples of such potentials are those $k\in C^3(\mathbb{R}^3)$ for which $\partial^\alpha k(x)/\partial x_\alpha \leqslant C\,|x|^{-1-|\alpha|}\forall\,|\alpha|\leqslant 3$. For such k, he proves that $V[k]\leqslant C(H_{N,B_R} + C\sum_{i=1}^s N_i)$ as operators on $L_N^2(B_R)$. This is given in Lemma 4 of Section 3 of his paper.[3] Lemma 4 actually establishes the inequality for a more general k satisfying

$$\begin{aligned} &|\partial_x^\alpha k(x)|\leqslant C_\alpha\,|x|^{-1-|\alpha|} && \text{for}\quad |\alpha|\leqslant 2 \text{ and all } x \\ \text{and } &|\partial_x^\alpha k(x)|\leqslant C_3\,|x|^{-4} && \text{for}\quad |\alpha| = 3 \text{ for all } x \text{ expect possibly} \end{aligned} \tag{4.15}$$

those in one of the annuli $A_i = B_{R_i+1}\setminus B_{R_i-1}$. Here R_1, R_2,... may be any sequence satisfying $R_{i+1}\geqslant 2R_i$ and $R_1\geqslant 1$. Since the proof is rather long and detailed, I refer the reader to Ref. 3. We will apply this result to prove that $V[k^\#]\leqslant V[|x|^{-1}] + (C/M)(H_{N,B_R} + \sum_{i=1}^s N_i)$.

$$\begin{aligned} |x|^{-1} - k^\#(x) &\geqslant \left(\frac{1}{M}\sum_{i=1}^M |x|^{-1}\right) - \left[\frac{1}{M+5} + O\left(\frac{1}{M^2}\right)\right]|x|^{-1}\sum_{i=1}^M \frac{\Phi_i^2 * \Phi_i^2}{|B_{R_i}|}(x) \\ &\geqslant \frac{c}{M^2}\,|x|^{-1} + \frac{c}{M}\,|x|^{-1}\sum_{i=1}^M\left[1 - \frac{\Phi_i^2 * \Phi_i^2}{|B_{R_i}|}(x)\right] \end{aligned} \tag{4.16}$$

Let us examine the potential $|x|^{-1}\sum_{i=1}^M [1 - (\Phi_i^2 * \Phi_i^2/|B_{R_i}|)(x)]$, which we denote $\tilde{k}$. As is easily calculated, $|\partial_x^\alpha(\Phi_i^2 * \Phi_i^2/|B_{R_i}|)(x)|\leqslant C/R_i^{|\alpha|+1}$ for $|\alpha|\leqslant 3$ except when $|\alpha| = 3$ and x the annulus $B_{2R_i+1}\setminus B_{2R_i-1}$, where it only satisfies $|\partial_x^\alpha(\Phi_i^2 * \Phi_i^2/|B_{R_i}|)(x)|\leqslant C$. [To see this, write $\Phi_i^2 = X_{B_R} * \Phi$ for some $\Phi\in C_0^\infty[B_1(0)]$ and notice that $(1/|B_R|)\,X_{B_R} * X_{B_R}(x) = X_{B_1} * X_{B_1}(X/R)$.] This means that $\tilde{k}$ satisfies the assumptions of Fefferman's Lemma 4 on Coulomb-type potentials. However, since we have to sum $i = 1$,..., M, the constants C_α in (4.15) are proportional to M. For example, for large x, $\tilde{k}(x) = M\,|x|^{-1}$. This will give a bound on the order $CM(H_{N,B_R} + \sum_{i=1}^s N_i)$, which is clearly not good enough.

Since k may be replaced by $-k$ in (4.15), the lemma in Fefferman's paper gives both an upper and lower bound. We only need to prove the lower bound $V[|x|^{-1} - k^\#]\geqslant (C/M)(H_{N,B_R} + \sum_{i=1}^s N_i)$. The potential $\tilde{\tilde{k}} = \sum_{i=1}^M \Phi_i^2 * 1/|x| * \Phi_i^2$ has the same quantitative behavior as $\tilde{k}$. Let $\tilde{k}_i$ and $\tilde{\tilde{k}}_i$ be the ith terms of $\tilde{k}$ and $\tilde{\tilde{k}}$, respectively. Using what we said above, it is easy to see that

$$\begin{aligned} \partial_x^\alpha(\tilde{k}_i \pm \tilde{\tilde{k}}_i)(x) &= 0 && \text{if}\quad |x| > 2R_i,\ \forall_\alpha \\ &\leqslant \frac{c}{R_i}\frac{1}{|X|^{|\alpha|+1}} && \text{if}\quad |x|\leqslant 2R_i \end{aligned}$$

and $|\alpha| \leqslant 3$ except when $|\alpha| = 3$ and $|x| \in (2R_i - 1, 2R_i + 1)$, where it is only bounded. Since $R_1 \geqslant 1$ and $R_{i+1} > 2R_i$ this implies that $\tilde{k} \pm \tilde{\tilde{k}}$ satisfies Fefferman's generalized Coulomb-type potential assumptions. His Lemma 4 applies to show

$$V[\tilde{k} \pm \tilde{\tilde{k}}] \leqslant C\left(H_{N,B_R} + \sum_{i=1}^{s} N_i\right) \tag{4.17}$$

where now C is independent of the number M of different radii.

Now, notice that $V[\tilde{\tilde{k}}]$ has the special feature that it is within an error $C(\sum_{i=1}^{s} N_i)$ of being a positive operator. Consider the ith term:

$$V[\tilde{\tilde{k}}_i](\ldots, X_i^k, \ldots) = \sum_{(i,k) \neq (j,l)} eiej\Phi_i^2 * \frac{1}{|x|} * \Phi_i^2(X_i^k - X_j^l)$$

$$= \int \cdots \int_{\mathbb{R}^3 \times \mathbb{R}^3} \left[\sum_{i,k} e_i \Phi_i^2(u - X_i^k)\right]\left[\sum_{i,k} e_i \Phi_i^2(v - X_i^k)\right] |u - v|^{-1}\, du dv$$

$$- \sum_{i,k} e_i^2 \int \cdots \int_{\mathbb{R}^3 \times \mathbb{R}^3} \Phi_i^2(u)\, \Phi_i^2(v)\, |u - v|^{-1}\, du dv$$

By elementary potential theory (actually the fact that $-\Delta$ has positive spectrum) the first term is positive. The second term is easily calculated to have absolute value $(C/R_i) \sum_{j=1}^{s} e_j^2 N_j$. If we sum over $i = 1, \ldots, M$ and use the facts that $R_1 \geqslant 1$ and $R_{i+1} > 2R_i$, we get

$$V[\tilde{\tilde{k}}] \geqslant -C \sum_{i=1}^{s} N_i \tag{4.18}$$

Now combine (4.16), (4.17), (4.18) to get

$$\begin{aligned} V[|x|^{-1}] - V[k^{\#}] &\geqslant \frac{C}{M^2} V[|x|^{-1}] + \frac{C}{M} V[\tilde{k}] \\ &= \frac{C}{M^2} V[|x|^{-1}] + \frac{C}{M} V[\tilde{\tilde{k}}] + \frac{C}{M} V[\tilde{\tilde{k}} - k] \\ &\geqslant \frac{C}{M^2} V[|x|^{-1}] - \frac{C}{M} \sum_{i=1}^{s} N_i - \frac{C}{M}\left(H_N, B_R + \sum_{i=1}^{s} N_i\right) \\ &\geqslant -\frac{C}{M}\left(H_{N,B_R} + C \sum_{i=1}^{s} N_i\right) \end{aligned}$$

as desired. ∎

Proof of Covering Lemma. Let $R_1,..., R_M$ be radii with $R_1 \geqslant 1$ and $R_{i+1} \geqslant 2\sqrt{3}\, R_i$. Let Q be a cube with $|Q| > 2M^2\, |B_{R_M}|$ and let $c_i \in [|Q|\ |B_{R_i}|^{-1}/(M+6),\ |Q|\ |B_{R_i}|^{-1}/(M+5)]$. I claim that Q can be placed with c_i balls of each radius R_i so that all the balls are disjoint. Prove this by induction. Assume that c_i balls of radius R_i have been packed into Q for $i = M,..., j+1$. Let $\Omega^2 = Q \setminus \bigcup_{i=j+1}^{M} \cup B_{R_i}$. It is enough to show that $1/(M+5) \cdot |Q| \cdot |\Omega^j|^{-1}$ proportion of the volume of Ω^j can be covered by disjoint balls of radius R_j. For since $|Q| > 2M^2\, |B_{R_M}|$ we can adjust the number of balls to put c_i in the proper range. As $|\Omega^j| = |Q| - \sum_{i=j+1}^{M} c_i\, |B_{R_i}| \geqslant |Q|\ [(j+5)/(M+6)]$, $1/(M+5) \cdot |Q| \cdot |\Omega^j|^{-1} \leqslant (M+6)/(M+5) \cdot [1/(j+5)]$. Using the notation $\Omega_d^j = \{x \,\|x - \Omega^j)^c| > d\}$, we must show that $|\Omega^j_{\sqrt{3}R_j}|/|\Omega^j| \geqslant (M+6)/(M+5)\, 1/(j+5)$. (Recall the discussion of Lebowitz and Lieb's packing in Section 3.1.) Let the side length of Q be denoted by l:

$$|\Omega^j| \leqslant l^3 - \sum_{i=j+1}^{M} c_i\, |B_{R_i}| \leqslant l^3$$

$$- \sum_{i=j+1}^{M} \frac{1}{M+6}\, l^3\, |B_{R_i}|^{-1} \cdot |B_{R_i}| = l^3 \left(1 - \frac{M-j}{M+6}\right)$$

$$|\Omega^0_{\sqrt{3}R_j}| \geqslant (l^3 - \sqrt{3}\, R_j)^3 - \sum_{i=j+1} \frac{1}{M+5}\, l^3\, |B_{R_i}|^{-1}\, |B_{R_i} + \sqrt{3}\, R_j|$$

$$\geqslant l^3 \left[\left(1 - \frac{\sqrt{3}\, R_j}{l}\right)^3 - \frac{1}{M+5} \sum_{i=j+1}^{M} \left(1 + \sqrt{3}\, \frac{R_j}{R_i}\right)^3\right]$$

The necessary inequality is

$$\frac{\left(1 - \sqrt{3}\, \frac{R_j}{l}\right)^3 - \frac{1}{M+5} \sum_{i=j+1}^{M} \left(1 + \sqrt{3}\, \frac{R_j}{R_i}\right)^3}{\frac{j+6}{M+6}} \geqslant \frac{M+6}{M+5}\, \frac{1}{j+5} \tag{4.19}$$

Elementary calculations show that $R_{i+1} > 2\sqrt{3}\, R_i$ and $l > MR_M$ give (4.19) for all $j = 1,..., M-1$. The case $j = M$ is trivial.

Now decompose $\mathbb{R}^3$ into disjoint cubes Q of side length l. Pack each with c_i balls of radius R_i for $i = 1,..., M$ so that all are disjoint. Then for large R (say, $R \approx cl^4$), the number of cubes which intersect ∂B_R is $\leqslant c(R^2/|Q_l|)$. Hence, $|\bigcup B_{R_i} \cap B_R|/|B_R| \leqslant 1/(M+5) + [1/(M+5)]\ |Q_l|/|B_R| \cdot cR^2/|Q_l| \leqslant 1/(M+5)(1 + c/R)$. Similarily, $|\bigcup B_{R_i} B_R|/|B_R| \geqslant 1/(M+6)(1 - c/R)$ and the lemma is proved. ∎

Notice that the $R_*(M, R_m)$ in Fefferman's Inequality can be taken as $cl^4 = c(M^{2/3}R_m)^4 = cM^{4/3}R_m^4$. This can certainly be improved. For the purpose of Section 5 (and hence of this paper) any crude but definite value is sufficient.

5. CONTINUITY OF $F(\rho)$ AT $\partial E^\perp$

In Section 5.1 I will show that $\lim_{R\to\infty} \Pi_R(u)$ is uniform as some components $u_i \to -\infty$. In Section 5.2 I will show how this resolves the problem at vanishing particle densities.

5.1. Uniformity of $\lim_{R\to\infty} \Pi_R(\mu)$

The proof combines the L. L. Inequality and Fefferman's Inequality in the manner indicated in the comments after the statement of Fefferman's Inequality in Section 5.1. For this to work, we need to work with neutral N.

Lemma ← (Neutrality Lemma). Let $\mu_n = \max_{e_j<0}\{\mu_j, 0\}$ and $\mu_\rho = \max_{e_i>0}\{\mu_i, 0\}$. Then

$$\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})] \leqslant k(\mu, \beta, R) \sum_{N\cdot E=0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_N, B_R)] \tag{5.1}$$

where $(1/|B_R|)\,|\log k(\mu, \beta, R)| \leqslant c(\mu, \beta)/R^2 + (\mu_n^2 + \mu_\rho^2)/R^2$ and $c(\mu, \beta)$ is uniform for all $\mu_i <$ const and $\beta >$ const.

Proof. Assume $e_1 < 0$, $e_2 > 0$, $\mu_n = \mu_1$, and $\mu_\rho = \mu_2$. By dividing H_{N,B_R} by e_1, we can assume $e_2 = -1$. The lemma is proved by associating to each $N \in \mathbb{Z}^s_{\geqslant 0}$ a unique neutral N and then estimating the contribution coming from all terms corresponding to a given neutral N by the neutral term itself. Let $N \in \mathbb{Z}^s_{\geqslant 0}$. If $N\cdot E = \rho > 0$ then $[N + (\rho, 0,..., 0)]\cdot E = 0$. In this case, associate N with $N + (\rho, 0,..., 0)$. If $N\cdot E = n < 0$, then for q the least integer greater than n/k and $\rho = qk - n$, $[N + (\rho, q, 0,..., 0)]\cdot E = 0$. In this case associate N with $N + (\rho, q, 0,..., 0)$. Now assume that $N\cdot E = 0$. For $\rho \leqslant N_1$, we can estimate the term in grand canonical partition function corresponding to $N^\rho = N - (\rho, 0,..., 0)$ by the one corresponding to N. By the analysis leading to the L. L. Inequality we can put ρ electrons in the domain $S_R = B_{R+1}\backslash B_R$ and the other $N - (\rho, 0,..., 0)$ particles in B_R and obtain

$$\sum_n \exp\{-\beta[\langle H_{N^\rho,B_R}\psi_n, \psi_n\rangle + W(\psi_n, \psi) + \langle H_{\rho,S_R}, \psi, \psi\rangle] \leqslant \mathrm{Tr}[\exp(-\beta H_{N,B_{R+1}})]\} \tag{5.2}$$

where $\{\psi_n\}$ are the eigenfunctions for H_{N^ρ, B_R}, ψ is any statistically correct function on S_R^ρ, and $W(\psi_n, \psi)$ is the Coulomb interaction between the N^ρ particles defined by ψ_n and the ρ electrons defined by ψ. Peierl's theorem tells that (5.2) dominates

$$\mathrm{Tr}[\exp(-\beta H_{N_\rho, B_R})]\cdot \exp(-\beta\langle H_{\rho, S_R}, \psi, \psi\rangle - \beta\langle W\rangle]$$

where $\langle W\rangle = \int_{B_R}\int [\Phi_{B_R}(x)\,\Phi_{S_R}(y)]/|x-y|\,dxdy$ for Φ_{B_R} the average charge density taken over the ensemble $\mathrm{Tr}[\exp(-\beta H_{N^\rho, B_R})]$ and Φ_{S_R} the charge density arising from the as yet unspecified ψ. We know that Φ_{B_R} is radial and $\int_{B_R}\Phi_{B_R}(x)\,dx = \rho$. This means that for each $y \in S_R$

$$\int_{B_R}\Phi_{B_R}(x)\,|x-y|^{-1}\,dx = \frac{\rho}{|y|}$$

Now pick ψ so that $\exp(-\beta\langle H_{\rho, S_R}, \psi, \psi\rangle - \beta\langle W\rangle)$ is reasonably large: Place ρ uniformly around the sphere $B_{R+1/2}$ and define $\psi_i(y) = \tilde{\psi}(y - y_i)$ for some $C_0^\infty(S_R)$ radial function $\tilde{\psi} \geqslant 0$ with $\int |\tilde{\psi}|^2 = 1$. Assume $\tilde{\psi}$'s support is chosen small enough that the supports of the ψ_j are mutually disjoint. The function

$$\psi(x_1,\dots, x_\rho) = \frac{1}{\rho!}\sum_{Б\in \Pi_\rho}(-1)^{\mathrm{sgn}\,Б}, \psi_{Б(1)}(x_1)\dots\psi_{Б(\rho)}(x_\rho)$$

is antisymmetric on S_R^ρ and has L^2 norm 1. As is easily checked, $\langle -\Delta\psi, \psi\rangle \approx \rho^{5/3}R^{-4/3}$. Also, $\int\cdots\int_{S_R^\rho}\psi\cdot\overline{V_\rho\psi}\,dx_1\cdots dx_\rho = \frac{1}{2}\sum_{i\neq j}|y_i - y_j|^{-1}\cdot \leqslant \frac{1}{2}(\rho^2/R)$. Also, $\langle W\rangle = -\rho^2/(R+\frac{1}{2}) \approx -\rho^2/R$. It follows that $\exp[-\beta(\langle H_{\rho, S_R}\psi, \psi\rangle + \langle W\rangle)] \geqslant \exp[\beta(\rho^2/2R - \rho^{5/3}/R^{4/3})] \geqslant \exp[\beta(\rho^2/3R)]$, which shows

$$\mathrm{Tr}[\exp(-\beta H_{N^\rho, B_R})] \leqslant \exp[-\beta(\rho^2/3R)]\,\mathrm{Tr}(\exp(-\beta H_{N, B_{R+1}})] \quad (5.3)$$

In an analogous way we can deal with the case in which nuclei must be added to neutralize the system. Define $N^{\rho,q} = N - (\rho, q, 0,\dots, 0)$. For $0 < q < N_2$ and $0 \leqslant \rho < \min\{e_2, N_1\}$. As with the electrons needed to neutralize N^ρ, place nuclei clouds $\Phi_k(y) = \tilde{\Phi}(y - y_k)$ uniformly around S_R. Now place the $\rho < e_2$ disjoint electron clouds $\psi_j(x) = \tilde{\psi}(x - x_j)$ uniformly around S_R independently of the nuclei. Assume that R is large enough (depending on e_2) that the disjointness of the electron clouds does not force $\tilde{\psi}$ to have support smaller than $B_1(0)$. The nuclei–nuclei interaction energy is $\leqslant (e_2 q)^2/2R$ and the electron–electron interaction energy is $\leqslant \rho^2/2R$. The electron–nuclei interaction energy is $\geqslant -e_2 q(1 - 1/CR^2)(\rho/R) = -e_2(\rho_q/R) + e_2(\rho_q/R^3)$. This is because q/CR^2 is approximately the number of nuclei which intersect $\mathrm{supp}(\psi_j)$ for a given j. If ψ is the appropriately symmetrized linear combination of products of electron and nuclei clouds, then the discussion above shows that $\iint_{S_R^{\rho+q}} \psi \cdot \overline{V_{\rho+q}\psi}\, dx_1^1 \ldots dx_1^\rho dx_2^1 \ldots dx_2^q \leqslant (e_2 q - \rho)^2/2R + e_2 \rho q/R^3$. Again $\langle W \rangle \approx -(e_2 q - \rho)^2/R$ and $\int -\Delta_{\rho,q}\psi \cdot \bar{\psi} \approx (q^{5/3} + \rho^{5/3})/R^{4/3}$. Therefore, for only a moderately large R we have

$$\operatorname{Tr}[\exp(-\beta H_{N^{\rho,q},B_R})] \leqslant \exp\left[-\beta \frac{(e_2 q - \rho)}{3R}\right]^2 \operatorname{Tr}[\exp(-\beta H_{N,B_{R+1}})] \qquad (5.4)$$

Finish off the argument in the obvious way. Let $N \cdot E = 0$. Then,

$$\begin{aligned}
&\sum_{\rho=0}^{N_1} \exp(\beta\mu \cdot N^\rho) \operatorname{Tr}[\exp(-\beta H_{N^\rho,B_R})] \\
&\quad + \sum_{\rho=1}^{e_2-1} \sum_{q=0}^{N_2} \exp(\beta\mu \cdot N^{\rho,q}) \operatorname{Tr}[\exp(-\beta H_{N^{\rho,q}B_R})] \\
&\quad \leqslant \left\{ \sum_{\rho=0}^{N_1} \exp -\beta\mu_n\rho \exp\left(-\beta \frac{\rho^2}{3R}\right) + \sum_{\rho=1}^{k-1} \sum_{q=0}^{N_2} \exp[-\beta(\mu_n\rho - \mu_\rho q)] \right. \\
&\quad \left. \times \exp\left[-\beta \frac{(e_2 q - \rho)^2}{3R}\right] \right\} \cdot \operatorname{Tr}[\exp(-\beta H_{N,B_{R+1}})] \\
&\quad \leqslant \left\{ \sum_{\rho=0}^{N_1} \exp\left[-\beta\left(\mu_n\rho + \frac{\rho^3}{3R}\right)\right] \right. \\
&\quad \left. + C \sum_{q=0}^{N_2} \exp\left[-\beta\left(\mu_\rho q + \frac{q^2}{3R}\right)\right] \right\} \cdot \operatorname{Tr}[\exp(-\beta H_{N,B_{R+1}})]
\end{aligned}$$

Complete the square:

$$\begin{aligned}
&\leqslant \left(\exp\left(\frac{3}{4}\beta R \mu_n^2\right) \sum_{\rho=0}^{\infty} \exp\left[-\frac{\beta}{3R}\left(\rho + \frac{\mu_n}{2}\right)^2\right] + C \exp\left(\frac{3}{4}\beta R \mu_\rho^2\right) \sum_{q=0}^{\infty} \right. \\
&\quad \left. \times \exp\left[-\frac{\beta}{3R}\left(q + \frac{\mu_\rho}{2}\right)^2\right] \right) \cdot \operatorname{Tr}[\exp(-\beta H_{N,B_{R+1}})] \\
&\leqslant C(R\beta^{-1})^{1/2} \exp[\beta R(\mu_n^2 + \mu_\rho^2)] \operatorname{Tr}[\exp(-\beta H_{N,B_{R+1}})]
\end{aligned}$$

The sum in the grand canonical ensemble is thus

$$\begin{aligned}
\sum_N e^{\beta\mu \cdot N} \operatorname{Tr}[\exp(-\beta H_{N,B_R})] &\leqslant C(R\beta^{-1})^{1/2} \exp[\beta R(\mu_n^2 + \mu_\rho^2)] \\
&\quad \times \sum_{N \cdot E = 0} \exp(\beta\mu \cdot N) \operatorname{Tr}[\exp(-\beta H_{N,B_{R+1}})]
\end{aligned}$$

We must prove the following.

Claim. $\mathrm{Tr}[\exp(-\beta H_{N,B_{R+1}})] \leqslant \exp\{\beta[C(N)\,R + C\,|N|\,R^{-2}]$ $\mathrm{Tr}[\exp(-\beta H_{N,B_R})]\}$, where $C(N)$ is uniform for β bounded below $|N| \leqslant M\,|B_R|$.

The constant $C(N)$ is the Lipshitz constant for $F_R(\rho, \beta)$ in the β variable. Since F_R is convex in β and uniformly (in R) bounded (3.7) for $\beta > C$ and $|\rho| < M$, it can be picked uniform there. Once the claim is proved, estimate (3.14) allows us to restrict to $|N| < M(\mu)\,|B_R|$, where $M(\mu)$ is uniform for μ bounded above. This translates the $\beta[C(N)\,R + C\,|N|\,R^{-2}]$ into a $\beta C(\mu)\,R$ and we will have

$$\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})] \leqslant C(R\beta^{-1})^{1/2}\exp[\beta R(\mu_n^2+\mu_\rho^2)+\beta C(\mu)\,R]$$

$$\times \sum_{N\cdot E=0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_N})]$$

and

$$\frac{1}{\beta\,|B_R|}\left|\log\{C(R\beta^{-1})^{1/2}\cdot\exp[\beta R(\mu_n^2+\mu_\rho^2)+\beta C(\mu)\,R]\}\right.$$

$$\leqslant \frac{1}{\beta\,|B_R|}\,[\log C(R\beta^{-1})^{1/2} + \beta R(\mu_n^2+\mu_\rho^2)+\beta C(\mu)\,R]$$

$$\leqslant \frac{C(\mu,\beta)}{R^2} + \frac{\mu_n^2+\mu_\rho^2}{R^2}$$

Notice that $C(\mu,\beta)/R^2$ is actually used to dominate $\log C(R\beta^{-1})^{1/2}/\beta\,|B_R| + \beta C(\mu)/R^2$. The dependence on β of the asymptotic behavior in R is not brought out.

Proof of Claim:

$$\mathrm{Tr}[\exp(-\beta H_{N,B_{R+1}})] = \sum_{\psi_n \text{ eigenvalues on } B_{R+1}} \exp[-\beta\langle H_{N,B_{R+1}}\psi_n, \psi_n\rangle]$$

$$= \sum_n \exp\left\{-\beta\left[\left(\frac{R}{R+1}\right)^2\right]\langle -\Delta_{N,B_R}\tilde{\psi}_n, \tilde{\psi}_n\rangle + \left(\frac{R}{R+1}\right)\langle V\tilde{\psi}_n, \tilde{\psi}_n\rangle\right\}$$

where

$$\tilde{\psi}_n(x) = \left(\frac{R+1}{R}\right)^{3\Sigma_{i=1}^s N_i}\psi_n\left(\frac{R}{R+1}\,x\right)$$

This quantity is

$$\leqslant \sum_n \exp\left\{-\beta\left(\frac{R}{R+1}\right)^2 \langle H_{N,B_R}\tilde{\psi}, \tilde{\psi}\rangle - \beta\left[\left(\frac{R}{R+1}\right) - \left(\frac{R}{R+1}\right)^2\right]\langle V\tilde{\psi}_n, \tilde{\psi}_n\rangle\right\}$$

As $\langle V\tilde{\psi}, \tilde{\psi}\rangle \geqslant -\langle H_{N,B_R}\tilde{\psi}, \tilde{\psi}\rangle - C\sum_{i=1}^{s} N_i$ (by stability of matter theorem for the operator $-\Delta_{N,B_R} + 2V_N$), this sum is

$$\leqslant \exp\left(\frac{C\beta}{R^2}\sum_{i=1}^{s} N_i\right)\sum_n \exp\left\{-\beta\left[\left(\frac{R}{R+1}\right)^2 + \frac{C}{R^2}\right]\langle H_{N,B_R}\tilde{\psi}, \tilde{\psi}\rangle\right\}$$

$$\leqslant \exp\left(\frac{C\beta}{R^2}\sum_{i=1}^{s} N_i\right)\operatorname{Tr}\left[\exp\left\{-\beta\left[\left(\frac{R}{R+1}\right)^2 + \frac{C}{R^2}\right] H_{N,B_R}\right\}\right]$$

$$\leqslant \exp\left[\frac{C\beta}{R^2}\sum_{i=1} N_i + \beta C(N)\, R\right]\operatorname{Tr}[\exp(-\beta H_{N,B_R})]$$

where $C(N)$ is the Lipshitz constant for $F_R(\beta, \rho)$ in the β variable. ∎

Remark. The error $(\mu_n^2 + \mu_\rho^2)/R^2$ is a shortcoming of this proof. It results because we correspond nonneutral systems to neutral systems by *adding* particle. If μ_n or $\mu_\rho \leqslant 0$, then this greatly decrease the corresponding terms in the sum. This error could be removed by a few pages of argument. As a stronger version of the Neutrality Lemma is not needed for the resolution of the continuity problem, I will not carry out these details.

Recalling Section 3.5, we already know that F is continuous at $\rho = 0$. Therefore, we are only concerned with continuity at $\rho \in \partial E^{\perp}$ away from zero. If a *neutral* ρ is nonzero then at least *two* components ρ_ρ, ρ_n must be nonzero, one corresponding to positive charge and the other to negative charge. Under the equivalence of ensembles, this translates into μ_ρ and μ_n being bounded below.

The Neutrality Lemma allows us to combine the L. L. Inequality and Fefferman's Inequality. Let $\{R_i\}_{i=1}^{M}$, $R_*(M, R_M)$ and $\{C_i\}_{i=1}^{M}$ be as in the statement of Fefferman's Inequality and let $R > R_*(M, R_M)$. The Covering Lemma implies that B_R can be packed with C_i balls of each radius R_i, all disjoint. If the L. L. Inequality is applied to these subdomains of B_R and we then use the Neutrality Lemma and Fefferman's Inequality we obtain

$$
\begin{aligned}
&\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})] \\
&\quad\geqslant \sum_{N\cdot E=0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})] \\
&\quad\geqslant \prod_{i=1}^{M}\left\{\sum_{N\cdot E=0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_{R_i}})]\right\}^{C_i} \\
&\quad\geqslant \prod_{i=1}^{M}\left\{K(\mu,\beta,R_i)\cdot\sum_{N\cdot E=0} e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_{R_i}})]\right\}^{C_i} \\
&\quad\geqslant \left[\prod_{i=1}^{M} K(\mu,\beta,R_i)^{C_i}\right]\cdot\exp\left[-k(\mu,\beta)\frac{C}{M}|B_R|\right] \\
&\qquad\times\sum_N e^{\beta\mu\cdot N}\,\mathrm{Tr}[\exp(-\beta H_{N,B_R})]
\end{aligned}
$$

Take logs and divide by $\beta\,|B_R|$ to obtain

$$
\begin{aligned}
\Pi_R(\mu,\beta) &\geqslant -\frac{C(\mu,\beta)}{R_1^2}-\frac{\mu_n^2+\mu_\rho^2}{R_1^2}+\sum_{i=1}^{M} C_i\frac{|B_{R_i}|}{|B_R|}\,\Pi_{R_i}(\mu) \\
&\geqslant -\frac{C(\mu,\beta)}{R_1^2}-\frac{\mu_n^2+\mu_\rho^2}{R_1^2}-k(\mu,\beta)\frac{C}{M}+\Pi_R(\mu,\beta)
\end{aligned}
$$

As stated in the Neutrality Lemma, $C(\mu,\beta)$ is uniform for $\mu_i<C$ and β bounded below. The constant $k(\mu,\beta)$ in Fefferman's Inequality is a sum $k(\mu,\beta)=C_1(\mu,\beta)+C_2(\mu,\beta)$. $C_1(\mu,\beta)$ depends on free particle pressure due to the Laplacian acting on the unit cubes [see discussion after (4.5)]. It clearly decreases as any μ_i decreases or as β increases. $C_2(\mu,\beta)$ depends on the Lipshitz continuity and, as was pointed out at the end of Section 4.2, also decreases as any μ_i decreases (for β in bounded sets). Hence, for μ_n, μ_ρ bounded below and all $\mu_i<C$ we can pick R_1 and M such that $C(\mu,\beta)/R_1^2+(\mu_n^2+\mu_\rho^2)/R_1^2-k(\mu,\beta)(C/M)$ is as small as we like, say, less than $\varepsilon>0$. If $R>R_*(M,R_1(2\sqrt{3})^M)$, $|\Pi_R(\mu,\beta)-\Pi(\mu,\beta)|<\varepsilon$ as long as μ is in this range and β is in a bounded set. In particular, the convergence is uniform as some $\mu_i\to-\infty$, as long as μ_n, μ_ρ remain bounded below. (As the Remark after the Neutrality Lemma indicates, we can even remove the restriction on μ_n, μ_ρ.)

5.2. Continuity of $F(\rho)$ at $\partial E^\perp$

As was pointed out in the last paragraph of Section 3.1 and discussed in the Remark after the Neutrality Lemma, we only need examine the continuity of F at some $\bar{\rho} \in \partial E^{\perp}$ away from $\rho = 0$. In particular this means that some $\bar{\rho}_p$ (corresponding to a positively charged species) and some $\bar{\rho}_n$ (corresponding to a negatively charged species) are nonzero. Let $a = \{i \mid \bar{\rho}_i = 0\}$. By assumption $a \neq \varnothing$. Let $\partial_a E^{\perp} = \{\rho \in \partial E^{\perp} \mid \rho_i = 0$ for all $i \in a\}$. For $\rho \in \partial_a E^{\perp}$ let ρ_t be any path in $E^{\perp}$ tending to ρ as $t \to 0$. We must show that $\lim_{t \to 0} F(\rho_t) = F(\rho)$. By possibly enlarging a we may assume that $\bar{\rho} \in \mathrm{int}(\partial_a E^{\perp})$. The *a priori* convexity of F's restrictions to $\partial_a E^{\perp}$ allows us to assume the $\rho^t \in \mathrm{int}(E^{\perp})$ for $t \neq 0$. Write $\rho = (\rho_a, \rho_b)$, $\mu = (\mu_a, \mu_b)$, where the subscript a denotes those ρ_i, μ_i with $i \in a$. In this notation ρ^t converges to $\bar{\rho} = (0, \bar{\rho}_b)$ as $t \to 0$. Let $\Pi_a(\mu_b) = \lim_{\mu_a \to -\infty} \Pi(\mu_a, \mu_b)$. By the uniform convergence of $\Pi_R(\mu)$ to $\Pi(\mu)$ for $\mu_a < c$ as $R \to \infty$ and the fact that $\lim_{\mu_a \to -\infty} \Pi_R(\mu_a, \mu_b) = (\beta\, |B_R|)^{-1} \sum_{N_b} \exp(\beta \mu_b \cdot N_b)$ $\mathrm{Tr}[\exp(-\beta H_{N_b, B_R})]$ is independent of the specific way in which $\mu_a \to -\infty$ for each R, $\Pi_a(\mu_b)$ is well defined. Furthermore, by the equivalence of ensembles for the system composed of only species for which $i \notin a$, $\Pi_a(\mu_b) = \sup_{\rho_b \cdot E_b = 0} \{\mu_b \cdot \rho_b - F(0, \rho_b)\}$. Equivalently, $F(0, \rho_b) = \sup_{\mu_b} \{\mu_b \cdot \rho_b - \Pi_a(\mu_b)\}$, $\rho_b \in \mathrm{int}(\partial_a E^{\perp})$. Since the Legendre transform of the limit of a sequence of convex functions is the limit of their Legendre transforms, this equals $\lim_{\mu_a \to -\infty} \sup_{\mu_b} \{\mu_b \cdot \rho_b - \Pi(\mu_a, \mu_b)\}$ independently of how μ_a approaches $-\infty$.

This paper is concluded by showing that $\lim_{t \to 0} F(\rho^t) = \sup_{\mu_b} \{\mu_b \cdot \overline{\rho_b} - \Pi_a(\mu_b)\}$. By equivalence of ensembles, $F(\rho^t) = \sup_{\mu} \{\mu \cdot \rho^t - \Pi(\mu)\}$. Since $F(\rho)$ is finite for all $\rho \in E^{\perp}$ this supremum is attained at some μ^t with $\mu_i^t < \text{const}$ for all i, independently of t. Since Π is bounded above by the free particle pressure (3.7), $\mu_b^t > \text{const}$ as well.

Now, let $\varepsilon > 0$. Write $F(\rho^t) = \mu_a^t \cdot \rho_a^t + \sup_{\mu_b} \{\mu_b \cdot \rho_b^t - \Pi(\mu_a^t, \mu_b)\}$. Since $\mu_a^t < \text{const}$, $\mu_a^t \cdot \rho_a^t < \varepsilon$ for all small enough t. Hence, for small t

$$F(\rho^t) < \varepsilon + \sup_{\mu_b} \{\mu_b \cdot \rho_b^t - \Pi(\mu_a^t, \mu_b)\}$$

As Π is a decreasing function of each variable μ_i, this is $< \varepsilon + \sup_{\mu_b} \{\mu_b \cdot \rho_b^t - \Pi_a(\mu_b)\}$. On the other hand, if we define a sequence $\tilde{\mu}_a^t \to -\infty$ for which $|\tilde{\mu}_a^t \cdot \rho_a^t| < \varepsilon$ then

$$F(\rho^t) > \tilde{\mu}_a^t \cdot \rho_a^t + \sup_{\mu_b} \{\mu_b \cdot \rho_b^t - \Pi(\tilde{\mu}_a^t, \mu_b)\}$$

$$> -\varepsilon + \sup_{\mu_b} \{\mu_b \cdot \rho_b^t - \Pi(\tilde{\mu}_a^t, \mu_b)\}$$

Letting $t \to 0$ gives

$$> -\varepsilon + \sup_{\mu_b} \{\mu_b \cdot \rho_b^t - \Pi_a(\mu_b)\}$$

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