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The Thermodynamic Limit for a Crystal

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Abstract. Consider a crystal with nucleii fixed at the lattice points in $\Omega \subset \mathbb{R}^3$, interacting by Coulomb forces with quantized electrons in Ω. We prove that the pressure tends to a limit as Ω grows infinitely large.

0. Introduction

A natural model for electrons in a crystal is as follows. We place a nucleus of charge $+1$ at each lattice point in a box $\Omega \subseteqq \mathrm{R}^3$. The basic Hamiltonian for N quantized electrons $x_1, \ldots, x_N$ in Ω is

$$H_{N,\Omega} = -\Delta_x + \sum_{j<k} |x_j - x_k|^{-1} + \sum_{j<k} |y_j - y_k|^{-1} - \sum_{j,k} |x_j - y_k|^{-1}$$

with Dirichlet boundary conditions on $\Omega \times \cdots \times \Omega$. Here $y_1 \ldots y_M$ are the nucleii, and $H_{N,\Omega}$ acts on antisymmetric wave functions $\psi(x_1 \ldots x_N)$. If the electrons have temperature β^{-1} and chemical potential μ/β, then up to trivial factors the pressure is given by

$$F = (\mathrm{Vol}\,\Omega)^{-1} \ln \left[\sum_N e^{\mu N} \operatorname{Trace} e^{-\beta H_{N,\Omega}} \right].$$

The purpose of this paper is to prove that F tends to a limit as the volume of Ω tends to infinity. This is called existence of the thermodynamic limit. See Sect. 2 for the precise statement of our result. The problem of the thermodynamic limit for crystals was posed by Lebowitz and Lieb, following their basic work [1] on real matter, with electrons and nucleii all quantized. Since a crystal is not rotationally symmetric, the method of [1] doesn't work here.

Of course one wants to allow periodic arrangements of nucleii more general than just charge $+1$ at each lattice point; also, we should introduce spin into our wave functions. These refinements can be easily incorporated into our proof. For that matter, it is enough to suppose that the placement of nucleii is asymptotically periodic; and our electrons could be Bosons (or even classical particles provided the nucleii have hard cores).

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In a later article, we shall apply our technique to show that quantized electrons and nucleii at suitable temperature and density form an ideal gas of hydrogen atoms or molecules.

1. Notation

Let $\Gamma = \{\Omega \subset R^3 | \Omega$ bounded, convex, with non-empty interior$\}$,

$\Gamma_0 = \{D \in \Gamma | \partial D$ is smooth and has strictly positive Gaussian curvature at every point$\}$.

For $D \in \Gamma$, $x \in R^3$, $R > 0$, write $D(x, R)$ for the translate and dilate, $\{Ry + x | y \in D\}$.
We write Q^0 for the unit cube in R^3.
Set $L_N^2(\Omega) = \{$square-integrable antisymmetric $\psi(x_1 \dots x_N)$ on $\Omega^N\}$,

$$L_*^2(\Omega) = \sum_{N \geqq 0} \oplus L_N^2(\Omega).$$

If $\psi \in L_N^2(\Omega)$ and $(x_1 \dots x_N) \notin \Omega^N$, then we interpret $\psi(x_1 \dots x_N)$ to be zero.

If $K(x)$ is a function on R^3, and we have electrons $x_1 \dots x_N$ and nucleii $y_1 \dots y_M$, then $V[K] = \frac{1}{2} \sum_{j \neq k} K(x_j - x_k) + \frac{1}{2} \sum_{j \neq k} K(y_j - y_k) - \sum_{j,k} K(x_j - y_k)$.

Thus, the Coulomb potential is $V[|x|^{-1}]$.

For $\Omega \subset R^3$, define
$H_{N,\Omega}^0 = -\Delta$ on $L_N^2(\Omega)$ with Dirichlet boundary conditions;
$H_{N,\Omega} = -\Delta + V[|x|^{-1}]$ on $L_N^2(\Omega)$ with Dirichlet boundary conditions, where the nucleii are placed at all the points of $Z^3 \cap \Omega$.

$$\text{Define} \quad F(\mu, \beta, \Omega) = |\Omega|^{-1} \ln \left[\sum_{N \geqq 0} e^{\mu N} \operatorname{Tr} e^{-\beta H_{N,\Omega}} \right].$$

If $\Omega = D(x, R)$ for $D \in \Gamma$, then we write $F(\mu, \beta, x, R, D)$ for $F(\mu, \beta, \Omega)$. Observe that F is invariant under translates of x by vectors in Z^3, but not by vectors in R^3.

When μ, β, D are kept fixed, we shall often write $F(x, R)$ for $F(\mu, \beta, x, R, D)$.

2. Reduction of the Theorem to Two Main Lemmas

The precise statement of our result is as follows.

Theorem. *For each* $\beta > 0$, $\mu \in R^1$, $\Omega \in \Gamma$, *the limit* $\lim_{R \to \infty} F(\mu, \beta, x, R, \Omega)$ *converges uniformly in x. Its value is independent of* Ω *and has the form* $\phi(\beta) + \mu$.

In this section, we shall state two main lemmas, and show how they imply the theorem. The rest of the paper is devoted to proving the lemmas.

Lemma 1. *Let* $D \in \Gamma_0, \Omega \in \Gamma$, $\varepsilon > 0$. *Suppose we have radii* $R_1 < R_2 < \dots < R_M < R_*$ *with* $R_1 > C\varepsilon^{-10}$, $R_{k+1} > 2R_k$, $M > C\varepsilon^{-10}$, *and* $R_* > M^{10} R_M$. *Then for* $x \in R^3$ *we have*

$$F(\mu, \beta, x, R_*, \Omega) < \varepsilon + \max_{1 \leqq k \leqq M} [\operatorname{Av}_{y \in Q^0} F(\mu, \beta, y, R_k, D)]. \tag{2.1}$$

The constants C in Lemma 1 depend on μ, β, D, Ω.

Lemma 2. *For $\Omega \in \Gamma$ there is a constant $C(\Omega)$ with the following property. Let $D \in \Gamma_0$, $0 < \varepsilon < 1$, $D_* = D(x', R')$, $\Omega_* = \Omega(x, R)$. Suppose $D_* \subseteqq \Omega_*$, $\operatorname{dist}(\partial D_*, \partial \Omega_*) > 10$, and $|\Omega_*| < (1 + \varepsilon^{10})|D_*|$. Then $F(\mu, \beta, \Omega_*) > F(\mu, \beta, D_*) - C(\Omega)\varepsilon$ if R' is sufficiently large.*

Very roughly, Lemma 1 says that $F(\mu, \beta, \Omega)$ is monotone decreasing in Ω over the long run, while Lemma 2 says that a small increase in Ω will not cause a large drop in $F(\mu, \beta, \Omega)$.

Let us check that Lemmas 1 and 2 imply the theorem. From Lemma 1 we get

Corollary 1. *For fixed $\mu, \beta, D \in \Gamma_0$, the quantity $\bar{F}(R) \equiv AV_{y \in Q^0} F(\mu, \beta, y, R, D)$ tends to a limit as $R \to \infty$.*

Proof. Let $l = \liminf_{R \to \infty} \bar{F}(R)$, and take $\varepsilon > 0$. It is trivial to show $l \neq -\infty$ (see estimate (3.20) below), so there are arbitrarily large R with $\bar{F}(R) \leqq l + \varepsilon$. So we can pick successively $R_1, R_2, \ldots, R_M$ to satisfy $R_1 > C\varepsilon^{-10}$, $R_{k+1} > 2R_k$, $M > C\varepsilon^{-10}$, and $\bar{F}(R_k) \leqq l + \varepsilon$. Here the constant C is taken from Lemma 1 with $\Omega = D$. Lemma 1 gives $F(\mu, \beta, x, R_*, D) \leqq \varepsilon + [l + \varepsilon]$ for all $x \in R^3$, $R_* > M^{10} R_M$. Averaging over $x \in Q^0$, we get $\bar{F}(R_*) \leqq l + 2\varepsilon$ for R_* large enough, so $\limsup_{R \to \infty} \bar{F}(R) \leqq 2\varepsilon + l = 2\varepsilon + \liminf_{R \to \infty} \bar{F}(R)$. Q.E.D.

Now let $\bar{F}(\mu, \beta, D) = \lim_{R \to \infty} \mathrm{Av}_{y \in Q^0} F(\mu, \beta, y, R, D)$. Corollary 1 and Lemma 1 together show at once

Corollary 2. *Given μ, β, $D \in \Gamma_0$, $\Omega \in \Gamma$ and $\varepsilon > 0$, we have $F(\mu, \beta, x, R, \Omega) \leqq \varepsilon + \bar{F}(\mu, \beta, D)$ if R is large enough.*

In particular,

$$F(\mu, \beta, x, R, D) \leqq \varepsilon + \bar{F}(\mu, \beta, D) \quad \text{if } R \text{ is large enough.} \tag{2.2}$$

On the other hand, Lemma 2 shows that for a large constant C we have $F(\mu, \beta, x, R, D) \geqq F(\mu, \beta, y, R - C, D) - C(D)\varepsilon$ if R is large enough and $|x - y| < 50$. Average this estimate over all y in a translate of Q^0 containing x. The result is $F(\mu, \beta, x, R, D) \geqq [\mathrm{Av}_{y \in Q^0} F(\mu, \beta, y, R - C, D)] - C(D)\varepsilon$ for large R. Recalling the definition of $\bar{F}(\mu, \beta, D)$, we conclude that

$$F(\mu, \beta, x, R, D) \geqq \bar{F}(\mu, \beta, D) - C'(D)\varepsilon \quad \text{if } R \text{ is large enough.}$$

Comparing with (2.2), we find that $F(\mu, \beta, x, R, D) \to \bar{F}(\mu, \beta, D)$ as $R \to \infty$, for each $D \in \Gamma_0$.

Next note that $\bar{F}(\mu, \beta, D)$ is independent of D. This is immediate from Corollary 2 with $\Omega \in \Gamma_0$. We write $\bar{F}(\mu, \beta)$ for $\bar{F}(\mu, \beta, D)$.

Finally, let $\Omega \in \Gamma$, $\varepsilon > 0$, and pick $D_\varepsilon \in \Gamma_0$ so that $\bar{D}_\varepsilon \subseteqq$ interior Ω, $|\Omega| < (1 + \varepsilon^{10})|D_\varepsilon|$. Lemma 2 shows that $F(\mu, \beta, x, R, \Omega) > F(\mu, \beta, x, R, D_\varepsilon) - C(\Omega)\varepsilon$ for R large enough. Hence $F(\mu, \beta, x, R, \Omega) > \bar{F}(\mu, \beta) - 2C(\Omega)\varepsilon$ for large R. On the other hand, Corollary 2 with $D = D_\varepsilon$ gives $F(\mu, \beta, x, R, \Omega) \leqq \bar{F}(\mu, \beta) + \varepsilon$ for large R. So $\lim_{R \to \infty} F(\mu, \beta, R, \Omega) = \bar{F}(\mu, \beta)$ uniformly in x, for any $\Omega \in \Gamma$. Our theorem is completely proved, except for the assertion $\bar{F}(\mu, \beta) = \mu + \phi(\beta)$, which follows trivially from estimate (3.6) below. Hence, the problem is reduced to proving Lemmas 1 and 2.

3. Estimates for Coulomb Systems

Consider a Coulomb system with electrons $x_1 \ldots x_N$ and nucleii $\omega_1 \ldots \omega_{N'}$. Assume $|\omega_k - \omega_{k'}| \geqq 1$ for $k \neq k'$. We shall compare the potential energy $V = V[|x|^{-1}]$ with the energy of a continuous charge distribution:

$$V_\rho = \frac{1}{2} \int\int \frac{\rho(x)\rho(y)}{|x-y|} dx\, dy, \qquad \rho(x) = \sum_k \phi(x - \omega_k) - \sum_j \phi(x - x_j),$$

$$\phi \in C_0^\infty(|x| \leqq 1/4), \qquad \int \phi = 1, \qquad \phi \geqq 0.$$

First of all, V_ρ contains N "self-energy" terms $\frac{1}{2} \int \phi(x - x_j)\phi(y - x_k)/|x-y|\, dx\, dy$ with $j = k$, as well as N' similar terms for the nucleii. These terms have no analogues in $V[|x|^{-1}]$; they total $CN + CN'$.

Next, compare the terms in V, V_ρ arising from repulsion of distinct electrons. We have

$$|x_j - x_k|^{-1} \geqq c|x_j - x_k|^{-1} \chi_{|x_j - x_k| < 1/10} + \int \frac{\phi(x - x_j)\phi(y - x_k)}{|x-y|} dx\, dy.$$

in view of the subharmonicity of the Coulomb potential.[1]

The terms in V, V_ρ arising from repulsion of distinct nucleii are exactly equal, since distinct nucleii are at least distance 1 apart. Finally, the electron–proton attraction gives rise to terms in V, V_ρ which compare as follows:

$$-|x_j - \omega_k|^{-1} \geqq -\int \frac{\phi(x - x_j)\phi(y - \omega_k)}{|x-y|} dx\, dy - |x_j - \omega_k|^{-1} \chi_{|x_j - \omega_k| < 1/2}.$$

Consequently,

$$V[|x|^{-1}] \geqq V_\rho + c \sum_{0 < |x_j - x_k| < 1/10} |x_j - x_k|^{-1} - \sum_{|x_j - \omega_k| < 1/2} |x_j - \omega_k|^{-1} - CN - CN'. \tag{3.1}$$

For functions ψ of three variables, we have an elementary inequality

$$\frac{1}{2} \int_{|x-\omega| < 1/2} |\nabla_x \psi|^2 dx \geqq 2 \int_{|x-\omega| < 1/2} |x - \omega|^{-1} |\psi(x)|^2 dx - C \int_{|x-\omega| < 1/2} |\psi(x)|^2 dx.$$

This amounts to the stability of a single hydrogen atom. Writing x_j for x, ω_k for ω; integrating against $\prod_{l \neq j} dx_l$; and summing over j, k we obtain

$$-\tfrac{1}{2}\Delta \geqq 2 \sum_{|x_j - \omega_k| < 1/2} |x_j - \omega_k|^{-1} - CN - CN' \tag{3.2}$$

as operators on $\psi(x_1 \ldots x_N)$. Adding (3.1) and (3.2), we get for $H = -\Delta + V[|x|^{-1}]$ the operator inequality

$$H + CN + CN' \geqq -\tfrac{1}{2}\Delta + c \sum_{0 < |x_j - x_k| < 1/10} |x_j - x_k|^{-1} + \sum_{|x_j - \omega_k| < 1/2} |x_j - \omega_k|^{-1} + V_\rho. \tag{3.3}$$

1 Here we assume $\phi(x) \geqq c$ when $|x| < 1/10$

The terms on the right are all positive, so (3.3) implies H-stability of the system. Note that we did not need antisymmetric wave functions.

Lemma 3. *Let F be a function of compact support on R^3, with one distributional derivative in L^2. Then*

$$\left|\sum_k \phi * F(\omega_k) - \sum_j \phi * F(x_j)\right|^2 \leqq C \|\nabla F\|_{L^2}^2 \cdot (H + CN + CN') \tag{3.4}$$

as operators on $L^2(R^{3N})$.

Corollary. *If the system is confined to a ball of radius R, then the net charge $N - N'$ satisfies*

$$(N - N')^2 \leqq CR(H + CN + CN'). \tag{3.5}$$

In particular, for nucleii at the lattice points of $\Omega(x, R)$, we have

$$H \geqq -\tfrac{1}{2}\Delta + c\delta^2 R^5 \tag{3.6}$$

if the net charge $|N - N'| > \delta R^3$, $\delta > CR^{-1}$.

Proof of the Corollary. Estimate (3.5) is just the special case of Lemma 3 with $F(x) = 1$ for x in a ball of radius $2R$, $F(x) = 0$ outside a ball of radius $3R$, $|\nabla F| \leqq CR^{-1}$ everywhere. To prove (3.6), note that $N' \sim (\mathrm{Vol}\,\Omega) \cdot R^3$, so if $|N - N'| > \delta R^3$ with $\delta > CR^{-1}$ then (3.5) shows that $H \geqq c\delta^2 R^5 + C_1 N$, while (3.3) gives $H \geqq -\tfrac{1}{2}\Delta - C_1 N - CR^3$. Estimate (3.6) follows by adding the last two inequalities. ∎

Proof of Lemma 3. We have $\sum_k \phi * F(\omega_k) - \sum_k \phi * F(x_j) = \langle \rho, F \rangle = \langle (-\Delta)^{-1/2}\rho, (-\Delta)^{1/2} F \rangle$. The formal manipulation is justified if $F \in C_0^\infty$, which we may assume. Thus,

$$\left|\sum_k \phi * F(\omega_k) - \sum_j \phi * F(x_j)\right|^2 \leqq \|(-\Delta)^{-1/2}\rho\|^2 \cdot \|(-\Delta)^{1/2} F\|^2 = \|\nabla F\|^2 \langle (-\Delta)^{-1}\rho, \rho \rangle$$
$$= \mathrm{const}\, \|\nabla F\|^2 V_\rho.$$

So (3.4) follows from (3.3). ∎

Next we give an estimate for $V[K]$ when K behaves roughly like $|x|^{-1}$ in the following rather technical sense.

$$|\partial_x^\alpha K(x)| \leqq C|x|^{-1-|\alpha|} \quad \text{for } |\alpha| \leqq 2 \text{ and all } x. \tag{3.7}$$

$$|\partial_x^\alpha K(x)| \leqq C|x|^{-4} \quad \text{for } |\alpha| = 3, \tag{3.8}$$

unless x belongs to one of the annuli $\mathscr{A}_k = D(0, R_k + 1) \backslash D(0, R_k - 1)$. Here we assume $D \in \Gamma_0$ and $R_1, R_1, \ldots$ are fixed radii satisfying $R_1 \geqq 10$, $R_{k+1} \geqq 2R_k$.

Lemma 4. *If K satisfies (3.7) and (3.8), then $V[K] \leqq C(H + CN + CN')$.*

Proof. First we check that (3.7), (3.8), imply a bound for the Fourier transform of K, namely $|\hat{K}(\xi)| \leqq C|\xi|^{-2}$. In fact, we can write $K = K_1 + K_2$ with K_1 supported in $|x| < 2|\xi|^{-1}$, K_2 supported in $|x| > |\xi|^{-1}$, and K_1, K_2 satisfying (3.7) and (3.8). Then one checks that $\|K_1\|_{L^1} \leqq C|\xi|^{-2}$ and $\int |\Delta K_2(x) - \Delta K_2(x-y)|\,dx \leqq C$ for $|y| < c|\xi|^{-1}$. Consequently $|\hat{K}_1(\xi)| \leqq C|\xi|^{-2}$, while $|[1-e^{iy\cdot\xi}]|\xi|^2\hat{K}_2(\xi)| \leqq C$ for $|y| < c|\xi|^{-1}$. Taking $y = (c/2)\xi|\xi|^{-2}$, we get $|\hat{K}_2(\xi)| \leqq C'|\xi|^{-2}$, and so $|\hat{K}(\xi)| \leqq C|\xi|^{-2}$ as claimed.

Now set $K^{\#} = |x|^{-1} - cK(x)$ with $0 < c \ll 1$. We know that $K^{\#}$ has positive Fourier transform, so that $\int K^{\#}(x-y)\rho(x)\rho(y)\,dx\,dy \equiv K^{\#}\{\rho\} \geqq 0$ for continuous charge distribution ρ.

We shall prove that

$$V[K^{\#}] \geqq -C(H + CN + CN'). \tag{3.9}$$

If (3.9) holds, then since $V[1/|x|] \leqq H$ and $V[cK - 1/|x|] \leqq C(H + CN + CN')$, we obtain the conclusion of Lemma 4 just by adding. So the problem reduces to proving (3.9).

Subdivide R^3 into a grid $\{Q_\nu\}$ of cubes of side 10^{-3}, and let N_ν be the number of particles (x_j and ω_k) in Q_ν. Evidently

$$\frac{1}{2}\sum_\nu N_\nu(N_\nu - 1) \leqq \sum_{0<|x_j-x_k|<10^{-2}} |x_j - x_k|^{-1} + \sum_{|x_j-\omega_k|<1/2} |x_j - \omega_k|^{-1} \leqq C(H + CN + CN')$$

by (3.3). Therefore

$$\sum_\nu N_\nu^2 \leqq C(H + CN + CN') \quad \text{since} \quad \sum_\nu N_\nu = N + N'. \tag{3.10}$$

Now we are ready to prove (3.9) by imitating the proof of (3.3). Fix an even approximate identity $\psi \in C_0^\infty(|x| < 10^{-3})$ with $\int x^\alpha \psi(x)\,dx = \delta_{\alpha 0}, |\alpha| < 10$. Then set $\rho^{\#}(x) = \sum_k \psi(x - \omega_k) - \sum_j \psi(x - x_j)$, and compare $V[K^{\#}]$ with the non-negative quantity $V^{\#} = \frac{1}{2}\int K^{\#}(x-y)\rho^{\#}(x)\rho^{\#}(y)\,dx\,dy$. As before, $V^{\#}$ contains self-energy terms which total $CN + CN'$. The difference between $K^{\#}(y_1 - y_2)$ and the corresponding term $\int K^{\#}(x-y)\psi(x-y_1)\psi(y-y_2)\,dx\,dy$ is $\varepsilon(y_1 - y_2)$ with $\varepsilon = K^{\#} - K^{\#} * \psi * \psi$. Therefore

$$V[K^{\#}] \geqq V^{\#} - CN - CN' - \sum_{y_j \neq y_k} |\varepsilon(y_j - y_k)|, \tag{3.11}$$

where $y_1 \ldots y_{N+N'}$ is a list of all the particles $x_1 \ldots x_N$, $\omega_1 \ldots \omega_{N'}$.

In view of the moment conditions on ψ, we have the estimates

$$\varepsilon(y)| \leqq C|y|^{-1} \text{ just from the size of } K^{\#}, \tag{3.12}$$

$$|\varepsilon(y)| \leqq C|y|^{-3} \text{ by Taylor-expanding } K^{\#} \text{ to first order using (3.7)}, \tag{3.13}$$

$$|\varepsilon(y)| \leqq C|y|^{-4} \text{ outside } \bigcup_{k=1}^{\infty} [D(0, R_k + 2) \backslash D(0, R_k - 2)], \tag{3.14}$$

by Taylor-expanding $K^{\#}$ to second order using (3.8).

$$\text{Set } \varepsilon(Q_\mu, Q_\nu) = \max\{|\varepsilon(y - y')| \quad |y \in Q_\mu, y' \in Q_\nu, |y - y'| > 10^{-3}\}.$$

From (3.13), (3.14) we get

$$\sum_\nu \varepsilon(Q_\mu, Q_\nu) < C \text{ for each } \mu; \sum_\mu \varepsilon(Q_\mu, Q_\nu) < C \text{ for each } \nu. \tag{3.15}$$

On the other hand (3.11) and (3.12) imply

$$V[K^{\#}] \geqq -CN - CN' - \sum_{\mu,\nu} \varepsilon(Q_\mu, Q_\nu) N_\mu N_\nu - \sum_{0<|y_j-y_k|<10^{-2}} C|y_j - y_k|^{-1}. \quad (3.16)$$

Now (3.15) shows that $\sum_{\mu,\nu} \varepsilon(Q_\mu, Q_\nu) N_\mu N_\nu \leqq C \sum_\mu N_\mu^2$, which we estimate by (3.10). Also

$$\sum_{0<|y_j-y_k|<10^{-3}} |y_j - y_k|^{-1} = \sum_{0<|x_j-x_k|<10^{-3}} |x_j - x_k|^{-1} + \sum_{|x_j-\omega_k|<10^{-3}} |x_j - \omega_k|^{-1},$$

which we estimate by (3.3). Hence (3.16) yields $V[K^{\#}] \geqq -C(H + CN + CN')$, which is the desired estimate (3.9). ■

We shall also need estimate on $\sum_{y\in J} \sum_{|x_j-y|<1/2} |x_j - y|^{-1}$ for various subsets $J \subseteqq Z^3$. Imitating the proof of (3.2), we first note that $\varepsilon^2 \int_{|x-y|<1/2} |\nabla_x \psi|^2 dx \geqq \int_{|x-y|<1/2} |x-y|^{-1} |\psi|^2 dx - C(\varepsilon) \int_{|x-y|<1/2} |\psi|^2 dx$, for functions ψ on R^3 and $\varepsilon > 0$ arbitrary. Set $x = x_j$, integrate against $\prod_{l \neq j} dx_l$, sum over j and sum over $y \in J$. We obtain

$$-\varepsilon^2 \Delta \geqq \sum_{y\in J} \sum_{|x_j-y|<1/2} |x_j - y|^{-1} - C(\varepsilon) \cdot \left[\text{Number of } x_j \in \bigcup_{y\in J} B(y, 1/2) \right] \quad (3.17)$$

as operators on $L^2(R^{3N})$. Setting $\mathfrak{N} = \{\nu | Q_\nu \text{ meets one of the } B(y, 1/2), y \in J\}$, we note that $|\mathfrak{N}| \leqq C|J|$, while the number of $x_j \in \bigcup_{y\in J} B(y, 1/2)$ is at most

$$\sum_{\nu\in\mathfrak{N}} N_\nu \leqq \left(\sum_\nu N_\nu^2 \right)^{1/2} \cdot |\mathfrak{N}|^{1/2} \leqq \frac{\varepsilon^2}{C(\varepsilon)} \sum_\nu N_\nu^2 + \frac{C(\varepsilon)}{\varepsilon^2} |\mathfrak{N}|$$

$$\leqq \frac{\varepsilon^2}{C(\varepsilon)} \sum_\nu N_\nu^2 + C'(\varepsilon)|J|.$$

Putting this into (3.17), we find that $\sum_{y\in J} \sum_{|x_j-y|<1/2} |x_j - y|^{-1} \leqq -\varepsilon^2 \Delta + \varepsilon^2 \sum_\nu N_\nu^2 + C''(\varepsilon)|J|$. Hence,

$$\sum_{y\in J} \sum_{|x_j-y|<1/2} |x_j - y|^{-1} \leqq C\varepsilon^2 (H + CN + CN') + C(\varepsilon)|J|, \quad (3.18)$$

by virtue of (3.3) and (3.10).

Next we record some trivial estimates on partition functions. Let $\Omega_* = \Omega(x, R)$ with $\Omega \in \Gamma$, and suppose we place the nucleii at a subset of $Z^3 \cap \Omega_*$. The corresponding N-electron Hamiltonian satisfies $H_N \geqq \frac{1}{2} H^0_{N,\Omega*} - CN - C|\Omega_*|$ by (3.3). Therefore, we have an upper bound

$$\frac{1}{|\Omega_*|} \ln \sum_N e^{\mu N} \operatorname{Tr} e^{-\beta H_N} \leqq C(\mu, \beta), \quad (3.19)$$

simply because there is a corresponding upper bound for H^0_N. Also, it is obvious that

$$\frac{1}{|\Omega_*|} \ln \sum_N e^{\mu N} \operatorname{Tr} e^{-\beta H_N} \geqq -C(\mu, \beta), \quad (3.20)$$

simply because there exists $N < C|\Omega|$ and $\psi_0 \in L^2_N(\Omega_*)$ with $\langle H\psi_0, \psi_0 \rangle \leqq CN$. In fact, we can write $\psi_0(x_1 \dots x_N)$ as an antisymmetrized product of one-electron wave functions, each describing a spherically symmetric electron cloud of radius 1/4 about each nucleus of distance $> 1/4$ from $\partial\Omega_*$.

From (3.19), (3.20) and convexity, we get

$$\left|\frac{\partial}{\partial\mu}F(\mu,\beta,x,R,\Omega)\right|, \quad \left|\frac{\partial}{\partial\beta}F(\mu,\beta,x,R,\Omega)\right| \leqq C(\mu,\beta,\Omega) \quad \text{for} \quad \Omega \in \Gamma. \tag{3.21}$$

The next lemma is a special application of (3.3) and Lemma 3. We fix $D \in \Gamma_0$, $\Omega \in \Gamma$, and numbers $R \gg 1$, $\sigma \ll 1$. Suppose θ is a function on R^3 satisfying $\theta(x) = 1$ in $D(0, R - \sigma)$, $\theta(x) = 0$ outside $D(0, R)$, $|\nabla\theta| \leqq C\sigma^{-1}$ everywhere. Define a kernel

$$S(x) = \frac{|x|^{-1}}{|D(0,R)|} \int_{D(0,R)} \theta(x+y)(\theta(y)-1)\,dy.$$

Place nucleii ω_k at the lattice points of $\Omega_* = \Omega(x_*, R_*)$. Then we have

Lemma 5. $\left|\sum_{j,l} S(x_j - \omega_l) - \sum_{l' \neq l} S(\omega_{l'} - \omega_l)\right| \leqq C\sigma(H_{N,\Omega_*} + CN + C|\Omega_*|)$ *on* $L^2_N(\Omega_*)$, *if* $R_* > CR$.

Proof. One computes that

$$|S(x)| \leqq \frac{C\sigma}{R|x|}\chi_{|x|<CR}, \tag{3.22}$$

$$|\nabla S(x)| \leqq \frac{C\sigma}{R|x|^2}\chi_{|x|<CR}. \tag{3.23}$$

Take functions ϕ_0, ϕ_1, η on R^3 with $\phi_0 + \phi_1 = 1$, ϕ_0 supported in $|x| < 1/4$, ϕ_1 supported in $|x| > 1/8$, $\int \eta = 1$, $\eta \geqq 0$, $\eta \in C_0^\infty(|x| \leqq 10^{-3})$. Then write

$$S = \phi_0 S + \eta * (\phi_1 S) + [\phi_1 S - \eta * (\phi_1 S)] \equiv S_1 + S_2 + S_3.$$

Estimates (3.22), (3.23) imply

$$|S_3(x)| \leqq \max_{|y-x|<10^{-3}} |\nabla(\phi_1 S)(y)| \leqq \frac{C\sigma}{R|x|^2}\chi_{1/10<|x|<CR}, \tag{3.24}$$

and

$$|\nabla(\phi_1 S)(x)| \leqq \frac{C\sigma}{R|x|^2}\chi_{1/10<|x|<CR}. \tag{3.25}$$

Now

$$\sum_{j,l} |S_1(x_j - \omega_l)| \leqq (C\sigma/R) \sum_{|x_j - \omega_l| < 1/4} |x_j - \omega_l|^{-1} \leqq (C\sigma/R)(H + CN + C|\Omega_*|) \text{ by (3.3)},$$

while $\sum_{l' \neq l} S_1(\omega_{l'} - \omega_l) = 0$. Hence

$$\left|\sum_{j,l} S_1(x_j - \omega_l) - \sum_{l' \neq l} S_1(\omega_{l'} - \omega_l)\right| \leqq \frac{C\sigma}{R}(H_{N,\Omega_*} + CN + C|\Omega_*|). \tag{3.26}$$

Next observe that

$$\sum_{j,l} S_2(x_j-\omega_l)-\sum_{l'\neq l} S_2(\omega_{l'}-\omega_l)=\sum_j \eta * \mathscr{S}(x_j)-\sum_{l'} \eta * \mathscr{S}(\omega_{l'})$$

with $\mathscr{S}(y)=\sum_l (\phi_1 S)(y-\omega_l)$; we have $|\nabla \mathscr{S}|<C\sigma$ by (3.25), and $\mathscr{S}$ is supported in the double of Ω_* since $R_*>CR$. Hence, Lemma 3 yields

$$\left|\sum_{j,l} S_2(x_j-\omega_l)-\sum_{l'\neq l} S_2(\omega_{l'}-\omega_l)\right|^2 \leqq C\sigma^2|\Omega_*|(H+CN+C|\Omega_*|),$$

and therefore

$$\left|\sum_{j,l} S_2(x_j-\omega_l)-\sum_{l'\neq l} S_2(\omega_{l'}-\omega_l)\right| \leqq C\sigma|\Omega_*|+\sigma^{-1}|\Omega_*|^{-1}.$$

$$\left[\left|\sum_{j,l} S_2(x_j-\omega_l)-\sum_{l'\neq l} S_2(\omega_{l'}-\omega_l)\right|^2\right] \leqq C'\sigma(H+C'N+C'|\Omega_*|). \tag{3.27}$$

Finally, (3.24) shows that $\sum_l |S_3(y-\omega_l)| \leqq C\sigma$ for any $y \in R^3$, so that trivially,

$$\left|\sum_{j,l} S_3(x_j-\omega_l)-\sum_{l'\neq l} S_3(\omega_{l'}-\omega_l)\right| \leqq C\sigma(N+C|\Omega_*|). \tag{3.28}$$

Since $S=S_1+S_2+S_3$, Lemma 5 follows from (3.26), (3.27), (3.28). ∎

4. A Swiss Cheese

Fix $D \in \Gamma_0$. To prove Lemma 1, we shall partition R^3 into $D(x_{k\alpha}, R_k)$ and a small residual part. See Lebowitz–Lieb [1], where such a "Swiss cheese" decomposition is used to get existence of the thermodynamic limit.

Lemma 6. *Let $1<R_1<R_2<\dots<R_M$ be radii with $R_{k+1}>2R_k$. Then any cube Q^+ of side greater than CMR_M may be decomposed into a disjoint union $Q^+=\bigcup_{k=1}^{M}\bigcup_\alpha B_{k\alpha} \cup \bigcup_\alpha Q_\alpha$ with the following properties.*

$$\text{Each } B_{k\alpha} \text{ has the form } B_{k\alpha}=D(x_{k\alpha}, R_k). \tag{4.1}$$

$$\text{Each } Q_\alpha \text{ is contained in a cube of side } 1. \tag{4.2}$$

$$\sum_\alpha |B_{k\alpha}| \leqq \frac{10}{M}|Q^+| \text{ for each } k. \tag{4.3}$$

$$\text{The number of } Q_\alpha\text{'s is at most } \frac{C}{M}|Q^+|. \tag{4.4}$$

Proof. We give an inductive procedure to construct successively the $B_{M\alpha}$, $B_{M-1\alpha}$, $B_{M-2\alpha}$, etc. We continue applying the procedure until it is impossible to continue, at which time we cut the remaining part of Q^+ into Q_α's.

Assuming we have already constructed the $B_{k\alpha}$ for all $k>j$, our inductive procedure is as follows. (Note that for $j=M$, the inductive hypothesis is fulfilled vacuously.) First cut Q^+ into a grid of cubes $\{Q_\nu\}$ of side $\sim C_1 R_j$. Here C_1 is a constant chosen so that $D(x_\nu, 2R_j) \subseteq Q$ when $x_\nu =$ centre of Q_ν. Let $J = \{\nu | Q_\nu$ meets none of the $B_{k\alpha}$ already constructed$\}$; at the centre of each Q_ν we place $B_\nu = D(x_\nu, R_j)$.

Case 1. If $\sum_{\nu \in J} |B_\nu| > 10/M|Q^+|$, then since each B_ν has volume $< |Q^+|/M$, one can pick a subset $\{B_{j\alpha}\} \subseteq \{B_\nu\}_{\nu \in J}$ so that

$$\frac{9}{M}|Q^+| < \sum_\alpha |B_{j\alpha}| < \frac{10}{M}|Q^+|. \tag{4.5}$$

Note that (4.1), (4.3) hold for $k = j$ if they held for $k > j$. Our inductive step is complete.

Case 2. If $\sum_{\nu \in J} |B_\nu| \leqq 10/M|Q^+|$, then we cut up Q^+ into a grid of unit cubes $\{Q_\nu^0\}$, and define $\{Q_\alpha\}$ to consist of the non-empty intersections of the Q_ν^0 with $Q^+ \setminus \bigcup_{k\alpha} B_{k\alpha}$. The construction of $B_{k\alpha}$'s and Q_α's is complete.

The first inequality in (4.5) shows that Case 2 must occur for some $j \geqq 1$. When it does occur, we note that the number of Q_ν^0 which meet a fixed $\partial B_{k\alpha}$ is at most $C|B_{k\alpha}|/R_k$. Hence the total number of Q_ν^0 which meet any of the $\partial B_{k\alpha}$ is at most $\sum_k CR_k^{-1}\left(\sum_\alpha |B_{k\alpha}|\right) \leqq (C|Q^+|/M) \cdot \sum_k R_k^{-1} \leqq C'/M|Q^+|$; here we used (4.3).

Similarly, for a fixed $B_{k\alpha}$, the total volume of all the Q_ν that meet $\partial B_{k\alpha}$ is at most $CR_j/R_k \cdot |B_{k\alpha}|$; hence the total volume of all the Q_ν that meet any $\partial B_{k\alpha}$ is at most

$$\sum_{k>j} \frac{CR_j}{R_k} \cdot \sum_\alpha |B_{k\alpha}| \leqq \frac{C'|Q^+|}{M} \sum_{k>j} R_j/R_k \leqq \frac{C''|Q^+|}{M}.$$

Also, since we are in Case 2, the total volume of the Q_ν which meet no $B_{k\alpha}$ is at most $C/M|Q^+|$. Consequently, $|Q^+ \setminus \bigcup_{k\alpha} B_{k\alpha}| < C/M|Q^+|$. So the total number of Q_ν^0 disjoint from all $B_{k\alpha}$ is at most $C/M|Q^+|$.

Since each Q_α is of the form $Q_\nu^0 \setminus \bigcup_{k\alpha} B_{k\alpha}$ with Q_ν^0 either disjoint from all $B_{k\alpha}$ or meeting some $\partial B_{k\alpha}$, property (4.4) is proved. The other properties, (4.1), (4.2), (4.3) are obvious from the construction. ■

Lemma 6 induces a decomposition of all R^3 into $B_{k\alpha}$'s and Q_α's. We just cut R^3 into congruent subcubes $\{Q_\nu^+\}$ of side $\sim 2CMR_M$, and cut each of the Q_ν^+ via Lemma 6. Thus, $R^3 = \bigcup_{k\alpha} B_{k\alpha} \cup \bigcup_\alpha Q_\alpha$. We can assume the decompositions of the different Q_ν^+ are all translates of one another. Also, we take the $\{Q_\nu^+\}$ to have their vertices at lattice points.

Next we introduce a partition of unity $1 = \sum_{k\alpha} \theta_{k\alpha}^2 + \sum_\alpha \theta_\alpha^2$ corresponding to the $B_{k\alpha}$ and Q_α. More precisely, with $\sigma = M^{-1/3}$, we define functions θ_k, $\theta_{k\alpha}$, θ_α on R^3 so that

$$\theta_{k\alpha}(x) = \theta_k(x - x_{k\alpha}), \quad \text{where} \quad B_{k\alpha} = D(x_{k\alpha}, R_k). \tag{4.6}$$

θ_k is constant on $\partial D(0, r)$ for each r, and θ_k is supported in $D(0, R_k)$. (4.7)

$$|\partial^\gamma \theta_k| \leqq C_\gamma \sigma^{-|\gamma|}. \tag{4.8}$$

$$\operatorname{Supp} \theta_\alpha \subseteqq \tilde{Q}_\alpha = \{x \mid \operatorname{dist}(x, Q_\alpha) < \sigma\}. \tag{4.9}$$

$$|\partial^\gamma \theta_\alpha| \leqq C_\gamma \sigma^{-|\alpha|}. \tag{4.10}$$

$$\sum_{k\alpha} \theta_{k\alpha}^2 + \sum_\alpha \theta_\alpha^2 = 1. \tag{4.11}$$

It is easy to define these; first construct θ_k so that (4.7), (4.8) hold and $(1-\theta_k^2)^{1/2}$ satisfies estimates analogous to (4.8); next define $\theta_{k\alpha}$ by (4.6); and finally construct the θ_α.

Note that $\theta_{k\alpha}(x) = 1$ for $x \in B_{k\alpha}$, $\operatorname{dist}(x, \partial B_{k\alpha}) > \sigma$.

For a vector $\tau \in R^3$, we can obviously translate the $B_{k\alpha}$, Q_α, $\theta_{k\alpha}$, θ_α by τ. Later on, it will be important to do this and then average our estimates over all $\tau \in Q^+ =$ one of the fundamental cubes $\{Q_\nu^+\}$. In particular, we shall need the following identities.

$$\operatorname{Av}_{\tau \in Q^+} \sum_{B_{k\alpha}} \theta_{k\alpha}^2(x-\tau)\theta_{k\alpha}^2(x'-\tau) = \sum_k \lambda_k(\theta_k^2 * \tilde{\theta}_k^2)(x-x'), \tag{4.12}$$

$$\operatorname{Av}_{\tau \in Q^+} \sum_{B_{k\alpha}} \theta_{k\alpha}^2(x-\tau)\chi_{B_{k\alpha}}(y'-\tau) = \sum_k \lambda_k(\theta_k^2 * \tilde{\chi}_{D(0,R_k)})(x-y), \tag{4.13}$$

$$\operatorname{Av}_{\tau \in Q^+} \sum_{B_{k\alpha}} \chi_{B_{k\alpha}}(y-\tau)\chi_{B_{k\alpha}}(y'-\tau) = \sum_k \lambda_k(\chi_{D(0,R_k)} * \tilde{\chi}_{D(0,R_k)})(y-y'), \tag{4.14}$$

where

$$\lambda_k = |Q^+|^{-1} \cdot [\text{Number of } x_{k\alpha} \in Q^+], \tag{4.15}$$

and $\tilde{\theta}(x) \equiv \theta(-x)$ for any function θ on R^3.

To prove (4.12), (4.13), (4.14), let B^0 be the set of $x_{k\alpha}$ in Q^+, and fix a lattice Λ^+ in R^3 so that the fundamental cubes Q_ν^+ are precisely the translates of Q^+ by vectors in Λ^+. Note that each $x_{k\alpha}$ can be written uniquely as $x_{k\alpha} \equiv x_{k\alpha'} + \omega$ with $x_{k\alpha'} \in B^0$ and $\omega \in \Lambda^+$. Now we can write

$$\begin{aligned}
&\operatorname{Av}_{\tau \in Q^+} \sum_{B_{k\alpha}} \theta_{k\alpha}^2(x-\tau)\theta_{k\alpha}^2(x'-\tau) \\
&= |Q^+|^{-1} \int_{\tau \in Q^+} \sum_{k\alpha} \theta_k^2(x-\tau-x_{k\alpha})\theta_k^2(x'-\tau-x_{k\alpha})\,d\tau \\
&= |Q^+|^{-1} \sum_{x_{k\alpha'} \in \mathscr{B}^0} \sum_{\omega \in \Lambda^+} \int_{\tau \in Q^+} \theta_k^2(x-\tau-\omega-x_{k\alpha'})\theta_k^2(x'-\tau-\omega-x_{k\alpha'})\,d\tau \\
&= |Q^+|^{-1} \sum_{x_{k\alpha'} \in \mathscr{B}^0} \int_{\xi \in R^3} \theta_k^2(x-\xi)\theta_k^2(x'-\xi)\,d\xi
\end{aligned}$$

(write $\xi = x_{k\alpha'} + \tau + \omega$ with $\tau \in Q^+$, $\omega \in \Lambda^+$). This proves (4.12). The proofs of (4.13) and (4.14) are similar.

Finally, with

$$\bar{\lambda}_k = \lambda_k |D(0,R_k)|, \quad \text{we obtain,} \tag{4.16}$$

$$0 \leqq \bar{\lambda}_k \leqq \frac{10}{M}, \tag{4.17}$$

$$1 \geqq \sum_{k=1}^M \bar{\lambda}_k \geqq 1 - \frac{C}{M}, \quad \text{by (4.3), (4.4), (4.15).} \tag{4.18}$$

In terms of the $\bar{\lambda}_k$, identities (4.12), (4.13), (4.14) become

$$\mathrm{Av}_{\tau\in Q^+}\sum_{B_{k\alpha}}\theta_{k\alpha}^2(x-\tau)\theta_{k\alpha}^2(x'-\tau)=\sum_k\bar{\lambda}_k\frac{\theta_k^2*\tilde{\theta}_k^2}{|D|R_k^3}(x-x'), \tag{4.19}$$

$$\mathrm{Av}_{\tau\in Q^+}\sum_{B_{k\alpha}}\chi_{B_{k\alpha}}(x-\tau)\chi_{B_{k\alpha}}(x'-\tau)=\sum_k\bar{\lambda}_k\frac{\theta_k^2*\tilde{\chi}_{D(0,R_k)}(x-y)}{|D|R_k^3}, \tag{4.20}$$

$$\mathrm{Av}_{\tau\in Q^+}\sum_{B_{k\alpha}}\chi_{B_{k\alpha}}(y-\tau)\chi_{B_{k\alpha}}(y'-\tau)=\sum_k\bar{\lambda}_k\frac{\chi_{D(0,R_k)}*\tilde{\chi}_{D(0,R_k)}(y-y')}{|D|R_k^3}. \tag{4.21}$$

5. An Exploded System

Fix a cube $Q^+=$ one of the Q_ν^+ from the last section, and let $\Omega_*=\Omega(x_*,R_*)$ with $\Omega\in\Gamma$ and $R_*\geqq CM^2R_M$. Let $\mathscr{B}=\{B=B_{k\alpha}$ or $\tilde{Q}_\alpha|B+\tau$ meets Ω_* for some $\tau\in Q^+\}$. To each $B\in\mathscr{B}$ we can associate a vector $\xi_B\in Z^3$ so that the translates $B+\xi_B$ $(B\in\mathscr{B})$ are pairwise disjoint. The ξ_B may grow large, but we do not care.

Now for each fixed $\tau\in Q^+$ we define a simplified statistical mechanics problem, in which Coulomb interactions between the translates $B+\tau$ $(B\in\mathscr{B})$ are turned off. More precisely, set $\hat{B}=B+\xi_B+\tau$ for $B\in\mathscr{B}$, and define the exploded set $\Omega_{\mathrm{ex}}=\bigcup_{B\in\mathscr{B}}\hat{B}$. Define

$$K_{\mathrm{ex}}(y,z)=\begin{pmatrix}|y-z|^{-1} & \text{if } y,z\in\hat{B}_{k\alpha} \text{ for some } B_{k\alpha}\in\mathscr{B}\\ 0 & \text{otherwise.}\end{pmatrix}$$

In particular, $K_{\mathrm{ex}}(y,z)=0$ if y and z belong to different components of Ω_{ex}, or if y,z both belong to $\hat{B}$ with $B=\tilde{Q}_\alpha$.

Next we place nucleii in Ω_{ex}. In each $\hat{B}_{k\alpha}\subset\Omega_{\mathrm{ex}}$ we place a nucleus at each lattice point $\omega\in\hat{B}_{k\alpha}\cap(\Omega_*+\xi_{B_{k\alpha}})$. In the $\tilde{Q}_\alpha$ we place no nucleii. Note that $\tilde{B}_{k\alpha}$ has a nucleus at each lattice point, unless $B_{k\alpha}+\tau$ intersects the complement of Ω_*. Let $\hat{y}_1\dots\hat{y}_{N'}$ be the nucleii in Ω_{ex}.

Now for N electrons $x_1\dots x_N\in\Omega_{\mathrm{ex}}$ we define a Hamiltonian H_N^{ex} on $L_N^2(\Omega_{\mathrm{ex}})$ by setting

$$H_N^{\mathrm{ex}}=-\Delta_x+\sum_{j<k}K_{\mathrm{ex}}(x_j,x_k)+\sum_{j<k}K_{\mathrm{ex}}(\hat{y}_j,\hat{y}_k)-\sum_{j,k}K_{\mathrm{ex}}(x_j,\hat{y}_k)$$

with Dirichlet boundary conditions. Note that the above constructions are not isomorphic for different τ, because nucleii were placed at lattice points of $B_{k\alpha}+\xi_{B_{k\alpha}}+\tau$.

Since the different components of Ω_{ex} act independently in H_N^{ex}, we have for the partition functions

$$\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta H_N^{\mathrm{ex}}}=\prod_{B\in\mathscr{B}}\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta h_{N,B}}\right) \tag{5.1}$$

for suitable Hamiltonians $h_{N,B}$ acting on $L_N^2(\hat{B})$. If $B=B_{k\alpha}\in\mathscr{B}$ and $(\mathscr{B}+\tau)\cap{}^c\Omega_*=\emptyset$, then $h_{N,B}$ is isomorphic to $H_{N,B+\tau}$, so that $\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta h_{N,B}}\right)=$

$|B_{k\alpha}|\cdot F(\mu,\beta,x_{k\alpha}+\tau,R_k,D)$, since $B_{k\alpha}=D(x_{k\alpha},R_k)$. If $B=B_{k\alpha}\in\mathscr{B}$, but $(B+\tau)\cap{}^c\Omega_*\neq\emptyset$, then in any event $\left|\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta h_{N,B}}\right)\right|\leqq C|B_k|$ by (3.19), (3.20). Note also that $|F(\mu,\beta,x_{k\alpha}+\tau,R_k,D)|\leqq C$, again by (3.19), (3.20). Finally, if $B=\tilde{Q}_\alpha$, then $h_{N,B}$ is the Hamiltonian for N free particles in B. Since B is contained in a cube of side 2, we have $\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta h_{N,B}}\right)\leqq C$ for $B=\tilde{Q}_\alpha$, since the partition function is monotone in the domain. Putting these remarks into (5.1), we find that

$$\begin{aligned}\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta H_N^{\mathrm{ex}}}\right)&=\sum_{B_{k\alpha}\in\mathscr{B}}|B_{k\alpha}|F(\mu,\beta,x_{k\alpha}+\tau,R_k,D)\\&\quad+\sum_{B_{k\alpha}\in\mathscr{B};(B_{k\alpha}+\tau)\cap{}^c\Omega_*\neq\emptyset}\left\{\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-h_{N,B}}\right)\right.\\&\quad\left.-|B_{k\alpha}|F(\mu,\beta,x_{k\alpha}+\tau,R_k,D)\right\}\\&\quad+\sum_{B=\tilde{Q}_{k\alpha}\in\mathscr{B}}\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta h_{N,B}}\right)\\&\leqq\sum_{B_{k\alpha}\in\mathscr{B}}|B_{k\alpha}|\cdot F(\mu,\beta,x_{k\alpha}+\tau,R_k,D)\\&\quad+C\sum_{B_{k\alpha}\in\mathscr{B}'}|B_{k\alpha}|+C\cdot[\text{Number of }\tilde{Q}_\alpha\in\mathscr{B}],\\&\quad\text{where }\mathscr{B}'=\{B_{k\alpha}\in\mathscr{B}\,|\,(B_{k\alpha}+\tau)\cap{}^c\Omega_*\neq\emptyset\}.\end{aligned}\tag{5.2}$$

Now each $B_{k\alpha}\in\mathscr{B}'$ is contained in $E=\{x\,|\,\operatorname{dist}(x+\tau,\partial\Omega_*)<2\operatorname{diam}Q^+\}$, since $B_{k\alpha}\subseteqq$ some Q_ν^+ so that $\operatorname{diam}B_{k\alpha}\leqq\operatorname{diam}Q_\nu^+$. Since $\operatorname{diam}Q^+\sim CMR_M$, while $\Omega_*=\Omega(x_*,R_*)$ with $R_*>CM^2R_M$, it follows that E has volume $<(C/M)|\Omega_*|$. Hence, $\sum_{B_{k\alpha}\in\mathscr{B}'}|B_{k\alpha}|<(C/M)|\Omega_*|$. Also, the number of $\tilde{Q}_\alpha\in\mathscr{B}$ is at most $(C/M)|\Omega_*|$ by virtue of (4.4). Hence we can rewrite (5.2) in the form

$$\ln\left(\sum_N e^{\mu N}\operatorname{Tr}e^{-\beta H_N^{\mathrm{ex}}}\right)\leqq\sum_{B_{k\alpha}\in\mathscr{B}}|B_{k\alpha}|F(\mu,\beta,x_{k\alpha}+\tau,R_k,D)+\frac{C}{M}|\Omega_*|.\tag{5.3}$$

Recall that the left-hand side depends on τ.

6. An Injection of Hilbert Spaces

We hope to exploit (5.3) by comparing the partition functions for H_N^{ex} and H_{N,Ω_*}. Since these Hamiltonians live on different Hilbert spaces, it is natural to inject $L_*^2(\Omega_*)$ into $L_*^2(\Omega_{\mathrm{ex}})$ by an isometry i and then quote the following remark.

Lemma 7. *Let $i:E_1\to E_2$ be an isometric injection of Hilbert spaces, and let H_2 be a self-adjoint operator on E_2. Define $H_1=i^*H_2i$ on E_i. Then* $\operatorname{Tr}e^{-\beta H_1}\leqq\operatorname{Tr}e^{-\beta H_2}$.

The proof is immediate by minimax.

Note that $L^2_N(\Omega_*)$ would be isomorphic to $L^2_N(\Omega_{ex})$, were it not for the slight overlaps of the $\tilde{Q}_\alpha \in \mathscr{B}$ with the $B_{k\alpha} \in \mathscr{B}$ and one another. This section is just a careful discussion of the technicalities arising from the overlaps.

To prepare for the definition of i, we introduce more notation, namely

$$\theta_B = \begin{pmatrix} \theta_{k\alpha} & \text{if } B = B_{k\alpha} \\ \theta_\alpha & \text{if } B = \tilde{Q}_\alpha \end{pmatrix}.$$

Thus, θ_B is supported in B, and $\sum_{B \in \mathscr{B}} \theta_B^2(x-\tau) = 1$ for $x \in \Omega_*$. Now let $\psi(x_1 \dots x_N) \in L^2_N(\Omega_*)$. We shall define $i\psi$ as a function in $L^2_N(\Omega_{ex})$. To do so, we must specify the value of $i\psi$ at a point $(y_1 \dots y_N) \in \Omega^N_{ex}$. Each y_k belongs to a single $\hat{B}_k$, so we can write $y_k = x_k + \xi_{B_k}$ with $x_k \in B_k + \tau$. We define

$$(i_N\psi)(y_1 \dots y_N) = \left(\prod_{k=1}^{N} \theta_{B_k}(x_k - \tau) \right) \cdot \psi(x_1 \dots x_N).$$

Here one interprets $\psi(x_1 \dots x_N) = 0$ if any of $x_1 \dots x_N$ lie outside of Ω.

One checks easily that i_N injects $L^2_N(\Omega_*)$ isometrically into $L^2_N(\Omega_{ex})$. In particular, $i_N\psi$ is antisymmetric if ψ is antisymmetric. Also if ψ has one derivative in $L^2(\Omega^N_*)$ and vanishes on $\partial(\Omega^N_*)$, then $i_N\psi$ will have one derivative in $L^2(\Omega^N_{ex})$ and vanish on $\partial(\Omega^N_{ex})$. This is because of the factors $\theta_B \in C^\infty_0(B)$ in $i_N\psi$. So i_N preserves Dirichlet boundary conditions. Define i as the direct sum of the i_N, $N \geqq 0$.

Lemma 7 and (5.3) now yield

$$\ln\left(\sum_N e^{\mu N} \operatorname{Tr} e^{-\beta h_{N,\tau}} \right) \leqq \sum_{B_{k\alpha} \in \mathscr{B}} |B_{k\alpha}| \cdot F(\mu, \beta, x_{k\alpha} + \tau, R_k, D) + \frac{C}{M} |\Omega_*| \tag{6.1}$$

for an auxiliary Hamiltonian $h_{N,\tau} = i^*_N H^{ex}_N i_N$ defined on $L^2_N(\Omega_*)$.

7. Calculation of the Auxiliary Hamiltonian

First we recall the definition of H^{ex}_N. We have

$$H^{ex}_N = \sum_{B \in \mathscr{B}} h_{N,B}, \quad \text{where } h_{N,B} \text{ acting on } \phi(y_1 \dots y_N) \tag{7.1}$$

is given by

$$\begin{aligned} h_{N,B} = & -\sum_k \chi_{\hat{B}}(y_k) \Delta_{y_k} + \sum_{j<k} |y_j - y_k|^{-1} \chi_{\hat{B}}(y_j) \chi_{\hat{B}}(y_k) \\ & + \sum_{j<k} |\hat{y}_j - \hat{y}_k|^{-1} \chi_{\hat{B}}(\hat{y}_j) \chi_{\hat{B}}(\hat{y}_k) \\ & - \sum_{j,k} |y_j - \hat{y}_k|^{-1} \chi_{\hat{B}}(y_j) \chi_{\hat{B}}(\hat{y}_k), \quad B = B_{k\alpha} \in \mathscr{B}, \end{aligned} \tag{7.2}$$

$$h_{N,B} = -\sum_k \chi_{\hat{B}}(y_k) \Delta_{y_k}, \quad B = \tilde{Q}_\alpha \in \mathscr{B}. \tag{7.3}$$

Recall that $\hat{y}_1 \dots \hat{y}_N$, are the nucleii in Ω_{ex}. The $h_{N,B}$ of (7.2), (7.3) are essentially the same as $h_{N,B}$ in (5.1).

By (7.1), we have

$$\begin{aligned}\langle h_{N,\tau}\psi,\psi\rangle &= \langle H_N^{\mathrm{ex}} i\psi, i\psi\rangle = \sum_{B_1\dots B_N\in\mathscr{B}} \langle H_N^{\mathrm{ex}} i\psi, i\psi\rangle_{L^2(\hat{B}_1\times\cdots\times\hat{B}_N)} \\ &= \sum_{B,B_1\dots B_N\in\mathscr{B}} \langle h_{N,B} i\psi, i\psi\rangle_{L^2(\hat{B}_1\times\cdots\times\hat{B}_N)}\end{aligned} \tag{7.4}$$

On $\hat{B}_1\times\cdots\times\hat{B}_N$ we apply (7.2), (7.3) to $\phi(y_1\dots y_N)=i\psi(y_1\dots y_N) = \left(\prod_{l=1}^N \theta_{B_l}(x_l-\tau)\right)\cdot\psi(x_1\dots x_N)$ with $y_l=x_l+\xi_{B_l}$. To evaluate the characteristic functions, note that $\chi_{\hat{B}}(y_l)=\begin{pmatrix}\chi_B(x_l-\tau) & \text{if } B=B_l \\ 0 & \text{otherwise}\end{pmatrix}$ for $(y_1\dots y_N)\in\hat{B}_1\times\cdots\times\hat{B}_N$. Also, the $\hat{y}_k\in\hat{B}$ are precisely the points $\omega+\xi_B$ for $\omega\in Z^3\cap\Omega_*\cap(B+\tau)$, if $B=B_{k\alpha}\in\mathscr{B}$. There are $\hat{y}_k\in\hat{B}$ if $B=\hat{Q}_\alpha\in\mathscr{B}$.

Consequently, the result of putting $\phi=i_N\psi$ in (7.2), (7.3) and then substituting into (7.4) is as follows

$$\begin{aligned}\langle h_{N,\tau}\psi,\psi\rangle &= \sum_{B_1\dots B_N\in\mathscr{B}} \left\| \nabla\left[\prod_{k=1}^N \theta_{B_k}(x_k-\tau)\cdot\psi(x_1\dots x_N)\right]\right\|^2_{L^2(R^{3N})} \\ &\quad + \sum_{B=B_{k\alpha}}\sum_{B_1\dots B_N\in\mathscr{B}} \int \prod_{l=1}^N \theta^2_{B_l}(x_l-\tau)\cdot\frac{1}{2}\sum_{j\neq j'}|x_j-x_{j'}|^{-1} \\ &\quad \times \chi_{B_j=B}\chi_{B_{j'}=B}|\psi(x_1\dots x_N)|^2\,dx_1\cdots dx_N \\ &\quad - \sum_{B=B_{k\alpha}}\sum_{B_1\dots B_N\in\mathscr{B}}\sum_{\omega\in\Omega_*\cap Z^3}\int\prod_{l=1}^N\theta^2_{B_l}(x_l-\tau) \\ &\quad \cdot\sum_j|x_j-\omega|^{-1}\chi_{B_j=B}\chi_{B+\tau}(\omega)|\psi(x_1\dots x_N)|^2\,dx_1\dots dx_N \\ &\quad + \sum_{B=B_{k\alpha}}\sum_{B_1\dots B_N\in\mathscr{B}}\int\prod_{l=1}^N\theta^2_{B_l}(x_l-\tau)\cdot\frac{1}{2}\sum_{\substack{\omega\neq\omega' \\ \omega\omega'\in Z^3\cap\Omega_*}}|\omega-\omega'|^{-1} \\ &\quad \cdot\chi_{B+\tau}(\omega)\chi_{B+\tau}(\omega')|\psi(x_1\dots x_N)|^2\,dx_1\dots dx_N \\ &\equiv T+V_1-V_2+V_3.\end{aligned} \tag{7.5}$$

Mercifully, the expressions on the right can be greatly simplified. Let us start with the V's.

Taking the sum over j,j' to the outside in the definition of V_1, we can carry out the inner sum over all the $B_1\dots B_N$ except $B_j, B_{j'}$. Recalling that $\sum_{B\in\mathscr{B}}\theta^2_B(x-\tau)=1$ for $x\in\Omega_*$, we obtain

$$\begin{aligned}V_1 &= \frac{1}{2}\sum_{j\neq j'}\int\sum_{B_{k\alpha}\in\mathscr{B}}\theta^2_{B_{k\alpha}}(x_j-\tau)\theta^2_{B_{k\alpha}}(x_{j'}-\tau)|x_j-x_{j'}|^{-1} \\ &\quad \cdot|\psi(x_1\dots x_N)|^2\,dx_1\dots dx_N \\ &= \left\langle\frac{1}{2}\sum_{j\neq j'}K^\tau_{ee}(x_j,x_{j'})\psi,\psi\right\rangle, \quad \text{with}\end{aligned} \tag{7.6}$$

$$K_{ee}^{\tau}(x,x') = \sum_{B_{k\alpha}\in\mathscr{B}} \theta_{k\alpha}^2(x-\tau)\theta_{k\alpha}^2(x'-\tau)\cdot|x-x'|^{-1}. \tag{7.7}$$

Similarly, in the definition of V_2, we can take the sum on j and ω to the outside, and then perform the inner sum over all the $B_1 \ldots B_N$ except B_j. The result is

$$V_2 = \sum_j \sum_{\omega\in Z^3\cap\Omega_*} \int \sum_{B_{k\alpha}\in\mathscr{B}} \theta_{B_{k\alpha}}^2(x_j-\tau)\chi_{B_{k\alpha}}(\omega-\tau)|x_j-\omega|^{-1}$$
$$\cdot|\psi(x_1\ldots x_N)|^2\,dx_1\ldots dx_N$$
$$= \left\langle \sum_j \sum_{\omega\in Z^3\cap\Omega_*} K_{ep}^{\tau}(x_j,\omega)\psi,\psi \right\rangle, \quad \text{with} \tag{7.8}$$

$$K_{ep}^{\tau}(x,\omega) = \sum_{B_{k\alpha}\in\mathscr{B}} \theta_{k\alpha}^2(x-\tau)\chi_{B_{k\alpha}}(\omega-\tau)\cdot|x-\omega|^{-1}. \tag{7.9}$$

The term V_3 is the simplest of all, since we can immediately carry out the sum over all the $B_1 \ldots B_N$ to obtain

$$V_3 = \left\langle \frac{1}{2} \sum_{\substack{\omega\neq\omega \\ \omega,\omega'\in Z^3\cap\Omega_*}} K_{pp}^{\tau}(\omega,\omega')\psi,\psi \right\rangle, \quad \text{with} \tag{7.10}$$

$$K_{pp}^{\tau}(\omega,\omega') = \sum_{B_{k\alpha}\in\mathscr{B}} \chi_{B_{k\alpha}}(\omega-\tau)\chi_{B_{k\alpha}}(\omega'-\tau)\cdot|\omega-\omega'|^{-1}. \tag{7.11}$$

Next we simplify T, using the elementary identity $\|\nabla(\theta\psi)\|^2 = \|\theta\nabla\psi\|^2 - \langle(\theta\Delta\theta)\psi,\psi\rangle$ for functions $\psi\in C'(R^3)$, $\theta\in C_0^\infty(R^3)$, θ real. The identity follows trivially from integration by parts. Substituting it into the definition of T yields

$$T = \sum_{B_1\ldots B_N\in\mathscr{B}} \left\| \prod_{k=1}^{N} \chi_{B_k}(x_k-\tau)\cdot\nabla(x_1\ldots x_N) \right\|_{L^2(R^{3N})}^2$$
$$-\sum_k \sum_{B_1\ldots B_N\in\mathscr{B}} \left\langle \prod_{l\neq k} \theta_{B_l}^2(x_l-\tau)\cdot\theta_{B_k}\Delta\theta_{B_k}(x_k-\tau)\psi,\psi \right\rangle.$$

In the first term on the right, we can sum over all the $B_1 \ldots B_N$, while in the second term, we can sum over the B_l for $l \neq k$. The result is

$$T = \|\nabla\psi\|^2 - \left\langle \sum_k G(x_k-\tau)\psi,\psi \right\rangle, \quad \text{with} \tag{7.12}$$
$$G = \sum_{B\in\mathscr{B}} \theta_B \Delta \theta_B. \tag{7.13}$$

Now we can substitute (7.6), (7.8), (7.10), (7.12) into (7.5) to obtain

$$h_{N,\tau} = -\Delta + V_{N,\tau}, \quad \text{with} \tag{7.14}$$

$$V_{N,\tau} = \frac{1}{2}\sum_{j\neq k} K_{ee}^{\tau}(x_j,x_k) + \frac{1}{2}\sum_{j\neq k} K_{pp}^{\tau}(\omega_j,\omega_k)$$
$$-\sum_{j,k} K_{ep}^{\tau}(x_j,\omega_k) - \sum_i G(x_j-\tau). \tag{7.15}$$

Here the ω_k denote the lattice points in Ω_*, and K_{ee}^{τ}, K_{ep}^{τ}, K_{pp}^{τ}, G are given by (7.7), (7.9), (7.11), (7.13). Note that the sums in these formulas can be extended from $B\in\mathscr{B}$ to all $B = B_{k\alpha}$ in the Swiss cheese; for, the new terms all vanish. The operator (7.14) acts on $L_N^2(\Omega_*)$ with Dirichlet boundary conditions.

8. Averaging over Translates

So far, we know estimate (6.1) for a Hamiltonian $h_{N,\tau}$ which somewhat resembles the desired H_{N,Ω_*} by virtue of (7.14), (7.15). We can improve the resemblance by averaging over $\tau \in Q^+$. Since $\ln \operatorname{Tr} e^{-\beta H}$ is a convex function of a self-adjoint operator H, (6.1) implies

$$\ln \sum_N e^{\mu N} \operatorname{Tr} e^{-\beta h_N} \leqq \operatorname{Av}_{\tau \in Q^+} \sum_{B_{k\alpha} \in \mathscr{B}} |B_{k\alpha}| F(\mu, \beta, x_{k\alpha} + \tau, R_k, D) + \frac{C}{M} |\Omega_*|, \tag{8.1}$$

where $h_N = \operatorname{Av}_{\tau \in Q^+} h_{N,\tau}$. Since $x \to F(\mu, \beta, x, R_k, D)$ is periodic with period lattice Z^3, while Q^+ is a large cube with its vertices at lattice points, the right-hand side of (8.1) may be rewritten as

$$\sum_{B_{k\alpha} \in \mathscr{B}} |B_{k\alpha}| \operatorname{Av}_{x \in Q^0} F(\mu, \beta, x, R_k, D) + \frac{C}{M} |\Omega_*|, \quad Q^0 = \text{unit cube}. \tag{8.2}$$

From the definition of $\mathscr{B}$ we have

$$\sum_{B_{k\alpha} \in \mathscr{B}} |B_{k\alpha}| \leqq \operatorname{vol}\{x \in R^3 \,|\, \operatorname{dist}(x, \Omega_*) < \operatorname{diam} Q^+\} \leqq \left(1 + \frac{C}{M}\right) |\Omega_*|,$$

since $\operatorname{diam} Q^+ \sim CMR_M$ while $\Omega_* = \Omega(x_*, R_*)$ with $R_* > CM^2 R_M$. Hence, expression (8.2) is dominated by $|\Omega_*| \cdot (1 + C/M) \cdot \max_{1 \leqq k \leqq M} [\operatorname{Av}_{x \in Q^0} F(\mu, \beta, x, R_k, D)] + C/M |\Omega_*|$. Since we already know that $F(\mu, \beta, x, R_k, D) \leqq C$ by (3.19), it follows that

$$|\Omega_*|^{-1} \ln \sum_N e^{\mu N} \operatorname{Tr} e^{-\beta h_N} \leqq \max_{1 \leqq k \leqq M} [\operatorname{Av}_{x \in Q^0} F(\mu, \beta, x, R_k, D)] + \frac{C}{M}. \tag{8.3}$$

Now

$$h_N = -\Delta + V_N, \quad \text{where } V_N = \operatorname{Av}_{\tau \in Q^+} V_{N,\tau} \tag{8.4}$$

with $V_{N,\tau}$ given by (7.15). To compute the τ-averages of the various terms in (7.15), we use (7.7) and (4.19), (7.9) and (4.20); and (7.11) and (4.21). The result is

$$V_N = \frac{1}{2} \sum_{j \neq k} \tilde{K}_{ee}(x_j - x_k) + \frac{1}{2} \sum_{j \neq k} \tilde{K}_{pp}(\omega_j - \omega_k) - \sum_{j,k} \tilde{K}_{ep}(x_j - \omega_k) - \sum_j \bar{G}(x_j), \tag{8.5}$$

where the ω_k are the lattice points in Ω_*, and

$$\tilde{K}_{ee}(x) = |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k \frac{\theta_k^2 * \tilde{\theta}_k^2(x)}{R_k^3 |D|}, \tag{8.6}$$

$$\tilde{K}_{ep}(x) = |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k \frac{\theta_k^2 * \tilde{\chi}_{D(0,R_k)}(x)}{R_k^3 |D|}, \tag{8.7}$$

$$\tilde{K}_{pp}(x) = |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k \frac{\chi_{D(0,R_k)} * \tilde{\chi}_{D(0,R_k)}(x)}{R_k^3 |D|}, \tag{8.8}$$

$$\bar{G}(x) = \operatorname{Av}_{\tau \in Q^+} \sum_{B \in \mathscr{B}} \theta_B \Delta \theta_B(x - \tau). \tag{8.9}$$

Note that (4.19), (4.20), (4.21) apply here because the restriction to $B\in\mathscr{B}$ in (7.7), (7.9), (7.11) is irrelevant. $\bar{G}$ is a constant, but we won't need to check that. Instead it is enough to note that

$$|\theta_B \Delta\theta_B(x)| \leqq C\sigma^{-2}\chi_{\mathrm{dist}(x,\partial B)<\sigma} \qquad \text{if } B = B_{k\alpha},$$
$$|\theta_B \Delta\theta_B(x)| \leqq C\sigma^{-2}\chi_{\tilde{Q}_\alpha} \qquad \text{if } B = \tilde{Q}_\alpha.$$

These estimates are immediate from (4.6)–(4.11) and the remarks immediately following. Integrating, we get

$$\int_{\tau\in Q^+} \sum_{B\in\mathscr{B}} |\theta_B \Delta\theta_B(x-\tau)|\,d\tau \leqq C\sigma^{-2}\cdot \sum_{k=1}^{M} \frac{C\sigma}{R_k} \sum_{B_{k\alpha}\cap(x-Q^+)\neq\emptyset} |B_{k\alpha}|$$
$$+ C\sigma^{-2}\cdot \sum_{\tilde{Q}_\alpha\cap(x-Q^+)\neq\emptyset} |\tilde{Q}_\alpha| \leqq \frac{C\sigma^{-2}|Q^+|}{M} \quad \text{by Lemma 6.}$$

Since we took $\sigma = M^{-1/3}$, we have

$$|\bar{G}(x) \leqq CM^{-1/3} \quad \text{for all } x\in R^3. \tag{8.10}$$

9. Proof of Lemma 1

The idea is to prove

$$h_N \leqq (1+C\varepsilon)H_{N,\Omega*} + C'\varepsilon N + C'\varepsilon|\Omega_*| \tag{9.1}$$

if $R_1\dots R_M$ and R_* are as in the statement of Lemma 1. Once we have this, (8.3) yields

$$\max_{1\leqq k\leqq N} [\mathrm{Av}_{x\in Q^0} F(\mu,\beta,x,R_k,D)] + \frac{C}{M}$$
$$\geqq |\Omega_*|^{-1} \ln\left[e^{-C'\beta\varepsilon|\Omega_*|}\sum_N e^{(\mu - C'\beta\varepsilon)N}\,\mathrm{Tr}\, e^{-\beta(1+C\varepsilon)H_{N,\Omega_*}}\right]$$
$$= -C'\beta\varepsilon + F(\mu - C'\beta\varepsilon, \beta(1+C\varepsilon), x_*, R_*, \Omega). \tag{9.2}$$

The right hand side is $\geqq F(\mu,\beta,x_*,R_*,\Omega) - C''\varepsilon$ by (3.21). Here, C'' depends on μ, β, Ω, D but not on x_*, R_*, $R_1\dots R_M$ or ε. Thus (9.2) implies

$$\max_{1\leqq k\leqq M} [\mathrm{Av}_{x\in Q^0} F(\mu,\beta,x,R_k,D)] + \left(\frac{C}{M} + C''\varepsilon\right) \geqq F(\mu,\beta,x_*,R_*,\Omega).$$

Since $M > C\varepsilon^{-10}$, Lemma 1 follows easily. So our problem is to prove (9.1).

Formulas (8.4), (8.5), (8.10) reduce (9.1) to the estimate

$$W_1 \leqq C\varepsilon H_{N,\Omega*} + C'\varepsilon N + C'\varepsilon|\Omega_*|, \tag{9.3}$$

with

$$W_1 = \frac{1}{2}\sum_{j\neq k} K_{ee}(x_j - x_k) + \frac{1}{2}\sum_{j\neq k} K_{pp}(\omega_j - \omega_k) - \sum_{j,k} K_{ep}(x_j - \omega_k), \tag{9.4}$$

$$K_{ee}(x) = -|x|^{-1} + |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k \frac{\theta_k^2 * \tilde{\theta}_k^2(x)}{R_k^3 |D|}, \tag{9.5}$$

$$K_{ep}(x) = -|x|^{-1} + |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k \frac{\theta_k^2 * \tilde{\chi}_{D(0,R_k)}(x)}{R_k^3 |D|}, \tag{9.6}$$

$$K_{pp}(x) = -|x|^{-1} + |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k \frac{\chi_{D(0,R_k)} * \tilde{\chi}_{D(0,R_k)}(x)}{R_k^3 |D|}. \tag{9.7}$$

To prove (9.3), we first correct W_1 so that electron–electron, electron–proton, and proton–proton all interact with the same potential. We write

$$W_1 = W_2 + W_3 + W_4 \quad \text{with} \tag{9.8}$$

$$W_2 = V[K_{ee}], \tag{9.9}$$

$$W_3 = \sum_{j,k} (K_{ee} - K_{ep})(x_j - \omega_k) - \sum_{j \neq k} (K_{ee} - K_{ep})(\omega_j - \omega_k), \tag{9.10}$$

$$W_4 = \sum_{j \neq k} (\tfrac{1}{2} K_{ee} + \tfrac{1}{2} K_{pp} - K_{ep})(\omega_j - \omega_k). \tag{9.11}$$

Now

$$(K_{ee} - K_{ep})(x) = |x|^{-1} \sum_{k=1}^{M} \bar{\lambda}_k (\theta_k^2 * [\tilde{\theta}_k^2 - \tilde{\chi}_{D(0,R_k)}](x)/R_k^3 |D|).$$

Since $\sum_k \bar{\lambda}_k \leqq 1$, we can prove that

$$W_3 \leqq C\sigma(H_{N,\Omega_*} + CN + C|\Omega_*|), \tag{9.12}$$

simply by quoting Lemma 5 with $\theta = \theta_k^2$, $R = R_k$ and summing against $\bar{\lambda}_k$. Also,

$$(\tfrac{1}{2} K_{ee} + \tfrac{1}{2} K_{pp} - K_{ep})(x) = \frac{1}{2} \sum_{k=1}^{M} \bar{\lambda}_k \frac{[\theta_k^2 - \chi_{D(0,R_k)}] * [\tilde{\theta}_k^2 - \tilde{\chi}_{D(0,R_k)}]}{|D| R_k^2} \cdot |x|^{-1}$$

$$+ [\text{Odd function of } x].$$

The odd function cancels when substituted into $\sum_{j \neq k} (\tfrac{1}{2} K_{ee} + \tfrac{1}{2} K_{pp} - K_{ep})(\omega_j - \omega_k)$. One checks that

$$\left| \frac{[\theta_k^2 - \chi_{D(0,R_k)}] * [\tilde{\theta}_k^2 - \tilde{\chi}_{D(0,R_k)}]}{R_k^3 |D|} \right| \leqq \frac{C\sigma^2}{R_k |x|} \chi_{|x| < CR_k}.$$

(Just use $|\tilde{\theta}_k^2 - \tilde{\chi}_{D(0,R_k)}| \leqq \tilde{\chi}_{D(0,R_k) \setminus D(0,R_k - \sigma)}$.) Multiplying this by $\bar{\lambda}_k / |x|$, setting $x = \omega_l - \omega_{l'}$, and summing over all $k = 1, \ldots, M$ and all $l \neq l'$, we obtain

$$|W_4| \leqq C\sigma^2 |\Omega_*|. \tag{9.13}$$

Recalling that $\sigma = M^{-1/3}$ and $M > C\varepsilon^{-10}$, we see that (9.8), (9.9), (9.12) and (9.13) reduce (9.3) to

$$V[K_{ee}] \leqq C\varepsilon H_{N,\Omega_*} + C'\varepsilon N + C'\varepsilon |\Omega_*|. \tag{9.14}$$

Let $\phi_k \in C_0^\infty(|x| \leqq R_k/10)$ be a radially symmetric approximate identity of total integral 1, satisfying natural estimates. Then with $\rho(x) = \sum_l \phi_k(x-\omega_l) - \sum_j \phi_k(x-x_j)$, we have

$$V[\phi_k * \phi_k * |x|^{-1}] = \tfrac{1}{2}\int \frac{\rho(x)\rho(y)}{|x-y|} - [\phi_k * \phi_k * |x|^{-1}(0)]$$

$$\cdot(\text{TOTAL NUMBER OF ELECTRONS AND NUCLEII})$$

$$\geqq -\frac{C}{R_k}(N + |\Omega_*|),$$

since the double integral is positive. Setting $m_k = (\theta_k^2 * \tilde{\theta}_k^2(0))/R_k^3|D|$, and recalling that $R_1 > C\varepsilon^{-10}$, we conclude that

$$\begin{aligned} V[K_{ee}] &\leqq C\varepsilon N + C\varepsilon|\Omega_*| + V\left[K_{ee} + \sum_{k=1}^M \bar{\lambda}_k m_k \phi_k * \phi_k * |x|^{-1}\right] \\ &= C\varepsilon N + C\varepsilon|\Omega_*| + \left(\sum_{k=1}^M \bar{\lambda}_k m_k - 1\right) V[|x|^{-1}] \\ &\quad + V\left[\sum_{k=1}^M \bar{\lambda}_k \left\{ m_k \phi_k * \phi_k * |x|^{-1} + |x|^{-1} \frac{\theta_k^2 * \tilde{\theta}_k^2}{R_k^3|D|} - m_k|x|^{-1}\right\}\right]. \end{aligned} \tag{9.15}$$

Now (4.18) and the obvious estimate $1 \geqq m_k \geqq 1 - C\sigma/R_k$ show that $-\varepsilon < \left(\sum_{k=1}^M \bar{\lambda}_k m_k - 1\right) < 0$, while Lemma 4 shows that $V[-|x|^{-1}] \leqq CH_{N,\Omega_*} + C'N + C'|\Omega_*|$. So (9.15) yields

$$V[K_{ee}] \leqq C\varepsilon(H_{N,\Omega_*} + C''N + C''|\Omega_*|) + V\left[\sum_{k=1}^M \bar{\lambda}_k H_k\right], \tag{9.16}$$

with

$$H_k(x) = m_k \phi_k * \phi_k * |x|^{-1} + |x|^{-1}\frac{\theta_k^2 * \tilde{\theta}_k^2}{R_k^3|D|} - m_k|x|^{-1}. \tag{9.17}$$

Elementary computation shows that

$$|\partial^\alpha H_k(x)| \leqq \frac{C}{R_k|x|^{|\alpha|}} \quad \text{if} \quad |\alpha| \leqq 2, \quad \text{or if} \quad |\alpha| = 3$$

and

$$x \notin [D^*(0, R_k) \backslash D^*(0, R_k - \sigma)]. \tag{9.18}$$

Here D^* is the convex set $\{x - y | x, y \in D\} \in \Gamma_0$. Also,

$$H_k(x) = 0 \quad \text{outside} \quad D^*(0, R_k). \tag{9.19}$$

Since $0 \leqq \bar{\lambda}_k \leqq C/M$, we see from (9.18), (9.19) that $K = M \cdot \sum_{k=1}^M \bar{\lambda}_k H_k$ satisfies the hypotheses of Lemma 4, with D^* in place of D. Hence, Lemma 4 yields

$$V\left[\sum_{k=1}^{M}\bar{\lambda}_k H_k\right] \leqq \frac{C}{M}(H_{N,\Omega_*} + C'N + C'|\Omega_*|).$$

Recalling that $M > C\varepsilon^{-10}$ and substituting (9.20) into (9.16), we obtain the desired estimate (9.14). The proof of Lemma 1 was already reduced to (9.14). ∎

10. Proof of Lemma 2

In this section, C denotes a constant independent of D, Ω; $C(\Omega)$ denotes a constant independent of D; and $C(\Omega, D)$ denotes a constant depending on both D and Ω.

Let $\hat{\omega}_1 \dots \hat{\omega}_L$ be the lattice points in $\Omega_* \backslash D_*$. We pick points $\hat{y}_1 \dots \hat{y}_L$ according to the following procedure.

(a) If $\operatorname{dist}(\hat{\omega}_l, \partial\Omega_*) < \frac{1}{10}$, then pick $\hat{y}_l \in \Omega_*$ to satisfy $|\hat{y}_l - \hat{\omega}_l| < \frac{1}{10}$, $\operatorname{dist}(\hat{y}_l, \partial\Omega_*) > c(\Omega)$. We can easily construct such a $\hat{y}_l$ by taking a convex combination of $\hat{\omega}_l$ with a point $y^0 \in \Omega_*$ of maximal distance to $\partial\Omega_*$.

(b) If $\operatorname{dist}(\hat{\omega}_l, \partial D_*) < \frac{1}{10}$, then pick $\hat{y}_l \in \Omega_* \backslash D_*$ to satisfy $|\hat{y}_l - \hat{\omega}_l| > \frac{1}{10}$, $\operatorname{dist}(\hat{y}_l, \partial D_*) > \frac{1}{20}$. This is easily done when R' is sufficiently large, because then ∂D_* will look almost flat around $\hat{\omega}_l$.

(c) If $\operatorname{dist}(\hat{\omega}_l, \partial D_*)$ and $\operatorname{dist}(\hat{\omega}_l, \partial\Omega_*) \geqq \frac{1}{10}$, then set $\hat{y}_l = \hat{\omega}_l$.

Note that the cases (a), (b), (c) are disjoint since $\operatorname{dist}(\partial D_*, \partial\Omega_*) \geqq 10$. In all cases we have $\hat{y}_l \in \Omega_* \backslash D_*$, $|\hat{y}_l - \hat{\omega}_l| < \frac{1}{10}$, $\operatorname{dist}(\hat{y}_l, \partial D_*) > \frac{1}{20}$, $\operatorname{dist}(\hat{y}_l, \partial\Omega_*) > c(\Omega)$. Since balls of radius $c(\Omega)$ about the y_l are pairwise disjoint and contained in $\Omega_* \backslash D_*$, the number L of $\hat{\omega}_l$ is at most $C(\Omega)\varepsilon^{10}|\Omega_*|$. Now fix a spherically symmetric $\phi_0 \in C_0^\infty(|x| \leqq c(\Omega))$ with $\|\phi_0\|_{L^2} = 1$ and $\|\nabla\phi_0\|_{L^2} < C(\Omega)$. Form an L-electron wave function

$$\psi_0(x_1 \dots x_L) = \frac{1}{\sqrt{L!}} \sum_{\pi} (\operatorname{sgn} \pi) \prod_{l=1}^{L} \phi_0(x_{\pi(l)} - \hat{y}_l), \tag{10.1}$$

where π runs over permutations of $1 \dots L$. We check easily that

$$\psi_0 \in C_0^\infty([\Omega_* \backslash D_*]^L), \quad \|\psi_0\| = 1, \quad \langle H_{L,\Omega_* \backslash D_*}\psi_0, \psi_0 \rangle < C(\Omega)\varepsilon^{10}|\Omega_*|.$$

Now define an isometric injection $i_N: L_N^2(D_*) \to L_{N+L}^2(\Omega_*)$ by

$$(i_N\psi)(x_1 \dots x_{N+L}) = \frac{1}{\sqrt{(N+L)!}} \sum_{\pi} (\operatorname{sgn} \pi) \psi(x_{\pi(1)} \dots x_{\pi(N)}) \cdot \psi_0(x_{\pi(N+1)} \dots x_{\pi(N+L)}),$$

where π runs over permutations of $1 \dots N+L$.

For $\|\psi\| = 1$, one compute that

$$\langle H_{N+L,\Omega_*} i_N\psi, i_N\psi \rangle = \langle H_{N,D_*}\psi, \psi \rangle + \langle H_{L,\Omega_* \backslash D_*}\psi_0, \psi_0 \rangle + \left\langle \left[\sum_k F(\omega_k) - \sum_j F(x_j)\right]\psi, \psi \right\rangle, \tag{10.2}$$

where ω_k runs over the lattice points of D_*, and

$$F(x)=\sum_{l=1}^{L}(|x-\hat{\omega}_l|^{-1}-|x-\hat{y}_l|^{-1}). \tag{10.3}$$

The proof of (10.2) uses the mean-value property of $|x|^{-1}$, radial symmetry of ϕ_0, and the fact that $\phi_0(x-\hat{y}_l)$ is supported away from D_*.

Now with ϕ as in (3.18), we have

$$\begin{aligned}&\left|\sum_k \phi*\phi*F(\omega_k)-\sum_j \phi*\phi*F(x_j)\right|\\ &\leqq CR^{2.5}+CR^{-2.5}\left|\sum_k \phi*\phi*F(\omega_k)-\sum_j \phi*\phi*F(x_j)\right|^2\\ &\leqq CR^{2.5}+CR^{-2.5}\|\nabla(\eta\cdot[\phi*F])\|_{L^2}^2\cdot(H_{N,D_*}+CN+C(\Omega)\cdot|\Omega_*|) \end{aligned}\tag{10.4}$$

by Lemma 3. Here we are using $C(\Omega)\cdot|\Omega_*|$ as an upper bound on the number of nucleii in D_*; and we take $\eta(x)=1$ if $\operatorname{dist}(x,\Omega_*)\leqq R$, $\eta(x)=0$ if $\operatorname{dist}(x,\Omega_*)\geqq 2R$, and $|\nabla\eta|\leqq C(\Omega)R^{-1}$ everywhere. We introduced η because Lemma 3 applies to functions of compact support.

The obvious estimates

$$|\phi*F(x)|\leqq\sum_{\hat{y}_l\neq\hat{\omega}_l}(|x-\hat{\omega}_l|+1)^{-2}C\leqq C(\Omega,D)\quad\text{for }\operatorname{dist}(x,\Omega_*)>R$$

and

$$|\nabla\phi*F(x)|\leqq\sum_{\hat{y}_l\neq\hat{\omega}_l}(|x-\hat{\omega}_l|+1)^{-3}C\leqq\frac{C(\Omega,D)}{1+\operatorname{dist}(x,\partial\Omega_*\cup\partial D_*)}\quad\text{for all }x,$$

show that

$$\|\nabla(\eta\cdot[\phi*F])\|_{L^2}^2\leqq C(\Omega,D)\cdot R^2.$$

So (10.4) yields

$$\begin{aligned}\left|\sum_k \phi*\phi*F(\omega_k)-\sum_j \phi*\phi*F(x_j)\right|&\leqq C(\Omega,D)R^{-1/2}(H_{N,D_*}+CN+C(\Omega)|\Omega_*|)\\ &<\varepsilon^{10}(H_{N,D_*}+CN+C(\Omega)|\Omega_*|)\end{aligned}\tag{10.5}$$

if R is large enough. On the other hand,

$$\begin{aligned}\left|\sum_k F(\omega_k)-\sum_j F(x_j)\right|&\leqq\left|\sum_k \phi*\phi*F(\omega_k)-\sum_j \phi*\phi*F(x_j)\right|\\ &\quad+C\sum_{y\in J}\sum_j |x_j-y|^{-1}\chi_{|x_j-y|<1/3},\ J\\ &=\{\hat{\omega}_l\text{ of distance }<1/20\text{ from }\partial D_*\}.\end{aligned}\tag{10.6}$$

To see (10.6), note that the ω_k have distance at least 1 to the $\hat{\omega}_l$ and hence also distance at least 9/10 to the $\hat{y}_l$, while the $\hat{y}_l$ have distance at least 1/20 to the D_* and hence also to the x_j. So if $z=x_j$ or ω_k and $z'=\hat{y}_l$ or $\hat{\omega}_l$, then $|z-z'|^{-1}=(\phi*\phi*|x|^{-1})(z-z')$ unless $z=x_j$, $z'=\hat{\omega}_l$.

Now estimate (3.8) gives an upper bound $C\varepsilon^2(H_{N,D_*}+CN+C(\Omega)|\Omega_*|)+C(\varepsilon)\cdot C(D)R^2$ for the last term on the right-hand side of (10.6). For R large enough, $C(\varepsilon)\cdot C(D)R^2<\varepsilon^2|\Omega_*|$, so that (10.5) and (10.6) yield

$$\left|\sum_k F(\omega_k)-\sum_j F(x_j)\right|\leqq C\varepsilon^2(H_{N,D}+CN+C(\Omega)\cdot|\Omega_*|).$$

Therefore, by (10.2) and our estimate for the energy of ψ_0, we know

$$i_N^* H_{N+L,\Omega_*} i_N \leqq (1+C(\Omega)\varepsilon^2)H_{N,D_*}+C'(\Omega)\varepsilon^2 N+C'(\Omega)\varepsilon^2|\Omega_*|. \tag{10.7}$$

Using Lemma 7 and (10.7), we can assert

$$\begin{aligned}\sum_N e^{\bar{\mu}N}\operatorname{Tr} e^{-\bar{\beta}H_{N,\Omega_*}} &\geqq \sum_N e^{\bar{\mu}(N+L)}\operatorname{Tr} e^{-\bar{\beta}H_{N+L,\Omega_*}}\\ &\geqq e^{\bar{\mu}L}\sum_N e^{\bar{\mu}N}\operatorname{Tr} e^{-\bar{\beta}i_N^* H_{N+L,\Omega_*}i_N}\\ &\geqq e^{\bar{\mu}L-C'(\Omega)\varepsilon^2\bar{\beta}|\Omega_*|}\sum_N e^{(\bar{\mu}-C'(\Omega)\varepsilon^2\bar{\beta})N}\operatorname{Tr} e^{-\bar{\beta}(1+C(\Omega)\varepsilon^2)H_{N,N_*}}.\end{aligned} \tag{10.8}$$

Pick $\bar{\mu}$, $\bar{\beta}$ so that $\bar{\beta}(1+C(\Omega)\varepsilon^2)=\beta$ and $\bar{\mu}-C'(\Omega)\varepsilon^2\bar{\beta}=\mu$. Thus, $|\beta-\bar{\beta}|$, $|\mu-\bar{\mu}|\leqq C''(\Omega)\varepsilon^2$, and (10.8) yields

$$|\Omega_*|F(\bar{\mu},\bar{\beta},\Omega_*)>|D_*|F(\mu,\beta,D_*)-C''(\Omega)\varepsilon^2|\Omega_*|. \tag{10.9}$$

Estimates (3.21) give $|F(\mu,\beta,\Omega_*)-F(\bar{\mu},\bar{\beta},\Omega_*)|\leqq C(\Omega)\varepsilon^2$, and $|D_*|<|\Omega_*|<(1+\varepsilon^{10})|D_*|$. Therefore (10.9) implies $F(\mu,\beta,\Omega_*)\geqq F(\mu,\beta,D_*)-C(\Omega)\varepsilon^2$, which is stronger than the conclusion of Lemma 2. ■

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