

The Atomic and Molecular Nature of Matter

Dedicated to Julie

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1. Introduction

The purpose of this article is to show that electrons and protons, interacting by Coulomb forces and governed by quantum statistical mechanics at suitable temperature and density, form a gas of Hydrogen atoms or molecules. Let us first recall elementary quantum statistical mechanics. (See [6].) We start with a box $\Omega \subset R^3$ and two parameters, $\beta > 0$ and μ real, related to temperature and density. The Hamiltonian for electrons $x_1 \dots x_N$ and protons $y_1 \dots y_{N'}$ in Ω is

$$H_{N,N'}^\Omega = -\kappa_1 \Delta_x - \kappa_2 \Delta_y + \sum_{j < k} |x_j - x_k|^{-1} + \sum_{j < k} |y_j - y_k|^{-1} - \sum_{j,k} |x_j - y_k|^{-1}. \quad (1.1)$$

Here $H_{N,N'}^\Omega$ acts on wave functions $\psi(x_1 \dots x_N, y_1 \dots y_{N'})$, antisymmetric in the x_j and y_k separately, and satisfying Dirichlet boundary conditions on $\Omega \times \Omega \times \dots \times \Omega$. (The coefficients κ_1, κ_2 are related to the electron and proton mass, and one has $\kappa_2 \sim (\kappa_1/2000)$. We pick units in which $\kappa_1 + \kappa_2 = 1$.)

Now $H_{N,N'}^\Omega$ has eigenfunctions $\psi_{N,N',1}, \psi_{N,N',2}, \dots$ with eigenvalues $E_{NN'1}, E_{NN'2}, \dots$. The basic idea of quantum statistical mechanics is to pick

an (N, N', k) according to the probability law

$$\text{Prob. } (N, N', k) = \frac{\exp[(N + N')\mu - \beta E_{NN'k}]}{Z}, \quad (1.2)$$

where Z is a normalizing constant (the partition function) which makes $\text{Prob}(N, N', k)$ sum to 1.

Once we have picked a $\psi = \psi_{N, N', k}$ by (1.2), the probability density for finding the particles at given positions is

$$d\text{Prob} = |\psi(x_1 \dots x_N, y_1 \dots y_{N'})|^2 dx_1 \dots dx_N dy_1 \dots dy_{N'}. \quad (1.3)$$

In principle (1.2) and (1.3) give a complete probabilistic description of the particles in the box Ω under given β, μ . The natural mathematical problem is to describe how the particles behave for fixed β, μ as the box Ω grows large. Up to now, no rigorous results were known for this difficult problem. (See, however, important ideas in Lebowitz-Lieb [7] on the asymptotic behavior of the partition function Z , which is fundamental in thermodynamics.)

In this paper we introduce a new technique to understand the behavior of (1.2) and (1.3). For suitable β, μ we can show that quantum statistical mechanics leads to a dilute gas of isolated electrons and protons. Under an assumption to be explained in a moment, we prove that a different range of β, μ leads to a gas of isolated Hydrogen atoms, while a third range of β, μ gives a gas of diatomic Hydrogen molecules.

An estimate crucial for quantum statistical mechanics is stability of matter (Dyson-Lenard [1], Lieb-Thirring; see [8]), which we state in the form

$$H_{N, N'}^{\Omega} \geq -E_* \cdot (N + N' - 1) \quad \text{with } E_* \text{ independent of } N, N', \Omega. \quad (1.4)$$

The best value of the constant E_* in (1.4) profoundly influences the outcome of (1.2), (1.3). To get Hydrogen atoms, we need to assume:

$$\text{We can take } E_* < \frac{1}{4} \quad \text{for } N + N' > 2. \quad (1.5)$$

Estimate (1.5) is well established by experimental observation of Hydrogen crystals, but a rigorous mathematical proof will be hard to find. See Lieb [8] for the best results known so far. To get Hydrogen molecules requires an assumption even sharper than (1.5). For the rest of the paper, we discuss only the monatomic Hydrogen gas. The discussion for diatomic molecules is essentially the same, while the case of isolated particles is much easier.

In a later article [4], we generalize from Hydrogen to nuclei with higher charges.

2. Statement of the Theorem

Let us give a precise meaning to the idea of a gas of Hydrogen atoms. First of all, the particles must arrange themselves in electron-proton pairs. So for small $\epsilon > 0$ and large $R > 1$ we demand

All but at most ϵ percent of the particles come in pairs $\{x_k, y_k\}$ with x_k an electron, y_k a proton, and

$$|x_k - z|, |y_k - z| > R|x_k - y_k| \quad (2.1)$$

for any particle $z \neq x_k, y_k$.

Call such a pair $\{x_k, y_k\}$ an *atom*, and define its *displacement vector* to be $\xi_k = x_k - y_k$. We want the displacement vectors ξ_k to be distributed by the probability law $d\text{Prob} = ce^{-|\xi|} d\xi$, as in the ground state of a single Hydrogen atom. Hence, for $E \subset R^3$ we demand

$$\left| \frac{\text{Number of atoms with } \xi_k \in E}{\text{Total number of atoms}} - c \int_E e^{-|\xi|} d\xi \right| < \epsilon. \quad (2.2)$$

Finally, we want the positions and displacement vectors of the different atoms to be nearly independent. To formulate this, let $\rho = (\text{Expected number of particles})/|\Omega|$ be the density of the system, and subdivide Ω into a grid of congruent subcubes $\{Q_\alpha\}$ of volume comparable to $1/\rho$. Then subdivide each Q_α into two halves, Q'_α and Q''_α . For $E \subset R^3$, we study the events

ϵ'_α : Q'_α contains a single atom and nothing else; and the displacement vector for that atom lies in E .

ϵ''_α : Q''_α contains a single atom and nothing else; and the displacement vector for that atom lies in E .

Let

$$\begin{aligned} p' &= \frac{\text{Number of } \alpha \text{ for which } \epsilon'_\alpha \text{ occurs}}{\text{Total number of } \alpha} \\ p'' &= \frac{\text{Number of } \alpha \text{ for which } \epsilon''_\alpha \text{ occurs}}{\text{Total number of } \alpha} \\ p^* &= \frac{\text{Number of } \alpha \text{ for which } \epsilon'_\alpha, \epsilon''_\alpha \text{ both occur}}{\text{Total number of } \alpha}. \end{aligned}$$

Then the idea of independence of distinct atoms is expressed by

$$|p^* - p'p''| < \epsilon. \quad (2.3)$$

If (2.1), (2.2), (2.3) hold, then we have the right to say that our system is a gas of Hydrogen atoms. Under our assumption $E_* < \frac{1}{4}$, we shall prove the following.

Theorem. *Given $\epsilon > 0$ and $R > 1$, there exist μ, β so that on a large enough box Ω , we have (2.1) with probability at least $(1 - \epsilon)$. Moreover, for any $E \subset \mathbb{R}^3$, (2.2) and (2.3) hold with probability at least $(1 - \epsilon)$.*

To prove the theorem, we shall study the range of μ, β given by $-1/4 + \delta < \mu/\beta < -E_* - \delta$, $\beta \rightarrow \infty$, $\mu \rightarrow -\infty$. This corresponds to a temperature small compared to that required to ionize Hydrogen atoms ($\sim 10^5$ degrees K) and density small compared to that of a solid. These conditions are certainly reasonable for the study of a gas. In particular, we expect that if the density increases from zero and the temperature stays fixed and low, then we shall see first a gas of isolated electrons and protons, then a gas of Hydrogen atoms, next a gas of diatomic Hydrogen molecules, and ultimately, we leave the low-density regime. We make no attempt to derive practical values for β, μ .

Before passing to the proof of our theorem, we point out some respects in which it ought to be sharpened. For a fixed $\epsilon > 0$ and suitable β, μ , the probability that (2.1), (2.2) or (2.3) is violated should tend to zero as $|\Omega|$ tends to infinity. Our theorem states that these probabilities are at most ϵ . However, β, μ depend on ϵ , so that ϵ does not tend to zero for fixed β, μ as Ω grows. Thus, we know how the particles will look for suitable β, μ with probability 99%, but we still have a 1% chance of being utterly wrong, no matter how large the box may grow. I hope this defect may be soon remedied. In the same spirit, it would be interesting to show that no phase transitions occur in the range of β, μ under study. (In particular, the transition from atoms to diatomic molecules with increasing density occurs smoothly.)

Another point worth mentioning is that we have been speaking of scalar wave-functions ψ , i.e., spinless electrons. It is trivial to change our proofs to the case of spin-1/2 electrons and protons, but I hesitate to complicate matters further. Of course, the analogue of our theorem for H_2 -molecules is stated in terms of spinning electrons. We could also have defined the events $\epsilon'_\alpha, \epsilon''_\alpha$ using two different measurable sets E, F instead of a single E . There are also variants of (3) involving events $\epsilon'_\alpha, \epsilon''_\alpha, \epsilon'''_\alpha, \dots, \epsilon^{(L)}_\alpha$ in place of $\epsilon'_\alpha, \epsilon''_\alpha$.

There is a small literature on thermodynamics, i.e., the behavior of $\lim_{|\Omega| \rightarrow \infty} \ln Z/|\Omega|$, for very low density. The reader should be warned that this literature is not entirely correct. See Hughes [5] for a correct discussion.

Here is a very crude summary of the way our proof works. Suppose first we look at statistical mechanics on a fixed large ball B of radius R . If B is held fixed while the temperature and density are taken very small depending on R , then it is easy to understand what will happen. In particular, for a suitable balance between density and temperature, B will most likely contain no particles at all; but if it contains something, then most likely it contains exactly one atom. This is where we use our assumption $E_* < \frac{1}{4}$.

Now take a huge box Ω , and cut Ω as in [7] into a huge number of balls

$\{B_{k\alpha}\}$ of various sizes R_k , and a negligible residual part. We shall compare the real system with a much simpler fictitious system in which all forces between particles in different $B_{k\alpha}$ are turned off. If the temperature and density are low enough, depending on the R_k , then each $B_{k\alpha}$ can be analyzed by the methods of the preceding paragraph. Since distinct $B_{k\alpha}$ do not interact in the fictitious system, the statistical mechanics of that system will be easy to understand. The point is to make the comparison with the real system. We succeed in doing this by showing that each observable (i.e., self-adjoint operator) A on the fictitious system induces an observable \mathcal{Q} on the real system, whose expected value $\langle \mathcal{Q} \rangle$ can be estimated in terms of A . In particular, if A is «negative» in the sense that

$$\text{Tr exp}\{A + \mu(N + N') - \beta H_{\text{fictitious}}\} \leq \text{Tr exp}\{\mu(N + N') - \beta H_{\text{fictitious}}\},$$

then in the real system, $\langle \mathcal{Q} \rangle$ will be negative modulo small error terms. The proof of this uses ideas from [2], [3], [7]. Once we can estimate $\langle \mathcal{Q} \rangle$, the game is to pick A so that \mathcal{Q} expresses detailed information about the real system.

The reader should be warned that our brief summary is inaccurate and oversimplified.

Finally a fascinating problem about which almost nothing is known is to understand why matter at high density and low temperature forms a crystal, i.e., a configuration with long-range order. The frontier in our knowledge of this question involves placing points $x_1, x_2, \dots, x_N \in R^n$ to minimize a potential $V = \sum_{j \neq k} W(x_j - x_k)$. For certain special W , both positive and negative results are available in two dimensions. Nothing is known about the three-dimensional case. See, e.g., Radin and Schulman [9]. If these matters could be settled and our present results sharpened, then maybe one could give a rigorous proof that matter undergoes phase transitions. It will take a long time to reach such deep understanding.

We now present our proof.

3. Notation

For $\Omega \subset R^3$, define $L_{N,N'}^2(\Omega)$ as the space of all square-integrable functions $\psi(x_1 \dots x_N, y_1 \dots y_{N'})$ on $\Omega^{N+N'}$, antisymmetric in the x 's and y 's separately. Define

$$H_{N,N'}^{0,\Omega} = -\kappa_1 \sum_j \Delta_{x_j} - \kappa_2 \sum_k \Delta_{y_k} \quad \text{acting on} \quad L_{N,N'}^2(\Omega)$$

with Dirichlet boundary conditions, and

$$H_{N,N'}^\Omega = H_{N,N'}^{0,\Omega} + \sum_{j < k} |x_j - x_k|^{-1} + \sum_{j < k} |y_j - y_k|^{-1} - \sum_{j,k} |x_j - y_k|^{-1}.$$

Define

$$\begin{aligned}
L_*^2(\Omega) &= \sum_{N, N'} \oplus L_{N, N'}^2(\Omega) \\
L_{\text{neutral}}^2(\Omega) &= \sum_N \oplus L_{N, N}^2(\Omega) \\
H_*^\Omega &= \sum_{N, N'} \oplus H_{N, N'}^\Omega \\
H_{\text{neutral}}^\Omega &= H_*^\Omega | L_{\text{neutral}}^2(\Omega) \\
Z_0(\mu, \beta, \Omega, N, N') &= e^{\mu(N+N')} \text{Tr} \exp[-\beta H_{N, N'}^\Omega] \\
Z(\mu, \beta, \Omega, N, N') &= e^{\mu(N+N')} \text{Tr} \exp[-\beta H_{N, N'}^\Omega] \\
Z_0(\mu, \beta, \Omega) &= \sum_{N, N'} Z_0(\mu, \beta, \Omega, N, N') \\
Z(\mu, \beta, \Omega) &= \sum_{N, N'} Z(\mu, \beta, \Omega, N, N') \\
Z_{\text{neutral}}(\mu, \beta, \Omega) &= \sum_N Z(\mu, \beta, \Omega, N, N).
\end{aligned}$$

If $x_1 \dots x_N, y_1 \dots y_{N'}$ are electrons and protons, then we sometimes write $z_1 \dots z_{N+N'}$ for a list of all the particles, with charges $\epsilon(j) = \epsilon(z_j) = 1$ if z_j is one of the y_k , -1 if z_j is one of the x_j . If $K(\cdot)$ is a kernel on R^3 , and $x_1 \dots x_N, y_1 \dots y_{N'}$ are electrons and protons, then define

$$V[K] = \frac{1}{2} \sum_{j \neq k} \epsilon(j)\epsilon(k)K(z_j - z_k).$$

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

If A is an observable, i.e., a self-adjoint operator on $L_*^2(\Omega)$ then the expected value of A is

$$\langle A \rangle = \frac{\text{Tr}(A e^{\mu(N+N') - \beta H_*^\Omega})}{\text{Tr}(e^{\mu(N+N') - \beta H_*^\Omega})}.$$

In all that follows, μ will be large negative and β will be large positive.

4. The Partition Function for a Single Ball

Fix a ball B of radius R , satisfying $e^{c_2\beta} < R < e^{c_1\beta}$, $0 < c_2 < c_1 \ll 1$. We shall estimate $\text{Tr} \exp[-\beta H_{N, N'}^B]$. From (1.1), (1.4) and rescaling, we get

$$-\kappa_1(1 - \delta)\Delta_x - \kappa_2(1 - \delta)\Delta_y + V[|x|^{-1}] \geq -E_*(1 + C\delta) \cdot (N + N' - 1)$$

for $N + N' > 2$ and $0 < \delta \ll 1$. Hence

$$H_{N, N'}^B \geq -\kappa_1\delta\Delta_x - \kappa_2\delta\Delta_y - E_*(1 + C\delta)(N + N' - 1).$$

Taking $\delta = \beta^{-1}$, we find that

$$\begin{aligned}
 \text{Tr exp}[-\beta H_{N, N'}^B] &\leq e^{(\beta E_* + C)(N + N' - 1)} \text{Tr exp}(-H_{N, N'}^{0, B}) \\
 &\leq e^{(\beta E_* + C) \cdot (N + N' - 1)} (\text{Tr exp}(-H_1^0; B))^N (\text{Tr exp}(-H_0^0; B))^{N'} \\
 &\leq e^{(\beta E_* + C) \cdot (N + N' - 1)} \cdot (C|B|)^{N + N'} \\
 &\leq C' \exp\{[(E_* + 3c_1)\beta + C'] \cdot (N + N' - 1)\} \\
 &\quad \text{when } N + N' > 2. \quad (4.1)
 \end{aligned}$$

Next we look more carefully at $\text{Tr exp}[-\beta H_{1, 1}^B]$. First we use the textbook separation of variables

$$H_{1, 1}^B = -\kappa_1 \Delta_x - \kappa_2 \Delta_y - |x - y|^{-1} = -(\text{const})\Delta_z + (-\Delta_w - |w|^{-1}) \quad (4.2)$$

where

$$z = \text{center of mass} = \frac{\kappa_1^{-1}x + \kappa_2^{-1}y}{\kappa_1^{-1} + \kappa_2^{-1}}, \quad w = x - y.$$

For the Hilbert space $L_{1, 1}^2(B)$ we have inclusions

$$L_{1, 1}^2(B) \subset L^2\{(z, w) \mid z \in B, w \in B_1\} \quad (4.3)$$

if B_1 is the ball about zero of radius $2R$ and $B_0 = B$;

$$L_{1, 1}^2(B) \supset L^2\{(z, w) \mid z \in B_0, w \in B_1\} \quad (4.4)$$

if B_1 is a ball about zero and $B_0 + B_1 \subset B$. Hence we can derive upper and lower bounds for $\text{Tr exp}[-\beta H_{1, 1}^B]$ by computing $I = \text{Tr exp}[(\text{const})\beta\Delta_z - \beta(-\Delta_w - |w|^{-1})]$ on $L^2(B_0 \times B_1)$. The latter breaks up as $[\text{Tr exp}((\text{const})\beta\Delta_z)$ on $L^2(B_0)] \cdot [\text{Tr exp}(-\beta(-\Delta_w - |w|^{-1}))$ on $L^2(B_1)]$. The first factor here has the form $(c|B_0|/\beta^{3/2})(1 + 0(\beta^{-1}))$, in view of the eigenvalue asymptotics of the Laplacian on B_0 ($|B_0| > e^{3c_2\beta}$). It remains to understand $\Pi = \text{Tr exp}(-\beta(-\Delta_w - |w|^{-1}))$ on $L^2(B_1)$. Write $L^2(B_1) = C\psi_0 \oplus X$ where ψ_0 is the ground-state eigenvector of $-\Delta_w - |w|^{-1}$ with Dirichlet boundary conditions on B_1 , and X is the orthocomplement of ψ_0 . Now $-\Delta_w - |w|^{-1} \geq -c_3 \cdot \Delta_w - [1/4(1 - c_3)]$, $0 < c_3 < 1$ and $-\Delta_w - |w|^{-1} \geq (c_4 - \frac{1}{4})$ on X , with $c_4 > 0$. These estimates come from the elementary theory of the Hydrogen atom. Taking $c_3 \sim c_4/100$ and averaging, we obtain $\langle (-\Delta_w - |w|^{-1})\psi, \psi \rangle \geq \langle (-c_3\Delta_w + c_5 - \frac{1}{4})\psi, \psi \rangle$ for $\psi \in X$ and $c_3, c_5 > 0$. Hence by minimax,

$$\begin{aligned}
 \text{Tr exp}(-\beta(-\Delta_w - |w|^{-1})|_X) &\leq \text{Tr exp}(-\beta(-c_3\Delta_w + c_5 - \frac{1}{4})|_{L^2(B_1)}) \leq \\
 &\leq e^{[(1/4) - c_6]\beta}
 \end{aligned}$$

for large β , since $|B_1| < e^{3c_1}$ with $c_1 \ll 1$. So $\Pi = e^{-\beta E_0} + O(e^{[(1/4) - c_6]\beta})$, $E_0 =$ lowest eigenvalue of $-\Delta_w - |w|^{-1}$ with Dirichlet boundary conditions

on B_1 . On the other hand, one sees easily that $E_0 = -\frac{1}{4} + O(e^{-c\beta})$. In fact, comparison of $-\Delta_w - |w|^{-1}$ on B_1 and on R^3 shows $E_0 \geq -\frac{1}{4}$; while the trial wave function $\psi(x) = \theta(x)e^{-|x|/2}$, $\theta(x) = 1$ for $x \in$ Middle half of B_1 , $\theta(x) = 0$ on ∂B_1 gives $E_0 \leq -\frac{1}{4} + O(e^{-\text{const. radius}(B_1)})$. Therefore $\Pi = e^{\beta/4} \cdot (1 + O(e^{-c\beta}))$, and so

$$I = \frac{c|B_0|}{\beta^{3/2}} e^{\beta/4} (1 + O(\beta^{-1})), \quad (4.5)$$

provided B_0 and B_1 have radii bounded between $e^{c_2\beta}$ and $e^{c_1\beta}$, $c_1 \ll 1$.

From (4.2), (4.3), (4.5) we get $\text{Tr exp}(-\beta H_{1,1}^B) \leq (c|B|/\beta^{3/2})(e^{\beta/4}(1 + C\beta^{-1}))$, while (4.2) (4.4), (4.5) with $B_0 = B$ dilated by $(1 - \beta^{-1})$, $B_1 = B$ dilated by a factor β^{-1} yields $\text{Tr exp}(-\beta H_{1,1}^B) \geq (c|B|/\beta^{3/2})(e^{\beta/4}(1 - C\beta^{-1}))$ with the same c . That is

$$\text{Tr exp}(-\beta H_{1,1}^B) = \frac{c|B|}{\beta^{3/2}} e^{\beta/4} (1 + O(\beta^{-1})). \quad (4.6)$$

Finally when $(N, N') = (1, 0)$ or $(0, 1)$ we have $H_{N, N'}^B = H_{N, N'}^{0, B}$, so that $\text{Tr exp}(-\beta H_{N, N'}^B) \leq (c|B|/\beta^{3/2})$. Analogous estimates hold for $(N, N') = (2, 0)$ or $(0, 2)$. Hence we can make a table

$$\begin{aligned} Z(\mu, \beta, B, N, N') &= 1 \quad \text{if } N = N' = 0 & (a) \\ &= (1 + O(\beta^{-1})) \frac{c e^{2\mu + \beta/4}}{\beta^{3/2}} |B| \quad \text{if } N = N' = 1 & (b) \\ &\leq \frac{C e^\mu}{\beta^{3/2}} |B| \quad \text{if } (N, N') = (1, 0) \text{ or } (0, 1) & (c) \\ &\leq \frac{C e^{2\mu}}{\beta^{3/2}} |B| \quad \text{if } (N, N') = (2, 0) \text{ or } (0, 2) & (c') \\ &\leq C \exp\{\mu(N + N') + [(E_* + 3c_1)\beta + C'] \cdot (N + N' - 1)\} & (d) \end{aligned}$$

if (N, N') is not one of the above. If $E_* < \frac{1}{4}$, then the quantity in braces in (d) will be less than

$$2\mu + \frac{\beta}{4} - c'(N + N' - 2) \quad \text{for } \beta \text{ large and } \frac{\mu}{\beta} < -\frac{1}{4} + c''.$$

Here c' , c'' are positive constants. Therefore, since $e^{c_2\beta} < \text{radius } B < e^{c_1\beta}$ with $c_1 \ll 1$, we have

$$\sum_{N+N'>2} Z(\mu, \beta, B, N, N') < \frac{1}{\beta} Z(\mu, \beta, B, 1, 1)$$

for β large, $\frac{\mu}{\beta} < -\frac{1}{4} + c''$.

Bringing in $(N, N') = (0, 0), (1, 0), (0, 1), (2, 0), (0, 2)$ also, we can find a nonempty interval \hat{I} of the form $(-\frac{1}{4} + c''', -\frac{1}{4} + c'')$ so that if β is large enough, c_1 is small enough, and $\mu/\beta \in \hat{I}$, then

$$\sum_{N+N' \neq (0,0) \text{ or } (1,1)} Z(\mu, \beta, B, N, N') < \frac{1}{\beta} Z(\mu, \beta, B, 1, 1) \quad (4.7)$$

$$Z(\mu, \beta, B, 1, 1) < \frac{1}{\beta} Z(\mu, \beta, B, 0, 0). \quad (4.8)$$

So the grand canonical ensemble on B consists most probably of a vacuum; but if it contains anything, the contents will most likely be a single Hydrogen atom.

From (a), (b), (4.7), (4.8) we get the important equation

$$Z(\mu, \beta, B) = \exp(\rho|B|) \cdot (1 + O(\beta^{-1})), \quad (4.9)$$

where

$$\rho = \frac{\text{const } e^{2\mu + (\beta/4)}}{\beta^{3/2}} \ll 1. \quad (4.10)$$

Evidently, we may replace Z by Z_{neutral} in (4.9).

We shall need also the following generalization of the partition function. Suppose we have balls $B_1 \dots B_{L_0}$ with $e^{c_2\beta} < \text{radius}(B_k) < e^{c_1\beta}$ as before. Fix a subset $E \subset R^3$ and a number t .

Define a Hilbert space $L^2_{1,1}(B_1 \dots B_{L_0})$ to consist of all square integrable $\psi(x_1, y_1, x_2, y_2, \dots, x_{L_0}, y_{L_0})$ supported in $\{x_k, y_k \in B_k (k = 1, \dots, L_0)\}$.

On this Hilbert space, define a Hamiltonian

$$\overset{\circ}{H} = \sum_{k=1}^{L_0} (-x_1 \Delta_{x_k} - x_2 \Delta_{y_k} - |x_k - y_k|^{-1}), \text{ Dirichlet boundary conditions.}$$

Thus, each B_k contains an electron and a proton which attract each other but do not interact with the particles in the other B_k .

Next define an observable

$$G = \begin{cases} 1 & \text{if } x_k - y_k \in E \text{ for } k = 1, \dots, s_0 \text{ but not for } k = s_0 + 1, \dots, L_0 \\ 0 & \text{otherwise} \end{cases}$$

Then for c_1 and $|t|$ less than some small constant $c(L)$ we have

Lemma 4.1. *The trace of $\exp(tG - \beta \overset{\circ}{H})$ on $L^2_{1,1}(B_1 \dots B_{L_0})$ is given by*

$$\prod_{k=1}^{L_0} \left(\frac{\text{const } e^{\beta/4} |B_k|}{\beta^{3/2}} \right) e^{tG_0} (1 + O(\beta^{-1}) + O(t^2))$$

with $G_0 = ((\text{const}) \int_E e^{-|x|} dx)^{s_0} ((\text{const}) \int_{cE} e^{-|x|} dx)^{L_0 - s_0}$.

Here $O(\beta^{-1})$ means less than $C(L_0) \cdot \beta^{-1}$ in absolute value, and similarly for $O(t^2)$.

We sketch the proof of Lemma 3.1. Again we can separate variables using $z_k =$ center of mass of x_k, y_k and $w_k = x_k - y_k$. Then

$$tG - \beta \overset{\circ}{H} = +(\text{const}) \beta \sum_k \Delta_{z_k} - \beta \left[\sum_k (-\Delta_{w_k} - |w_k|^{-1}) - \frac{t}{\beta} G(w_1 \dots w_{L_0}) \right]$$

with

$$G(w_1 \dots w_{L_0}) = \begin{cases} 1 & \text{if } w_1 \dots w_{s_0} \in E \text{ but } w_{s_0+1} \dots w_{L_0} \notin E \\ 0 & \text{otherwise} \end{cases}$$

As in the proof of (6), one can estimate $\text{Tr} \exp(tG - \beta \overset{\circ}{H})$ above and below by

$$\prod_{k=1}^{L_0} \left(\frac{\text{const}}{\beta^{3/2}} |B_k| \right) \cdot e^{-\beta \tilde{E}} (1 + O(\beta^{-1})), \quad (4.11)$$

where \tilde{E} is the lowest eigenvalue of

$$\sum_{k=1}^{L_0} (-\Delta_{w_k} - |w_k|^{-1}) - \frac{t}{\beta} G(w_1 \dots w_{L_0})$$

on a suitable product of large balls $B_1^1 \times \dots \times B_{L_0}^1$ about the origin.

If $t = 0$ then the w_k decouple and $\tilde{E} = -\frac{1}{4}L_0(1 + O(e^{-c\beta}))$. Perturbation theory yields

$$\tilde{E} = -\frac{L_0}{4} + O(e^{-c\beta}) - \frac{t}{\beta} G_0 + O\left[\left(\frac{t}{\beta}\right)^2\right] \quad \text{for } \left|\frac{t}{\beta}\right| < c(L_0).$$

Substituting this into (4.11), we obtain the conclusion of Lemma 4.1, even with a better error term than stated there.

5. Estimates for Coulomb Systems

Take an even approximate identity $\varphi_R(x)$ of total integral one, supported in $|x| < \frac{1}{2}R$, and set $\bar{K}(x, R) = |x|^{-1} * \varphi_R * \varphi_R$. Then define

$$V_{LR}(R) = \frac{1}{2} \sum_{j,k} \epsilon(j)\epsilon(k) \bar{K}(z_j - z_k, R) = \text{“Long-Range Part of the Coulomb Potential”}. \quad (5.1)$$

Our goal in this section is to show that if $K(\cdot)$ is a kernel on R^3 which behaves roughly like $|x|^{-1}$, then $V[K] \leq C(H_{N,N'}^0 + CN + CN')$. Also if $K(x)$ is supported in $|x| \geq R$, then $V[K]$ is dominated by $V_{LR}(R) + (\text{small constant}) \cdot (H_{N,N'}^0 + CN + CN')$. The precise statements are given by Lemmas 3 and 4 below.

Now fix nuclei $y_1 \dots y_{N'} \in R^3$, and let $\psi(x_1 \dots x_N)$ be antisymmetric of norm 1. Let Q° be an enormous cube containing the system, take $K \geq 1$ to be picked later, and make a Calderón-Zygmund decomposition $\{Q_\nu\}$ of Q° as follows. (See [2]). We bisect Q° repeatedly, stopping at the cube Q_ν when its triple Q_ν^* contains at most K nuclei. Thus, $Q^\circ = \cup_\nu Q_\nu$, and

- (a) Q_ν^* contains at most K nuclei.
- (b) Q_ν^{**} contains more than K nuclei, or else the cutting process would not have reached Q_ν .
- (c) $\bar{Q}_\mu \cap \bar{Q}_\nu \neq \phi$ implies that the side lengths δ_μ, δ_ν are comparable. Otherwise, (b) for the smaller cube contradicts (a) for the larger.
- (d) Call Q_ν *active* if Q_ν contains at least $c \cdot K$ nuclei. Then

$$\sum_{\nu \text{ active}} \delta_\nu^{-1} \geq c \sum_{\nu} \delta_\nu^{-1}.$$

To prove (d), say that Q_ν has *good geometry* if $\delta_\mu \sim \delta_\nu$ for any Q_μ intersecting Q_ν^{**} . We first check that

$$\sum_{\nu \text{ active}} \delta_\nu^{-1} \geq c \sum_{\nu \text{ good geom.}} \delta_\nu^{-1}. \quad (5.2)$$

In fact, take Q_ν with good geometry and note that only a bounded number of Q_μ can intersect Q_ν^{**} . The pigeon-hole principle therefore shows that one of these Q_μ must be active, by virtue of (b). Hence,

$$\sum_{\nu \text{ good geom.}} \delta_\nu^{-1} \leq C \sum_{\substack{\mu \text{ active} \\ \nu \text{ good geom.} \\ Q_\mu \cap Q_\nu^{**} \neq \phi}} \delta_\mu^{-1} \leq C' \sum_{\mu \text{ active}} \delta_\mu^{-1}, \text{ which proves (5.2).}$$

Next we show

$$\sum_{\nu \text{ good geom.}} \delta_\nu^{-1} \geq c \sum_{\nu} \delta_\nu^{-1}, \quad (5.3)$$

which together with (5.2) completes the proof of (d).

Observe that if Q_ν doesn't have good geometry, then some $Q_{\nu'}$ intersecting Q_ν^{**} must be much bigger or much smaller than Q_ν . If $Q_{\nu'}$ were much bigger, then $Q_\nu^{**} \subset Q_{\nu'}^*$, contradicting (a) and (b). Hence $\delta_{\nu'} < 10^{-3}\delta_\nu$, and $10^3 Q_{\nu'} \subset CQ_\nu$, where $CQ_\nu = Q_\nu$ dilated about its center by a factor C . Now either $Q_{\nu'}$ has good geometry, or else we can repeat the process to find a $Q_{\nu''}$ with $\delta_{\nu''} < 10^{-3}\delta_{\nu'}$, $10^3 Q_{\nu''} \subset 10^3 Q_{\nu'}$. Continue in this way until we reach a cube

with good geometry. This must happen eventually, since there are only finitely many cubes $\{Q_\nu\}$. Hence for each cube Q_ν there is a Q_μ with good geometry with $10^3 Q_\mu \subset 10^3 Q_\nu$. So

$$\begin{aligned} \sum_\nu \delta_\nu^{-1} &\leq \sum_{\substack{\mu, \nu \\ \mu \text{ good geom.} \\ 10^3 Q_\mu \subset 10^3 Q_\nu}} \delta_\nu^{-1} \leq \sum_{\mu \text{ good geom.}} \left(\sum_{\substack{\text{all dyadic } Q \\ 10^3 Q_\mu \subset 10^3 Q}} \text{side}(Q)^{-1} \right) \leq \\ &\leq C \sum_{\mu \text{ good geom.}} \delta_\mu^{-1}, \end{aligned}$$

which proves (5.3). Since (5.2) and (5.3) hold, we know (d).

We shall need the following estimate for functions on R^3 .

Lemma 5.1. *If Q is a cube of side δ , and $\psi \in L^2(Q)$, then*

$$\begin{aligned} \int_Q \left\{ \frac{1}{40} |\nabla \psi(x)|^2 - \sum_{k=1}^K |x - y_k|^{-1} |\psi(x)|^2 \right\} dx &\geq \\ &\geq - \left(\frac{CK}{\delta} + C(K) \right) \|\psi\|_{L^2(Q)}^2. \end{aligned} \quad (5.4)$$

PROOF. Look first at the case $\delta \leq \delta_0(K)$ with $\delta_0(K)$ to be picked in a moment. Set

$$V(x) = \sum_{k=1}^K |x - y_k|^{-1} \quad \text{and} \quad \psi_Q = |Q|^{-1} \int_Q \psi.$$

Then

$$\begin{aligned} \int_Q V(x) |\psi(x)|^2 dx &\leq 2 \int_Q V(x) |\psi_Q|^2 dx + 2 \int_Q V(x) |\psi(x) - \psi_Q|^2 dx \leq \\ &\leq \frac{CK}{\delta} \|\psi\|_{L^2(Q)}^2 + 2 \int_Q V(x) |\psi(x) - \psi_Q|^2 dx, \quad \text{since} \quad |Q|^{-1} \int_Q V(x) dx \leq \frac{CK}{\delta}. \end{aligned}$$

The last term on the right is at most

$$2 \|V\|_{L^{3/2}(Q)} \cdot \|\psi(\cdot) - \psi_Q\|_{L^6(Q)}^2 \leq CK\delta \|\nabla \psi\|_{L^2(Q)}^2$$

by Holder and Sobolev. If $\delta_0(K)$ is small enough, then $CK\delta < (1/40)$, and Lemma 5.1 follows for $\delta \leq \delta_0(K)$. For a cube Q of side $\delta > \delta_0(K)$, we just cut Q into subcubes $\{Q^\alpha\}$ of side $\sim \delta_0(K)$. We already know (5.4) for each of the Q^α ; summing over α completes the proof of Lemma 5.1.

Antisymmetry of the wave function enters via the following observation.

Lemma 5.2. *Let L_ν denote the number of electrons x_j in Q_ν . Then*

$$\frac{1}{20} \|\nabla \psi\|^2 \geq c \left\langle \sum_{L_\nu \geq 2} L_\nu^{5/3} \delta_\nu^{-2} \psi, \psi \right\rangle.$$

PROOF. Suppose first that φ is antisymmetric on Q^L for a cube $Q \subset R^3$ of side δ . Then

$$\|\nabla\varphi\|_{L^2(Q^L)}^2 \geq cL^{5/3}\delta^{-2}\|\varphi\|_{L^2(Q^L)}^2 \quad \text{for } L \geq 2.$$

This follows by expanding φ in eigenfunctions of the Neumann Laplacian on Q^L . Consequently, on $I = Q_{\nu_1} \times Q_{\nu_2} \times \dots \times Q_{\nu_N}$ we have

$$\|\nabla\psi\|_{L^2(I)}^2 \geq c\left(\sum_{L_\nu \geq 2} L_\nu^{5/3}\delta_\nu^{-2}\right)\|\psi\|_{L^2(I)}^2,$$

with $L_\nu = (\text{number of } \nu_k \text{ equal to } \nu) = (\text{number of electrons in } Q_\nu)$ for $(x_1 \dots x_N) \in I$. This may be rewritten as

$$\|\nabla\psi\|_{L^2(I)}^2 \geq c\left\langle \left(\sum_{L_\nu \geq 2} L_\nu^{5/3}\delta_\nu^{-2}\right)\psi, \psi \right\rangle_{L^2(I)}.$$

Summing over all possible choices of $\nu_1 \dots \nu_N$, we obtain Lemma 5.2.

Next we compare the potential energy of point charges $x_1 \dots x_N, y_1 \dots y_N$ with that of a continuous charge density $\rho(x) = \sum_k \epsilon(k)\varphi_k(x - z_k)$. Here $\varphi_k \geq 0$ is a spherically symmetric smooth charge density of total charge +1, supported in a ball of radius $(1/10)\delta(k)$, where $\delta(k) = \delta_\nu$ for the Q_ν containing z_k . Observe that

$$V(\rho) = \frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|} dx dy = c \int |\xi|^{-2} |\hat{\rho}(\xi)|^2 d\xi \geq 0.$$

How do $V[|x|^{-1}]$ and $V(\rho)$ differ?

(α) $V(\rho)$ contains "self-energy terms" of the form

$$\frac{1}{2} \int \frac{\varphi_k(x - z_k)\varphi_k(y - z_k)}{|x-y|} dx dy$$

with no analogues in $V[|x|^{-1}]$. The self-energy terms total at most $C\sum_\nu (K + L_\nu)/\delta_\nu$.

The mean-value properties of the Coulomb potential yield

$$\begin{aligned} (\beta) \quad |z_j - z_k|^{-1} &\geq \int \frac{\varphi_j(x - z_j)\varphi_k(y - z_k)}{|x-y|} dx dy + \\ &\quad + c|z_j - z_k|^{-1}\chi_{|z_j - z_k| < 10^{-2}\delta(k)} \end{aligned}$$

which we use when $\epsilon(j) = \epsilon(k)$, $j \neq k$; and

$$\begin{aligned}
(\gamma) \quad -|z_j - z_k|^{-1} &\geq - \int \frac{\varphi_j(x - z_j)\varphi_k(y - z_k)}{|x - y|} dx dy - \\
&\quad - |z_j - z_k|^{-1} \chi_{|z_j - z_k| < \frac{1}{2}\delta(k)}
\end{aligned}$$

which we use when $\epsilon(j) \neq \epsilon(k)$.

From (α) , (β) , (γ) we obtain

$$\begin{aligned}
V[|x|^{-1}] &\geq V(\rho) - C \sum_{\nu} \frac{K + L_{\nu}}{\delta_{\nu}} + \\
&\quad + c \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{0 < |x_j - x_k| < 10^{-2}\delta_{\nu}} |x_j - x_k|^{-1} + \\
&\quad + c \sum_{\nu} \sum_{y_j \in Q_{\nu}} \sum_{0 < |y_k - y_j| < 10^{-2}\delta_{\nu}} |y_j - y_k|^{-1} - \\
&\quad - \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{y_k \in Q_{\nu}^*} |x_j - y_k|^{-1}
\end{aligned} \tag{5.5}$$

If ν is active (see (d)), then by the pigeon-hole principle, some subcube of Q_{ν} of diameter $< 10^{-2}\delta_{\nu}$ will contain at least $c'K$ nuclei. Hence

$$\frac{1}{2} \sum_{y_j \in Q_{\nu}} \sum_{0 < |y_k - y_j| < 10^{-2}\delta_{\nu}} |y_j - y_k|^{-1} \geq \frac{c''K^2}{\delta_{\nu}}.$$

Similarly, if $L_{\nu} \geq K$, then

$$\frac{1}{2} \sum_{x_j \in Q_{\nu}} \sum_{0 < |x_k - x_j| < 10^{-2}\delta_{\nu}} |x_j - x_k|^{-1} \geq \frac{c''L_{\nu}^2}{\delta_{\nu}}.$$

Consequently, (5.5) implies

$$\begin{aligned}
V[|x|^{-1}] &\geq \left[V(\rho) + c \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{0 < |x_k - x_j| < \delta_{\nu} \cdot 10^{-2}} |x_j - x_k|^{-1} + \right. \\
&\quad \left. + c \sum_{\nu} \sum_{y_j \in Q_{\nu}} \sum_{0 < |y_k - y_j| < 10^{-2}\delta_{\nu}} |y_j - y_k|^{-1} \right] + \\
&\quad + \left[\sum_{\nu \text{ active}} \frac{c''K^2}{\delta_{\nu}} + \sum_{L_{\nu} \geq K} \frac{c''L_{\nu}^2}{\delta_{\nu}} - C \sum_{\nu} \frac{K + L_{\nu}}{\delta_{\nu}} \right] - \\
&\quad - \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{y_k \in Q_{\nu}^*} |x_j - y_k|^{-1}.
\end{aligned} \tag{5.6}$$

Lemma (5.1) and (a) imply

$$-\frac{1}{20} \Delta_x \geq 2 \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{y_k \in Q_{\nu}^*} |x_j - y_k|^{-1} - \sum_{\nu} \left(\frac{CK}{\delta_{\nu}} + C(K) \right) L_{\nu}.$$

Adding this and the conclusion of Lemma 5.2 to (5.6), we obtain

$$\begin{aligned}
 -\frac{1}{10}\Delta_x + V[|x|^{-1}] \geq & \left[V(\rho) + \right. \\
 & + c \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{0 < |x_k - x_j| < 10^{-2}\delta_{\nu}} |x_j - x_k|^{-1} + \\
 & + c \sum_{\nu} \sum_{y_j \in Q_{\nu}} \sum_{0 < |y_k - y_j| < 10^{-2}\delta_{\nu}} |y_j - y_k|^{-1} + \\
 & \left. + \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{y_k \in Q_{\nu}^*} |x_j - y_k|^{-1} \right] + \\
 & + \left[\sum_{\nu} \frac{\tilde{c}K^2}{\delta_{\nu}} + \sum_{L_{\nu} \geq K} \frac{c''L_{\nu}^2}{\delta_{\nu}} - \sum_{\nu} \frac{CKL_{\nu}}{\delta_{\nu}} - \right. \\
 & - \sum_{\nu} C(K)L_{\nu} - \sum_{\nu} \frac{CK + CL_{\nu}}{\delta_{\nu}} + \\
 & \left. + \sum_{L_{\nu} \geq 2} cL_{\nu}^{5/3}\delta_{\nu}^{-2} \right]. \tag{5.7}
 \end{aligned}$$

Here we used (d) in the term with constant \tilde{c} . Now if K is large enough, then we have the elementary inequality

$$\begin{aligned}
 \left(cL_{\nu}^{5/3}\delta_{\nu}^{-2}\chi_{L_{\nu} \geq 2} + \frac{c''L_{\nu}^2\chi_{L_{\nu} \geq K}}{\delta_{\nu}} + \frac{\tilde{c}K^2}{\delta_{\nu}} \right) - \frac{CKL_{\nu}}{\delta_{\nu}} - \frac{CK + CL_{\nu}}{\delta_{\nu}} - \\
 - C(K)L_{\nu} \geq -E(K)L_{\nu} + \frac{cL_{\nu}}{\delta_{\nu}} + \frac{cK}{\delta_{\nu}}. \tag{5.8}
 \end{aligned}$$

To check (5.8), we note that $c''L_{\nu}^2\chi_{L_{\nu} \geq 2} + \tilde{c}K^2 - CKL_{\nu} - CK - CL_{\nu} \geq cL_{\nu} + cK$ unless $L_{\nu} \sim K$. So (5.8) is obvious unless $L_{\nu} \sim K$. If $L_{\nu} \sim K$, then

$$cL_{\nu}^{5/3}\chi_{L_{\nu} \geq 2}\delta_{\nu}^{-2} - \frac{CKL_{\nu}}{\delta_{\nu}} - \frac{(CK + CL_{\nu})}{\delta_{\nu}} \geq \frac{cL_{\nu} + cK}{\delta_{\nu}}$$

as long as $\delta_{\nu} < \delta_0(K)$. So (5.8) is obvious unless $L_{\nu} \sim K$ and $\delta_{\nu} \geq \delta_0(K)$. In this last case, (5.8) is again obvious if we just take $E(K)$ large enough. So (5.8) holds in all cases.

Substituting (5.8) into (5.7) and recalling that $\sum_{\nu} L_{\nu} = N$, we find that

$$\begin{aligned}
 -\frac{1}{10}\Delta_x + V[|x|^{-1}] + E(K) \cdot N \geq & V(\rho) + \sum_{\nu} \frac{cL_{\nu}}{\delta_{\nu}} + \sum_{\nu} \frac{cK}{\delta_{\nu}} + c \sum_{\nu} \\
 & \sum_{x_j \in Q_{\nu}} \sum_{0 < |x_k - x_j| < 10^{-2}\delta_{\nu}} |x_j - x_k|^{-1} + \sum_{\nu} \sum_{y_j \in Q_{\nu}} \sum_{0 < |y_k - y_j| < 10^{-2}\delta_{\nu}} |y_j - y_k|^{-1} + \\
 & + \sum_{\nu} \sum_{x_j \in Q_{\nu}} \sum_{y_k \in Q_{\nu}^*} |x_j - y_k|^{-1}. \tag{5.9}
 \end{aligned}$$

The terms on the right are all positive, so (5.9) implies stability of matter. Now let $\delta_+(z_j) = \min_{k \neq j} |z_j - z_k|$ = distance from z_j to its nearest neighbor. One checks easily that

$$\sum_{\substack{z_j \text{ electrons} \\ \text{in } Q_\nu}} \frac{c}{\delta_+(z_j)} \leq \sum_{x_j \in Q_\nu} \sum_{0 < |x_k - x_j| < 10^{-2}\delta_\nu} |x_j - x_k|^{-1} + \\ + \sum_{x_j \in Q_\nu} \sum_{y_k \in Q_\nu^*} |x_j - y_k|^{-1} + \frac{C(K + L_\nu)}{\delta_\nu}.$$

So (5.9) yields

$$c \sum_{z_j \text{ electrons}} (\delta_+(z_j))^{-1} \leq -\frac{1}{10} \Delta_x + V[|x|^{-1}] + E(K) \cdot N.$$

The analogous estimate for protons follows similarly (there are slight changes because of the asymmetry between electrons and protons in the last term on the right in (5.9)). Hence

$$\sum_j \delta_+^{-1}(z_j) \leq C \left(-\frac{1}{10} \Delta_x + V[|x|^{-1}] + C \cdot N \right). \quad (5.10)$$

From here on, we simply fix K large enough to make sure (5.9) holds, and we denote K , $E(K)$ simply by C .

Set $\delta(z_j) = \min(1, \delta_+(z_j))$. Obviously, then,

$$\sum_j \delta^{-1}(z_j) \leq C \left(-\frac{1}{10} \Delta_x + V[|x|^{-1}] + CN + CN' \right). \quad (5.11)$$

So far, we have regarded the nucleii $y_1 \dots y_{N'}$ as fixed. However (5.11) for fixed nucleii implies the corresponding estimate for quantized nucleii, namely

$$\sum_j \delta^{-1}(z_j) \leq C(H_{N, N'}^\Omega + CN + CN'), \quad \text{any } \Omega \subset R^3. \quad (5.12)$$

We did not even need the kinetic energy of the nucleii in (5.12). Estimate (5.12) shows that in a quantum state ψ of moderate energy, the particles are not too closely packed.

Now we are ready to estimate $V[K]$ in terms of $H_{N, N'}^\Omega$ for Coulomb-like potentials $K(\cdot)$. Our assumptions on K are the following rather technical estimates.

$$|\partial^\alpha K(x)| \leq C|x|^{-1-|\alpha|} \quad \text{for } |\alpha| \leq 3 \quad (5.13)$$

and all x outside the annuli $\mathcal{G}_k = \{||x| - R_k| < R_0\}$, $k = 1, 2, 3, \dots$

$$|\partial^\alpha K(x)| \leq CR_0|x|^{-1-|\alpha|} \quad \text{for } |\alpha| \leq 2 \quad \text{and all } x. \quad (5.14)$$

Here $100 < R_0 < R_1 < \dots$ are fixed radii with $R_{k+1} \geq 100R_k$ and $R_1 > R_0^{10}$.

Lemma 5.3. *For K satisfying (5.13), (5.14), we have*

$$V[K] \leq C(H_{N,N'}^0 + CN + CN'). \quad (5.15)$$

PROOF. We first check that $|\hat{K}(\xi)| \leq C|\xi|^{-2}$. In fact, write $K = K_0 + K_1$ with both terms satisfying (5.13), (5.14), $K_0(x)$ supported in $|x| < 2|\xi|^{-1}$, and $K_1(x)$ supported in $|x| > |\xi|^{-1}$. From (5.13), (5.14) we get $\|K_0\|_{L^1} \leq C|\xi|^{-2}$, $\|\Delta K_1(x) - \Delta K_1(x-y)\|_{L^1(dx)} \leq C$ for $|y| \leq (1/20)|\xi|^{-1}$. Hence $|\hat{K}_0(\xi)| \leq C|\xi|^{-2}$, $|[e^{iy\xi} - 1]\hat{K}_1(\xi)|\xi|^2 \leq C$. Taking $y = (1/20)\xi|\xi|^{-2}$, we get $|\hat{K}_0(\xi)|, |\hat{K}_1(\xi)| \leq C|\xi|^{-2}$, so that $|\hat{K}(\xi)| \leq C|\xi|^{-2}$ as claimed.

Next set $K^\#(x) = |x|^{-1} - cK(x)$. For $c \ll 1$ we have $K^\#\{\rho\} = \frac{1}{2} \int K^\#(x-y)\rho(x)\rho(y) dx dy \geq 0$ for any charge density ρ . We shall prove

$$V[K^\#] \geq -C(H_{N,N'}^0 + CN + CN'). \quad (5.16)$$

This means $cV[K] \leq V[|x|^{-1}] + C(H_{N,N'}^0 + CN + CN')$. Since evidently $V[|x|^{-1}] \leq H_{N,N'}^0$, (5.16) implies (5.15) and so proves Lemma 5.3.

To establish (5.16), we construct a suitable charge density ρ and compare $V[K^\#]$ with $K^\#\{\rho\} \geq 0$. To make ρ , first take an even, smooth function $\varphi(x)$, supported in $|x| \leq \frac{1}{3}$ and satisfying $\int \varphi(x) dx = 1$, $\int x^\gamma \varphi(x) dx = 0$ for $0 < |\gamma| < 20$. Then set $\varphi_j(x) = [\delta(z_j)]^{-3} \varphi(x/\delta(z_j))$, and define $\rho(x) = \sum_j \epsilon(z_j) \varphi_j(x - z_j)$. Comparing $V[K^\#]$ with $K^\#\{\rho\}$, we first discover self-energy terms in $K^\#\{\rho\}$ with no analogues in $V[K^\#]$. These amount to $C \cdot \sum_j \delta^{-1}(z_j)$. Next, for distinct particles z_j, z_k we compare $K^\#(z_j - z_k)$ with the analogous term $K^\# * \varphi_j * \varphi_k(z_j - z_k)$ in $K^\#\{\rho\}$. These differ by at most

$$\begin{aligned} |K^\#(z_j - z_k) - K^\# * \varphi_j * \varphi_k(z_j - z_k)| &\leq \\ &\leq \frac{C(\delta(z_j) + \delta(z_k))^3}{|z_j - z_k|^4} + C(\delta(z_j) + \delta(z_k))^2 H(z_j - z_k), \end{aligned} \quad (5.17)$$

where

$$H(x) = R_0|x|^{-3} \cdot \sum_{k=1}^{\infty} \chi_{|x| - R_k < 2R_0}.$$

(To check (5.17), just Taylor-expand $K^\#$ about $z_j - z_k$ to order 1 or 2, and invoke (5.13), (5.14), and the moment properties of φ .)

Consequently,

$$\begin{aligned} V[K^\#] \geq K^\#\{\rho\} - C \sum_j \delta^{-1}(z_j) - C \sum_{j \neq k} \frac{(\delta(z_j) + \delta(z_k))^3}{|z_j - z_k|^4} - \\ - C \sum_{j \neq k} (\delta(z_j) + \delta(z_k))^2 H(z_j - z_k). \end{aligned} \quad (5.18)$$

To handle the last two terms on the right, set

$$F(x) = \sum_j \delta^{-3}(z_j) \chi_{|x-z_j| < (1/3)\delta(z_j)}, \quad G(x) = \sum_j \delta^{-1}(z_j) \chi_{|x-z_j| < (1/3)\delta(z_j)}.$$

Thus

$$\int F^{4/3} = \int G^4 \leq C \sum_j \delta^{-1}(z_j).$$

On the other hand,

$$\begin{aligned} \sum \frac{\delta^3(z_j)}{(\delta(z_j) + |z_j - z_k|)^4} &\leq \\ &\leq C \sum_j \int_{|x-z_j| < (1/3)\delta(z_j)} G(x) \left[\int \frac{\delta(z_j)}{(\delta(z_j) + |x-y|)^4} F(y) dy \right] dx \leq \\ &\leq C \sum_j \int_{|x-z_j| < (1/3)\delta(z_j)} G(x) F^*(x) dx \end{aligned}$$

(with F^* = maximal function of F ; see Stein [10]) $= C \int_{\mathbb{R}^3} G F^* dx \leq C (\int G^4)^{1/4} (\int F^{4/3})^{3/4}$ (by the maximal theorem) $\leq C \sum_j \delta^{-1}(z_j)$. So

$$\sum_{j \neq k} \frac{\delta^3(z_j)}{|z_j - z_k|^4} \leq C' \sum_j \delta^{-1}(z_j).$$

Switching the roles of j and k , we conclude that

$$\sum_{j \neq k} \frac{(\delta(z_j) + \delta(z_k))^3}{|z_j - z_k|^4} \leq C'' \cdot \sum_j \delta^{-1}(z_j). \quad (5.19)$$

Similarly,

$$\sum_{j,k} \delta^2(z_j) H(z_j - z_k) \leq \sum_j \int_{|x-z_j| < (1/3)\delta(z_j)} G(x) \left[\int_{\mathbb{R}^3} H^+(x-y) F(y) dy \right] dx$$

with $H^+(x) = \max_{|w| \leq 2} H(x+w)$. So

$$\begin{aligned} \sum_{j,k} \delta^2(z_j) H(z_j - z_k) &\leq \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} G(x) H^+(x-y) F(y) dy dx \leq \\ &\leq \|H^+\|_{L^1} \|G\|_{L^4} \|F\|_{L^{4/3}} \leq C \sum_j \delta^{-1}(z_j). \end{aligned}$$

Again switching the roles of z_j, z_k , we get

$$\sum_{j,k} (\delta(z_j) + \delta(z_k))^2 H(z_j - z_k) \leq C' \sum \delta^{-1}(z_j).$$

Put this and (5.19) into (5.18), and recall that $K^\# \{\rho\} \geq 0$. The result is $V[K^\#] \geq -C \sum_j \delta^{-1}(z_j)$, which implies (5.16) by virtue of (5.12).

Lemma 5.3 is proved.

We conclude this section by relating $V[K]$ to $V_{LR}(R)$ defined by (5.1), when $K(x)$ is a Coulomb-like potential supported in $|x| \gg R$. Note that

$$V_{LR}(R_0) = \frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|} dx dy \geq 0,$$

where $\rho(x) = \sum_j \epsilon(j) \varphi_{R_0}(x - z_j)$. As before, assume $100 < R_0 < R_1 < R_2 < \dots$ with $R_{k+1} > 100 R_k$ and $R_1 > R_0^{10}$. Now, however, let $K(\cdot)$ be a kernel on R^3 satisfying

$$|\partial^\alpha K(x)| \leq C|x|^{-1-|\alpha|} \quad \text{for } |\alpha| \leq 2 \quad \text{and all } x. \quad (5.20)$$

$$|\partial^\alpha K(x)| \leq C|x|^{-1-|\alpha|} \quad \text{for } |\alpha| \leq 4 \quad \text{and all } x \quad (5.21)$$

outside the annuli $\mathcal{Q}_k = \{|x| - R_k < R_0\}$, $k = 1, 2, 3, \dots$

$$K(x) \text{ is supported in } |x| \geq R_1. \quad (5.22)$$

Lemma 5.4. *If K satisfies (5.20), (5.21) and (5.22), then*

$$V[K] \leq C V_{LR}(R_0) + \frac{C}{R_0} (H_{N, N'}^0 + CN + CN'). \quad (5.23)$$

PROOF. Write $K = \tilde{K} + K'$ with $\tilde{K} = K^* \varphi_{R_0} * \varphi_{R_0}$.

Then

$$\begin{aligned} V[\tilde{K}] &= \frac{1}{2} \sum_{j \neq k} \tilde{K}(z_j - z_k) \epsilon(j) \epsilon(k) = \frac{1}{2} \sum_{j, k} \tilde{K}(z_j - z_k) \epsilon(j) \epsilon(k) - \frac{1}{2} \sum_j \tilde{K}(0) = \\ &= \frac{1}{2} \int K(x-y) \rho(x) \rho(y) dx dy - \frac{1}{2} \tilde{K}(0) \cdot (N + N') \end{aligned}$$

with $\rho(x) = \sum_j \epsilon(j) \varphi_{R_0}(x - z_j)$. Now K satisfies (5.20), (5.21), which are stronger than (5.13), (5.14). In the proof of Lemma 5.3, we saw that $|\tilde{K}(\xi)| \leq C|\xi|^{-2}$. Also, $\tilde{K}(0) = 0$ by (5.22). Hence,

$$\begin{aligned} V[\tilde{K}] &= \frac{1}{2} \int \tilde{K}(\xi) |\hat{\rho}(\xi)|^2 d\xi \leq C \int |\xi|^{-2} |\hat{\rho}(\xi)|^2 d\xi = \\ &= C' \int \frac{\rho(x)\rho(y) dx dy}{|x-y|} = C'' V_{LR}(R_0). \quad (5.24) \end{aligned}$$

On the other hand, $K^* = R_0 K'$ satisfies (5.13) and (5.14). In fact, (5.14) is immediate from (5.20), while (5.13) follows by writing $\partial^\alpha K^*(x) = R_0 \int [\partial^\alpha K(x) - \partial^\alpha K(x-y)] \varphi_{R_0} * \varphi_{R_0}(y) dy$ and $|\partial^\alpha K(x) - \partial^\alpha K(x-y)| \leq$

$r|y| \cdot \sup_{0 \leq t \leq 1} |\nabla \partial^\alpha K(x - ty)|$. Here we recall that $R_1 \geq R_0^{10}$. Applying Lemma 5.3 to K^* , we find that

$$V[K'] \leq \frac{C}{R_0} (H_{N, N'}^\alpha + CN + CN').$$

Combining this with (5.24) and recalling that $K = \tilde{K} + K'$, we obtain (5.23).

6. A Swiss Cheese

Fix radii $100 < R_1 < R_2 < \dots < R_M$ with $R_{k+1} > 100 R_k$, and take a cube Q^+ of diameter $\sim M^{10} R_M$. For \bar{M} between $M/2$ and M , we describe how to cut Q^+ into balls of radii $R_1, R_2, \dots, R_{\bar{M}}$ and a small left-over part.

First cut Q^+ into a grid $\{Q_\nu\}$ of cubes of side $\sim 10R_{\bar{M}}$, and place a ball B_ν of radius $R_{\bar{M}}$ in the center of each Q_ν . Next, cut Q^+ into a grid $\{Q'_\nu\}$ of cubes of side $\sim 10R_{\bar{M}-1}$, and place a ball B'_ν of radius $R_{\bar{M}-1}$ in the center of each Q'_ν which does not meet any of the balls already introduced. Continue in this way until we have a family $\{B_{k\alpha}\}$ of balls of radius R_k ($2 \leq k \leq \bar{M}$) in Q^+ . Finally, cut Q^+ into a grid of cubes $\{Q_\alpha\}$ of side $\sim R_1$, and retain those Q_α which are not contained in any of the balls $B_{k\alpha}$. In this way, we cover Q^+ by balls $B_{k\alpha}$ and cubes Q_α . Note the following properties.

Distinct balls $B_{k\alpha}, B_{k'\alpha'}$ have distance > 50 from each other. (6.1)

$$\sum_\alpha |B_{k\alpha}| \leq e^{-c(\bar{M}-k)} |Q^+| \quad \text{for } 2 \leq k \leq \bar{M}. \quad (6.2)$$

$$\sum_\alpha |Q_\alpha| \leq e^{-c\bar{M}} |Q^+|. \quad (6.3)$$

Next suppose R^3 is cut into a grid of cubes $\{Q_\nu^+\}$, all congruent to Q^+ . We can translate our covering of Q^+ to cover each of the Q_ν^+ , thus obtaining a covering of all R^3 by balls $B_{k\alpha}$ of radius R_k , and cubes Q_α of side $\sim R_1$.

We introduce a partition of unity $1 = \sum_{k\alpha} \theta_{k\alpha}^2 + \sum_\alpha \theta_\alpha^2$ with the following properties.

Each $\theta_{k\alpha}(x) = \theta_k(x - x_{k\alpha})$, where $x_{k\alpha}$ is the center of $B_{k\alpha}$; and $\theta_k(x)$ is spherically symmetric, supported in $|x| \leq R_k$, and satisfies $|\partial^\gamma \theta_k(x)| \leq C_\gamma$ uniformly in k . (6.4)

Each $\theta_\alpha(x)$ is supported in $\{\text{dist}(x, Q_\alpha) < 1\} = \tilde{Q}_\alpha$ and satisfies $|\partial^\gamma \theta_\alpha| \leq C_\gamma$. (6.5)

It is easy to construct such a partition. One picks the θ_k first so that $\theta_k(x) = 1$ in $|x| < R_k - 1$, and $(1 - \theta_k^2)^{1/2} \in C^\infty$. Then the $\theta_{k\alpha}$ are defined, and $\sum_{k\alpha} \theta_{k\alpha}^2(x) + \varphi^2(x) = 1$ for some smooth function φ . Finally, one defines θ_α so that $\sum_\alpha \theta_\alpha^2 = \varphi^2$. Recall that $B_{k\alpha}, Q_\alpha, \theta_{k\alpha}, \theta_\alpha$ all depend on $\bar{M}((M/2) \leq \bar{M} \leq M)$. In all that follows, we will take radii $R_1 < R_2 < \dots < R_M$ so that

$e^{c_2\beta} < R_1$ and $R_M < e^{c_1\beta}$ with $0 < c_2 < c_1 \ll 1$ to be picked later. Thus, $M \sim \beta$, and the results of Section 3 apply to all the $B_{k\alpha}$.

7. Comparison with an Exploded System

Fix \bar{M} and Q^+ as in the preceding section. Thus, R^3 is covered by balls $B_{k\alpha}$ and cubes Q_α . Recall $\bar{Q}_\alpha = \{\text{dist}(x, Q_\alpha) < 1\}$. Define

$$\begin{aligned} \mathcal{Q}^{\bar{M}} &= \mathcal{Q} = \{D = B_{k\alpha} \text{ or } \bar{Q}_\alpha \mid D + \tau \text{ meets } \Omega \text{ for some } \tau \in Q^+\} \\ \mathcal{Q}^{0\bar{M}} &= \mathcal{Q}^0 = \{D \in \mathcal{Q} \mid D + \tau \subset \Omega \text{ for every } \tau \in Q^+\}. \end{aligned}$$

For $D \in \mathcal{Q}$, define a vector $\xi(D)$ so that the translates $\hat{D} = D + \xi(D)$ are pairwise disjoint for distinct $D \in \mathcal{Q}$. Then define the exploded set $\Omega_{ex}^{\bar{M}} = \bigcup_{D \in \mathcal{Q}} \hat{D}$. Often, we shall omit the superscript and just speak of Ω_{ex} . On Ω_{ex} we define a two-particle potential

$$K(z, z') = \begin{cases} |z - z'|^{-1} & \text{if } z, z' \in \hat{D} \text{ with } D = \text{one of the } B_{k\alpha} \\ 0 & \text{otherwise.} \end{cases}$$

Thus, $K = 0$ if z, z' belong to different components of Ω_{ex} , or if both particles belong to the same \hat{D} with $D = \bar{Q}_\alpha$. For particles $z_1 \dots z_{N+N'}$ in Ω_{ex} , with charges $\epsilon(1), \dots, \epsilon(N+N')$, define the potential $V_{ex} = \frac{1}{2} \sum_{j \neq k} \epsilon(j)\epsilon(k)K(z_j, z_k)$. Then define the Hamiltonian

$$H_{NN'}^{ex\bar{M}} = -\kappa_1 \Delta_x - \kappa_2 \Delta_y + V_{ex}, \text{ acting on } L^2_{N, N'}(\Omega_{ex}^{\bar{M}})$$

with Dirichlet boundary conditions.

For fixed \bar{M} and $\tau \in Q^+$, there is a natural injection $\iota_\tau^{\bar{M}} = \iota: L^2_*(\Omega) \rightarrow L^2_*(\Omega_{ex})$, which we use to relate observables on Ω_{ex} to those on Ω . Preparing to define ι , we set $\theta(x, D) = \theta_{k\alpha}(x)$ if $D = B_{k\alpha}$, $\theta(x, D) = \theta_\alpha(x)$ if $D = \bar{Q}_\alpha$. Thus, $\theta(x, D)$ is supported in $x \in D$, and $\sum_{D \in \mathcal{Q}} \theta^2(x - \tau, D) = 1$ for $x \in \Omega$, $\tau \in Q^+$. Now we define ι . This means that for $\psi \in L^2_{N, N'}(\Omega)$ and $\hat{x}_1 \dots \hat{x}_N \hat{y}_1 \dots \hat{y}_{N'} \in \Omega_{ex}$, we have to define $(\iota\psi)(\hat{x}_1 \dots \hat{x}_N \hat{y}_1 \dots \hat{y}_{N'})$. Each \hat{x}_j belongs to a unique \hat{D}_j , so we can write $\hat{x}_j = x_j + \xi(D_j)$ for $x_j \in D_j$ and $D_j \in \mathcal{Q}$. Similarly, we can express $\hat{y}_k = y_k + \xi(D'_k)$ for $y_k \in D'_k$ and $D'_k \in \mathcal{Q}$. We define

$$\begin{aligned} (\iota\psi)(\hat{x}_1 \dots \hat{x}_N, \hat{y}_1 \dots \hat{y}_{N'}) &= \\ &= \prod_{j=1}^N \theta(x_j - \tau, D_j) \prod_{k=1}^{N'} \theta(y_k - \tau, D'_k) \cdot \psi(x_1 \dots x_N, y_1 \dots y_{N'}). \end{aligned}$$

Here, the right-hand side is interpreted as zero if any of the $x_1 \dots x_N y_1 \dots y_{N'}$ fail to belong to Ω . This is an isometry from $L^2_{N, N'}(\Omega)$ into $L^2_{N, N'}(\Omega_{ex})$.

It is important to compare the Hamiltonian $H_{N,N'}^{\Omega}$ with

$$\mathfrak{h} = Av_{\overline{M}\tau}[(\overline{M}) * H_{N,N'}^{ex\overline{M}}, (\overline{M})].$$

Here, $Av_{\tau, \overline{M}}$ means an average over all $\tau \in Q^+$ and all \overline{M} between $M/2$ and M . A computation analogous to that in [3] shows that

$$\mathfrak{h} = -\varkappa_1 \Delta_x - \varkappa_2 \Delta_y + V[K] + G \cdot (\varkappa_1 N + \varkappa_2 N')$$

where

$$\begin{aligned} K(x) &= |x|^{-1} \sum_{2 \leq k \leq M} \lambda_k \frac{\theta_k^2 * \theta_k^2(x)}{\frac{4}{3} \pi R_k^3} \\ \lambda_k &= Av_{\overline{M}} \left[\sum_{\alpha \ni B_{k\alpha} \subset Q^+} |B_{k\alpha}| / |Q^+| \right] \\ G &= -Av_{\overline{M}} Av_{\tau} \left[\sum_{k\alpha} \theta_{k\alpha} \Delta \theta_{k\alpha}(\tau) + \sum_{\alpha} \theta_{\alpha} \Delta \theta_{\alpha}(\tau) \right] \end{aligned}$$

Here, θ_k is as in (5.4). Note that unlike [3], we are able to treat electrons and protons in the same way. Therefore, our potential energy term has exactly the form $V[K]$ without the extra error terms arising in [3].

Next we use the above formulas to compare \mathfrak{h} with $H_{N,N'}^{\Omega}$. Recall that the radii for our Swiss cheese satisfy

$$e^{c_2\beta} < R_1 < R_2 < \dots < R_M < e^{c_1\beta} \quad \text{with } c_1 \ll 1 \text{ and } M \sim \beta.$$

We have $|G| \leq e^{-c\beta}$ by the geometric properties (6.1), (6.2), (6.3). Also with

$$m_k = \frac{\theta_k^2 * \theta_k^2(0)}{\frac{4}{3} \pi R_k^3},$$

we have $m_k = 1 + O(R_k^{-1})$ so that $1 \geq \sum_k \lambda_k m_k \geq 1 - e^{-c\beta}$, again by (6.1), (6.2), (6.3).

Now write

$$\mathfrak{h} = H_{N,N'}^{\Omega} + G(\varkappa_1 N + \varkappa_2 N') + V[K_1 + K_2 - K_3] \quad (7.1)$$

with

$$\begin{aligned} K_1(x) &= \sum_{k=1}^M \lambda_k [|x|^{-1} \frac{\theta_k^2 * \theta_k^2(x)}{\frac{4}{3} \pi R_k^3} - m_k (|x|^{-1} - |x|^{-1} * \varphi_{R_k} * \varphi_{R_k})] \\ K_2(x) &= \left(\sum_{k=1}^M \lambda_k m_k - 1 \right) |x|^{-1} \\ K_3(x) &= \sum_{k=1}^M \lambda_k m_k |x|^{-1} * \varphi_{R_k} * \varphi_{R_k}. \end{aligned}$$

Here φ_{R_k} is as in the definition (5.1) of $V_{LR}(R_k)$. As in [3], we find that MK_1 and $e^{c\beta}K_2$ satisfy (5.13), (5.14) with $R_0 = 10^3$. Therefore, Lemma 5.3 yields

$$\begin{aligned} V[K_1] &\leq \frac{C}{M}(H_{N,N'}^\Omega + CN + CN') \sim C\beta^{-1}(H_{N,N'}^\Omega + CN + CN') \\ V[K_2] &\leq Ce^{-c\beta}(H_{N,N'}^\Omega + CN + CN'). \end{aligned}$$

From (6.1) we get $\mathfrak{h} \leq H - V[K_3] + C\beta^{-1}(H + CN + CN')$, so that

$$\begin{aligned} \ln \operatorname{Tr} \exp\{\mu(N + N') - \beta(H - V[K_3] + \frac{C}{\beta}(H + CN + CN'))\} &\leq \\ \ln \operatorname{Tr} \exp\{\mu(N + N') - \beta\mathfrak{h}\} &\leq Av_{\bar{M}}\tau \ln \operatorname{Tr} \exp\{\mu(N + N') - \beta H^{ex \bar{M}}\}. \end{aligned}$$

The last inequality holds because $\operatorname{Tr} \exp\{\iota^* A \iota\} \leq \operatorname{Tr} \exp A$ for injections ι of Hilbert spaces, and because $A \rightarrow \ln \operatorname{Tr} \exp A$ is convex; again, see [3]. We are now regarding all operators as acting on L_*^2 . Our estimate may be rewritten as

$$\begin{aligned} \ln \operatorname{Tr} \exp\{(\mu - C')(N + N') - (\beta + C_1)H^\Omega + \beta V[K_3]\} &\leq \\ &\leq Av_{\bar{M}} \ln \operatorname{Tr} \exp\{\mu(N + N') - \beta H^{ex \bar{M}}\} \\ &= Av_{\bar{M}} \ln \prod_{B_{k\alpha} \in \mathbb{Q}^{\bar{M}}} Z(\mu, \beta, B_{k\alpha}) \cdot \prod_{\tilde{Q}_\alpha \in \mathbb{Q}^{\bar{M}}} Z_0(\mu, \beta, \tilde{Q}_\alpha), \end{aligned} \quad (7.2)$$

since the system is made of the non-interacting subsystems \hat{D} , $D \in \mathbb{Q}^{\bar{M}}$. Now (3.9) and its analogue for Z_{neutral} show that

$$\begin{aligned} Z(\mu, \beta, B_{k\alpha}) &\leq Z_{\text{neutral}}(\mu, \beta + C_1, B_{k\alpha}) \cdot r(\mu, \beta, k) \quad \text{for some } r(\mu, \beta, k) < 1, \\ \text{while } Z_0(\mu, \beta, \tilde{Q}_\alpha) &\leq \exp(Ce^\mu \beta^{-3/2} |\tilde{Q}_\alpha|). \end{aligned}$$

Hence (7.2) implies for some \bar{M}

$$\begin{aligned} \operatorname{Tr} \exp\{(\mu - C')(N + N') - (\beta + C_1)H^\Omega + \beta V[K_3]\} &\leq \\ &\leq \prod_{B_{k\alpha} \in \mathbb{Q}^{\bar{M}}} (Z_{\text{neutral}}(\mu, \beta + C_1, B_{k\alpha}) \cdot r(\mu, \beta, k)) \cdot \exp(Ce^\mu \beta^{-3/2} \sum_{\tilde{Q}_\alpha \in \mathbb{Q}^{\bar{M}}} |\tilde{Q}_\alpha|). \end{aligned} \quad (7.3)$$

By the method of Lebowitz-Lieb [7],

$$\prod_{B_{k\alpha} \in \mathbb{Q}^{0\bar{M}}} Z_{\text{neutral}}(\mu, \beta + C_1, B_{k\alpha}) \leq \operatorname{Tr} \exp\{\mu(N + N') - (\beta + C_1)H^\Omega\}.$$

Moreover, the product

$$\prod_{B_{k\alpha} \in \mathbb{Q}^{\bar{M}} \setminus \mathbb{Q}^{0\bar{M}}} Z_{\text{neutral}}(\mu, \beta + C_1, B_{k\alpha})$$

is absorbed by

$$\prod_{B_{k\alpha} \in \mathbb{Q}^{\bar{M}}} r(\mu, \beta, k),$$

provided Ω is big enough. (To be precise, we require that $\text{Vol}\{\text{dist}(x, \partial\Omega) < e^{c_1\beta}\}/\text{Vol}\Omega$ be less than a small constant depending on μ, β .) Therefore (7.3) implies

$$\begin{aligned} & \text{Tr} \exp\{(\mu - C')(N + N') - (\beta + C_1)H^\Omega + \beta V[K_3]\} \leq \\ & \leq \text{Tr} \exp\{\mu(N + N') - (\beta + C_1)H^\Omega\} \cdot \exp(Ce^\mu \beta^{-3/2} \sum_{\bar{Q}_\alpha \in \mathcal{Q}_M} |\bar{Q}_\alpha|). \end{aligned} \quad (7.4)$$

The last factor on the right is at most $\exp(Ce^{-\beta/4}\rho|\Omega|)$ by (4.10). Consequently, applying (7.4) to $\bar{\beta} = \beta - C_1$, we have

$$\begin{aligned} & \text{Tr} \exp\{\mu(N + N') - \beta H^\Omega + ((\beta - C_1)V[K_3] - C'(N + N'))\} \leq \\ & \leq \text{Tr} \exp\{\mu(N + N') - \beta H^\Omega\} \cdot \exp(Ce^{-\beta/4}\rho|\Omega|), \end{aligned}$$

which implies

$$\langle (\beta - C_1)V[K_3] - C'N - C'N' \rangle \leq Ce^{-\beta/4}\rho|\Omega|. \quad (7.5)$$

Recalling the definition of K_3 , we see that

$$V[K_3] = \sum_k \lambda_k m_k V_{LR}(R_k) + O(R_1^{-1} \cdot (N + N')),$$

the error arising from self-energy terms in $V_{LR}(R_k)$. Since $R_1^{-1} \leq e^{-c_2\beta}$, estimate (7.5) yields

$$\left\langle \sum_{k=1}^M \lambda_k m_k V_{LR}(R_k) \right\rangle \leq \frac{C}{\beta} \langle N + N' \rangle + Ce^{-\beta/4}\rho|\Omega|. \quad (7.6)$$

Next, fix radii $R'_1 < R'_2 < \dots < R'_M < R_1 < R_2 < \dots < R_M$, so that $R'_1 > e^{c_2\beta}$, $R'_{k+1} > 100R_k$, $R_1 > (R'_M)^{20}$, $R_{k+1} > 100R_k$, $R_M < e^{c_1\beta}$, $M \sim \beta$, for $0 < 30c_2 < c_1 \ll 1$. Since the R'_k give rise to an ensemble of Swiss cheeses, we have the analogue of (7.6), namely

$$\left\langle \sum_{k=1}^M \lambda_k m_k V_{LR}(R'_k) \right\rangle \leq \frac{C}{\beta} \langle N + N' \rangle + Ce^{-\beta/4}\rho|\Omega| \quad (7.7)$$

for Ω large enough. We use (7.7) to study the Swiss cheeses defined by $R_1 \dots R_M$. Our starting point is (7.1). As before, we know that $V[K_2] + G(x_1N + x_2N') \leq e^{-c\beta}(H^\Omega + CN + CN')$. Since $V_{LR}(R_k) \geq 0$, (7.1) implies

$$\mathfrak{h} \leq H^\Omega + V[K_1] + e^{-c\beta}(H^\Omega + CN + CN'). \quad (7.8)$$

Now take $R_0 =$ any of the R'_k , and define a cutoff function

$$\eta(x) = \begin{bmatrix} 1 & \text{for } |x| > 2 \cdot R_0^{12} \\ 0 & \text{for } |x| < R_0^{12} \\ \text{smooth in between} & \end{bmatrix}$$

Then Lemma 5.4 applies to $M\eta(x)K_1(x)$ if we use R_0^{12} , R_1, R_2, \dots in place of R_1, R_2, \dots in (5.21). Moreover, Lemma 5.3 applies to $e^{c\beta}(1 - \eta(x))K_1(x)$. Those Lemmas yield

$$\begin{aligned} V[\eta K_1] &< \frac{C}{M} V_{LR}(R_0) + \frac{C}{MR_0} (H^\Omega + CN + CN') \\ &< \frac{C}{\beta} V_{LR}(R_0) + e^{-c\beta} (H^\Omega + CN + CN') \end{aligned}$$

and $V[(1 - \eta)K_1] \leq e^{-c\beta} (H^\Omega + CN + CN')$. Putting these estimates into (7.8) gives

$$h \leq H + \frac{C}{\beta} V_{LR}(R_0) + e^{-c\beta} (H^\Omega + CN + CN').$$

Recall that R_0 here can be any of the R'_k , and that the coefficients $\lambda_k m_k$ sum approximately to 1. Therefore by taking a weighted sum of the last inequality over all the R'_k , we conclude that

$$h \leq H + \frac{C}{\beta} \left(\sum_{k=1}^M \lambda_k m_k V_{LR}(R'_k) \right) + e^{-c\beta} (H^\Omega + CN + CN'). \quad (7.9)$$

8. The Expected Value of Certain Observables

In this section, we explain how to estimate the expected value of certain observables \mathcal{Q} on $L_*^2(\Omega)$ in terms of information on the exploded system. Suppose for each τ , \bar{M} we specify an observable $A_{ex}(\tau, \bar{M})$ on the exploded system $L_*^2(\Omega_{ex}^{\bar{M}})$, and suppose

$$\begin{aligned} \text{Tr exp}\{A_{ex}(\tau, \bar{M}) + \mu(N + N') - \bar{\beta}H^{ex\bar{M}}\} &\leq \\ &\leq e^S \text{Tr exp}\{\mu(N + N') - \bar{\beta}H^{ex\bar{M}}\} \quad \text{for each } \tau, \bar{M}. \end{aligned} \quad (8.1)$$

Here S is a real number independent of τ, \bar{M} ; and $\bar{\beta}$ very near β is to be determined. There is an induced observable

$$\mathcal{Q} = Av_{\tau, \bar{M}}[(\iota_\tau^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_\tau^{\bar{M}})]$$

defined on $L_*^2(\Omega)$.

Our goal here is to estimate $\langle \mathcal{Q} \rangle$. Later on, we shall pick $A_{ex}(\tau, \bar{M})$ so that our estimate on $\langle \mathcal{Q} \rangle$ gives a strong hold on what most of the particles are doing.

Start with estimate (7.9). Setting $\bar{V}_{LR} = \sum_{k=1}^M \lambda_k m_k' V_{LR}(R_k)$, we have from (7.9)

$$\begin{aligned} \ln \operatorname{Tr} \exp\{\mathcal{Q} + \mu(N + N') - \bar{\beta}H^\Omega - C\bar{V}_{LR} - e^{-c\bar{\beta}}(H^\Omega + CN + CN')\} &\leq \\ &\leq \ln \operatorname{Tr} \exp\{\mathcal{Q} + \mu(N + N') - \bar{\beta}h\} \leq \\ &Av_{\tau\bar{M}} \ln \operatorname{Tr} \exp\{A_{ex}(\tau, \bar{M}) + \mu(N + N') - \bar{\beta}H^{ex\bar{M}}\}. \end{aligned} \quad (8.2)$$

The last estimate holds because $\operatorname{Tr} \exp(\iota^* A \iota) \leq \operatorname{Tr} \exp A$ for injections ι of Hilbert spaces, and because $A \rightarrow \ln \operatorname{Tr} \exp A$ is convex.

From (8.1) and (8.2) we obtain for at least one (τ, \bar{M}) that

$$\begin{aligned} \operatorname{Tr} \exp\{\mathcal{Q} + \mu(N + N') - \bar{\beta}H^\Omega - C\bar{V}_{LR} - e^{-c\bar{\beta}}(H^\Omega + CN + CN')\} &\leq \\ &\leq e^S \operatorname{Tr} \exp\{\mu(N + N') - \bar{\beta}H^{ex\bar{M}}\} = \\ &= e^S \cdot \prod_{B_{k\alpha} \in \mathcal{Q}^{\bar{M}}} Z(\mu, \bar{\beta}, B_{k\alpha}) \cdot \prod_{\bar{Q}_\alpha \in \mathcal{Q}^{\bar{M}}} Z_0(\mu, \bar{\beta}, \bar{Q}_\alpha). \end{aligned} \quad (8.3)$$

As in the discussion of (7.3), (7.4), (7.5), we know from (4.9), (4.10) that

$$Z(\mu, \bar{\beta}, B_{k\alpha}) \leq Z_{\text{neutral}}\left(\mu, \bar{\beta} + \frac{C'}{\bar{\beta}}, B_{k\alpha}\right) \cdot r(\mu, \beta, k)$$

with C' a fixed large constant and $r < 1$.

Also

$$\prod_{\bar{Q}_\alpha \in \mathcal{Q}^{\bar{M}}} Z_0(\mu, \bar{\beta}, \bar{Q}_\alpha) \leq \exp(Ce^{-\beta/4} \rho |\Omega|),$$

as in Section 7. Hence, as before, an application of the Lebowitz-Lieb technique [7] shows that

$$\begin{aligned} \operatorname{Tr} \exp\{\mathcal{Q} + \mu(N + N') - \bar{\beta}H^\Omega - C\bar{V}_{LR} - C'\bar{\beta}^{-1}(H^\Omega + CN + CN')\} &\leq \\ &\leq e^S \operatorname{Tr} \exp\{\mu(N + N') - (\bar{\beta} + C'\bar{\beta}^{-1})H^\Omega\} \cdot \exp(Ce^{-\bar{\beta}/4} \rho |\Omega|). \end{aligned}$$

In other words,

$$\begin{aligned} \operatorname{Tr} \exp\{\mu(N + N') - (\bar{\beta} + C'\bar{\beta}^{-1})H^\Omega + [\mathcal{Q} - C\bar{V}_{LR} - C'\bar{\beta}^{-1}(CN + CN')]\} &\leq \\ &\leq [\operatorname{Tr} \exp\{\mu(N + N') - (\bar{\beta} + C'\bar{\beta}^{-1})H^\Omega\}] \cdot \exp(S + Ce^{-\bar{\beta}/4} \rho |\Omega|). \end{aligned} \quad (8.4)$$

Now pick $\bar{\beta}$ near β so that $\bar{\beta} + C'\bar{\beta}^{-1} = \beta$. Then (8.4) implies

$$\langle \mathcal{Q} \rangle \leq C \langle \bar{V}_{LR} \rangle + \frac{C''}{\beta} \langle N + N' \rangle + Ce^{-\bar{\beta}/4} \rho |\Omega| + S.$$

Recalling

$$\bar{V}_{LR} = \sum_{k=1}^M \lambda_k m'_k V_{LR}(R_k)$$

and (7.7), we get from the last inequality

$$\langle \mathcal{Q} \rangle \leq S + \frac{C}{\beta} \langle N + N' \rangle + C e^{-\beta/4} \rho |\Omega|. \quad (8.5)$$

In the sections to follow, we pick $A_{ex}(\tau, \bar{M})$ so that (8.1) can be verified and (8.5) gives useful information.

9. The Density of the System

For fixed \bar{M} the partition function of the exploded system is

$$\begin{aligned} \text{Tr } e^{\mu(N+N') - \bar{\beta}H^{ex}} &= \prod_{B_{k\alpha} \in \mathcal{Q}} Z(\mu, \bar{\beta}, B_{k\alpha}) \cdot \prod_{\tilde{Q}_\alpha \in \mathcal{Q}} Z_0(\mu, \bar{\beta}, \tilde{Q}_\alpha) = \\ &= \exp \left\{ \frac{(\text{const})}{\bar{\beta}^{3/2}} e^{2\mu + (1/4)\bar{\beta}} |\Omega| \cdot (1 + O(\bar{\beta}^{-1})) \right\}, \end{aligned}$$

by the results of Section 3. Hence for $0 < t < 1$, we know that

$$\begin{aligned} \text{Tr } \exp \{ \pm t(N + N' - 2\bar{\rho}|\Omega|) + \mu(N + N') - \bar{\beta}H^{ex} \} &\leq \\ &\leq e^S \text{Tr } \exp \{ \mu(N + N') - \bar{\beta}H^{ex} \}, \quad (9.1) \end{aligned}$$

where

$$\bar{\rho} = \frac{(\text{const})e^{2\mu + (1/4)\bar{\beta}}}{\bar{\beta}^{3/2}}, \quad S = C\bar{\rho}|\Omega|(\bar{\beta}^{-1} + t^2). \quad (9.2)$$

Writing

$$L_*^2(\Omega_{ex}) = \left[\sum_{N+N' \geq \bar{\rho}|\Omega|} \oplus L_{N, N'}^2(\Omega_{ex}) \right] \oplus \left[\sum_{N+N' < \bar{\rho}|\Omega|} \oplus L_{N, N'}^2(\Omega_{ex}) \right]$$

and applying (9.1) with the two signs \pm for the two spaces in square brackets, we conclude that

$$\begin{aligned} \text{Tr } \exp \{ t|N + N' - 2\bar{\rho}|\Omega| + \mu(N + N') - \bar{\beta}H^{ex} \} &\leq \\ &\leq e^S \text{Tr } \exp \{ \mu(N + N') - \bar{\beta}H^{ex} \}. \end{aligned}$$

This holds for each \bar{M} . Moreover, the number operators N, N' commute with the injections $\iota_{\tau}^{\bar{M}}: L_*^2(\Omega) \rightarrow L_*^2(\Omega_{ex})$. So if we define

$$A_{ex}(\tau, \bar{M}) = t|N + N' - 2\bar{\rho}|\Omega|,$$

then $\mathcal{Q} = Av_{\tau, \bar{M}}(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_{\tau}^{\bar{M}}) = t|N + N' - 2\rho|\Omega|$ also. Therefore, estimate (7.5) yields

$$\begin{aligned} t\langle |N + N' - 2\bar{\rho}|\Omega| \rangle &\leq \frac{C}{\bar{\beta}} \langle N + N' \rangle + C\bar{\rho}|\Omega|(\bar{\beta}^{-1} + t^2) \leq \\ &\leq \frac{C}{\bar{\beta}} \langle |N + N' - 2\bar{\rho}|\Omega| \rangle + C'\bar{\rho}|\Omega|(\bar{\beta}^{-1} + t^2). \end{aligned}$$

Picking $t = \bar{\beta}^{-1/2}$, we can absorb the first term on the right into the left-hand side, leaving us with

$$\langle |N + N' - 2\bar{\rho}|\Omega| \rangle \leq C\bar{\beta}^{-1/2}\bar{\rho}|\Omega|.$$

Recalling (4.10), (9.2) and $\bar{\beta} + C'\bar{\beta}^{-1} = \beta$, we can rewrite the last estimate as

$$\langle |N + N' - 2\rho|\Omega| \rangle \leq C\beta^{-1/2}\rho|\Omega|. \quad (9.3)$$

Hence the total number of particles clusters around the obvious guess $2\rho|\Omega|$. In view of (9.3), we can rewrite estimate (8.5) in the simpler form

$$\langle \mathcal{Q} \rangle \leq S + \frac{C}{\beta}\rho|\Omega|. \quad (9.4)$$

Estimate (9.4) holds when $\mathcal{Q} = Av_{\tau, \bar{M}}[(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_{\tau}^{\bar{M}})]$ for $A_{ex}(\tau, \bar{M})$ satisfying (8.1), with $\bar{\beta} + C'\bar{\beta}^{-1} = \beta$ and $\bar{\beta}$ near β .

In addition to (9.3), we shall need to know later that if $F \subset \Omega$ with $F_* = \{ \text{dist}(x, F) < e^{c_1\beta} \}$ having volume $|F_*| < \beta^{-1}|\Omega|$, then

$$\langle \text{Number of particles in } F \rangle \leq C\beta^{-1}\rho|\Omega|. \quad (9.5)$$

To see this, let $A_{ex}(\tau, \bar{M}) = [\text{Number of particles in those } \hat{D} \text{ with } (D + \tau) \cap \Omega \neq \emptyset, D \in \mathcal{Q}^{\bar{M}}]$. Since $A_{ex}(\tau, \bar{M}) = \sum_j \chi_{F_{ex}}(z_j)$ with

$$F_{ex} = \bigcup \{ \hat{D} \mid (D + \tau) \cap \Omega \neq \emptyset, D \in \mathcal{Q}^{\bar{M}} \},$$

one computes easily that $(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_{\tau}^{\bar{M}}) = \sum_j V(z_j)$ with

$$V(x) = \sum_{\substack{(D+\tau) \cap \Omega \neq \emptyset \\ D \in \mathcal{Q}^{\bar{M}}}} \theta^2(x - \tau, D) \geq \chi_F(x).$$

Hence $\mathcal{Q} = Av_{\tau, \bar{M}}[(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_{\tau}^{\bar{M}})] \geq (\text{Number of particles in } F)$.

On the other hand, for fixed τ, \bar{M} we have

$$\begin{aligned} \text{Tr exp}\{A_{ex} + \mu(N + N') - \bar{\beta} \cdot \bar{H}^{ex}\} &= \\ &= \prod_{\substack{B_{k\alpha} \in \mathcal{Q} \\ (B_{k\alpha} + \tau) \cap F = \phi}} Z(\mu, \bar{\beta}, B_k) \cdot \prod_{\substack{\bar{Q}_\alpha \in \mathcal{Q} \\ (\bar{Q}_\alpha + \tau) \cap F = \phi}} Z_0(\mu, \bar{\beta}, \bar{Q}_\alpha) \cdot \\ &\cdot \prod_{\substack{B_{k\alpha} \in \mathcal{Q} \\ (B_{k\alpha} + \tau) \cap F \neq \phi}} Z(\mu + 1, \bar{\beta}, B_k) \cdot \prod_{\substack{\bar{Q}_\alpha \in \mathcal{Q} \\ (\bar{Q}_\alpha + \tau) \cap F \neq \phi}} Z_0(\mu + 1, \bar{\beta}, \bar{Q}_\alpha) \leq \\ &\leq e^S \text{Tr exp}\{\mu(N + N') - \bar{\beta} H^{ex}\} \quad \text{with } S = C\bar{\rho}|F_*|, \end{aligned}$$

by the results of Section 4. So (9.4) gives

$$\langle \text{Number of particles in } F \rangle \leq \langle \mathcal{Q} \rangle \leq \frac{C}{\bar{\beta}} \rho |\Omega| + C\rho |F_*|,$$

which proves (9.5).

10. Particles Form Atoms

The next application of the technique of Section 8 is to show that the vast majority of the electrons and protons pair up into ‘‘atoms’’. Our definition of ‘‘atom’’ is at first quite weak. For $0 < c' < c'' \ll 1$, we define an *atom of type* (c', c'') as an electron-proton pair $\{x_{j_0}, y_{k_0}\}$ with $|x_{j_0} - y_{k_0}| < e^{c'\beta}$ and $|x_{j_0} - z_l|, |y_{k_0} - z_l| > e^{c''\beta}$ for any particle z_l other than x_{j_0}, y_{k_0} .

To show that most of the particles belong to atoms, we use the observables

$$\begin{aligned} A_{ex}(\tau, \bar{M}) &= \sum_{B_{k\alpha} \in \mathcal{Q}_{\bar{M}}} (\text{Number of particles in } \hat{B}_{k\alpha}) \chi_{\hat{B}_{k\alpha} \text{ not of } ep\text{-type}}, \\ &\equiv \sum_{B_{k\alpha} \in \mathcal{Q}_{\bar{M}}} A_{ex}(\tau, \bar{M}, B_{k\alpha}) \end{aligned}$$

where $\hat{B}_{k\alpha}$ is of *ep-type* if it contains exactly one electron and one proton. For a fixed τ, \bar{M} we have

$$\begin{aligned} \text{Tr exp}\{A_{ex}(\tau, \bar{M}) + \mu(N + N') - \bar{\beta} H^{ex\bar{M}}\} &= \prod_{\bar{Q}_\alpha \in \mathcal{Q}_{\bar{M}}} Z_0(\mu, \bar{\beta}, \bar{Q}_\alpha) \cdot \\ &\cdot \prod_{B_{k\alpha} \in \mathcal{Q}_{\bar{M}}} \text{Tr exp}\{A_{ex}(\tau, \bar{M}, B_{k\alpha}) + \mu(N + N') - \bar{\beta} H^{B_{k\alpha}}\}, \end{aligned}$$

and

$$\begin{aligned} \text{Tr exp}\{A_{ex}(\tau, \bar{M}, B_{k\alpha}) + \mu(N + N') - \bar{\beta} H^{B_{k\alpha}}\} &= \\ Z(\mu, \bar{\beta}, B_{k\alpha}, 1, 1) + \sum_{(N, N') \neq (1, 1)} Z(\mu + 1, \bar{\beta}, B_{k\alpha}, N, N'). \end{aligned}$$

Hence the results of Section 4 show that

$$\begin{aligned} \text{Tr exp}\{A_{ex}(\tau, \bar{M}) + \mu(N + N') - \bar{\beta}H^{ex\bar{M}}\} &\leq \\ &\leq e^S \text{Tr exp}\{\mu(N + N') - \bar{\beta}H^{ex\bar{M}}\} \quad \text{with } S = C\beta^{-1}\rho|\Omega|. \end{aligned}$$

Estimate (9.4) therefore shows that

$$\langle \mathcal{Q} \rangle \leq \frac{C}{\beta} \rho |\Omega|, \quad \mathcal{Q} = Av\tau, \bar{M}[(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_{\tau}^{\bar{M}})]. \quad (10.0)$$

Now we compute \mathcal{Q} . It is convenient to work temporarily with operators which do not necessarily preserve antisymmetry of wave functions.

First let us fix $\tau, \bar{M}, B_{k\alpha} \in \mathcal{Q}^{\bar{M}}$ and $J \subset \{1 \dots N + N'\}$. Then define an operator A_J on $L_*^2(\Omega_{ex})$ by

$$A_J \psi(\hat{z}_1 \dots \hat{z}_{N+N'}) = \prod_{j \in J} \chi_{\hat{B}_{k\alpha}}(\hat{z}_j) \cdot \prod_{j \notin J} (1 - \chi_{\hat{B}_{k\alpha}}(\hat{z}_j)) \cdot \psi(\hat{z}_1 \dots \hat{z}_{N+N'}).$$

We have

$$(\iota\psi)(\hat{z}_1 \dots \hat{z}_{N+N'}) = \prod_j \theta(z_j - \tau, D_j) \psi(z_1 \dots z_{N+N'})$$

for $\psi \in L_*^2(\Omega)$, $\hat{z}_j = z_j + \xi(D_j)$ with $z_j \in D_j$, $D_j \in \mathcal{Q}^{\bar{M}}$. Hence

$$\begin{aligned} \langle A_J \iota\psi, \iota\psi \rangle &= \sum_{D_1 \dots D_{N+N'}} \int \prod_{j \in J} \theta^2(z_j - \tau, B_{k\alpha}) \chi_{D_j = B_{k\alpha}} \cdot \\ &\cdot \prod_{j \notin J} \theta^2(z_j - \tau, D_j) \chi_{D_j \neq B_{k\alpha}} |\psi(z_1 \dots z_{N+N'})|^2 dz_1 \dots dz_{N+N'} = \\ &= \int \left[\prod_{j \in J} \theta_{k\alpha}^2(z_j - \tau) \right] \left[\prod_{j \notin J} (1 - \theta_{k\alpha}^2)(z_j - \tau) \right] \cdot \\ &\cdot |\psi(z_1 \dots z_{N+N'})|^2 dz_1 \dots dz_{N+N'} \end{aligned} \quad (10.1)$$

Next fix $\tau, \bar{M}, B_{k\alpha} \in \mathcal{Q}^{\bar{M}}$, and integers n, n' . We define $A^{nn'}$ on $L_*^2(\Omega_{ex}^{\bar{M}})$ by

$$A^{nn'} \psi(\hat{z}_1 \dots \hat{z}_{N+N'}) = \chi \left(\begin{array}{l} \text{Number of electrons in } \hat{B}_{k\alpha} = n \\ \text{Number of protons in } \hat{B}_{k\alpha} = n' \end{array} \right) \cdot \psi(\hat{z}_1 \dots \hat{z}_{N+N'}).$$

Thus $A^{nn'} = \sum_J A_J$ over those J containing n electrons and n' protons. So (10.1) implies

$$\begin{aligned} \iota^* A^{nn'} \iota &= \sum_{\substack{|J| = n \\ |J'| = n'}} \prod_{j \in J} \theta_{k\alpha}^2(x_j - \tau) \cdot \prod_{j \notin J} (1 - \theta_{k\alpha}^2(x_j - \tau)) \cdot \\ &\cdot \prod_{j \in J'} \theta_{k\alpha}^2(y_j - \tau) \cdot \prod_{j \notin J'} (1 - \theta_{k\alpha}^2(y_j - \tau)). \end{aligned} \quad (10.2)$$

Hence, for

$$A_{ex}(\tau, \bar{M}, B_{k\alpha}) = \sum_{(n, n') \neq (1, 1)} (n + n') \cdot A^{nn'}$$

we can prove that

$${}^{\iota^*}A_{ex}(\tau, \bar{M}, B_{k\alpha})_{\iota} \geq \left(\begin{array}{l} \text{Number of particles in the middle half of} \\ B_{k\alpha} + \tau, \text{ assuming at least two of those} \\ \text{particles have the same charge} \end{array} \right) \quad (10.3)$$

and

$${}^{\iota^*}A_{ex}(\tau, \bar{M}, B_{k\alpha})_{\iota} \geq \chi \left(\begin{array}{l} \text{There is exactly one particle in } (B_{k\alpha} + \tau), \\ \text{and it lies in the middle half of } (B_{k\alpha} + \tau) \end{array} \right). \quad (10.4)$$

To check (10.3) and (10.4) we write down as a consequence of (10.2)

$$\begin{aligned} {}^{\iota^*}A_{ex}(\tau, \bar{M}, B_{k\alpha})_{\iota} &= \sum_{\substack{J, J' \\ (|J|, |J'|) \neq (1, 1)}} (|J| + |J'|) \cdot \prod_{j \in J} \theta_{k\alpha}^2(x_j - \tau) \cdot \\ &\cdot \prod_{j \notin J'} (1 - \theta_{k\alpha}^2(x_j - \tau)) \cdot \prod_{j \in J'} \theta_{k\alpha}^2(y_j - \tau) \cdot \prod_{j \notin J'} (1 - \theta_{k\alpha}^2(y_j - \tau)). \end{aligned} \quad (10.5)$$

If $J_0 = \{j \mid x_j \in \text{middle half of } B_{k\alpha} + \tau\}$, $J'_0 = \{j \mid y_j \in \text{middle half of } B_{k\alpha} + \tau\}$, then in the last equation, we restrict the sum to $J \supset J_0$ and $J' \supset J'_0$, and replace $|J| + |J'|$ by the smaller $|J_0| + |J'_0|$. If $|J_0|$ or $|J'_0| \geq 2$, then we never have $(|J|, |J'|) = (1, 1)$. Consequently,

$$\begin{aligned} {}^{\iota^*}A_{ex}(\tau, \bar{M})_{\iota} &\geq (|J_0| + |J'_0|) \sum_{\substack{G \subset \subset J_0 \\ G' \subset \subset J'_0}} \prod_{j \in G} \theta_{k\alpha}^2(x_j - \tau) \prod_{j \in \complement G} (1 - \theta_{k\alpha}^2(x_j - \tau)) \cdot \\ &\cdot \prod_{j \in G'} \theta_{k\alpha}^2(y_j - \tau) \cdot \prod_{j \in \complement G'} (1 - \theta_{k\alpha}^2(y_j - \tau)). \end{aligned}$$

Here we use $G = J \setminus J_0$, $G' = J' \setminus J'_0$. Now the big sum on the right is simply 1, so (10.3) follows. To prove (10.4), suppose say x_{j_0} belongs to the middle half of $B_{k\alpha}$, and no other particles lie in $B_{k\alpha}$. Then we take $J = \{j_0\}$, $J' = \emptyset$ in (10.5), and we find at once that ${}^{\iota^*}A_{ex}(\tau, \bar{M})_{\iota} \geq 1$. The same argument works if y_{j_0} is the only particle in $B_{k\alpha}$. So (10.3) and (10.4) are proved.

For a fixed \bar{M} we now sum (10.3), (10.4) over all $B_{k\alpha} \in \mathcal{Q}^{\bar{M}}$, and then average in τ . Recalling that the $B_{k\alpha}$ have radii between $e^{c_2\beta}$ and $e^{c_1\beta}$, we conclude that

$$Av_{\tau} \left[\left(\iota_{\tau}^{\bar{M}} \right)^* A_{ex}(\tau, \bar{M}) \iota_{\tau}^{\bar{M}} \right] \geq c. \quad \begin{array}{l} \text{(Number of particles } z_j \text{ for which at} \\ \text{least two particles } z_k, z_l \text{ of the same} \\ \text{charge lie within distance} \\ e^{(1/2)c_2\beta} \text{ of } z_j), \end{array} \quad (10.6)$$

and

$$Av_{\tau} \left[\left(\iota_{\tau}^{\bar{M}} \right)^* A_{ex}(\tau, \bar{M}) \iota_{\tau}^{\bar{M}} \right] \geq c. \quad \begin{array}{l} \text{(Number of particles which have} \\ \text{distance at least } e^{2c_1\beta} \text{ from all other} \\ \text{particles).} \end{array} \quad (10.7)$$

Average these estimates over \bar{M} , and apply (0). The conclusion is

$$\langle \text{Number of } z_j \text{ for which } B(z_j, e^{2c''\beta}) \text{ contains at least two particles of the same charge} \rangle \leq \frac{C}{\beta} \rho |\Omega| \quad (10.8)$$

$$\langle \text{Number of } z_j \text{ which have distance at least } e^{(1/2)c'\beta} \text{ from all other particles} \rangle \leq \frac{C}{\beta} \rho |\Omega| \quad (10.9)$$

provided c' , c'' are small. To derive (10.8), we take a Swiss cheese with $\frac{1}{2}c_2 = 2c''$, while (10.9) requires a Swiss cheese with $\frac{1}{2}c' = 2c_1$. Now when $c' < c''$, (10.8) and (10.9) show that

$$\langle \text{Number of particles not in atoms of type } (c', c'') \rangle \leq \frac{C}{\beta} \rho |\Omega|. \quad (10.10)$$

Comparing this with (9.3), we see that with probability nearly 1, the great majority of particles belong to atoms of type (c', c'') .

Finally, if $\{x_{j_0}, y_{k_0}\}$ form an atom of type (c', c'') , then define the *displacement vector* of the atom simply as $\vec{r} = x_{j_0} - y_{k_0}$.

11. A Special Observable

In this section we compute $\mathcal{Q} = Av_{\tau, \bar{M}}[(v_{\tau, \bar{M}})^* A_{ex}(\tau, \bar{M}) v_{\tau, \bar{M}}]$ for a special $A_{ex}(\tau, \bar{M})$ which is picked so that \mathcal{Q} will yield strong information on the positions of the particles. Then in the next section we shall compute $\langle \mathcal{Q} \rangle$ by the method of Section 8.

To construct $A_{ex}(\tau, \bar{M})$, we begin with a few simple definitions. Recall that for fixed \bar{M} , a ball $\hat{B}_{k\alpha}$ is of *ep-type* if it contains exactly one electron and one proton. Given $\mathcal{S} \subset \mathcal{Q}^{\bar{M}}$, we call \mathcal{S} *monatomic* if exactly one of the \hat{D}_i , $D \in \mathcal{S}$ contains some particles, and if that \hat{D} is of the form $\hat{B}_{k\alpha}$ rather than \hat{Q}_α , and if finally $\hat{B}_{k\alpha}$ is of ep-type. If $\hat{B}_{k\alpha}$ is of ep-type and contains the electron x_μ and the proton y_ν , then define the *displacement vector* $\vec{r}(B_{k\alpha}) = x_\mu - y_\nu$. Similarly, if $\mathcal{S} \subset \mathcal{Q}^{\bar{M}}$ is monatomic with $\hat{B}_{k\alpha}$ of ep-type, $B_{k\alpha} \in \mathcal{S}$, then define the displacement vector $\vec{r}(\mathcal{S}) = \vec{r}(B_{k\alpha})$.

Next, imagine Ω is partitioned into disjoint cubes $Q_1^j, Q_2^j, \dots, Q_L^j$ of volume

$$|Q^j| = \frac{\lambda}{\rho}, \quad \lambda \text{ a constant to be determined.} \quad (11.1)$$

Here L is a fixed large number to be determined, and the number of distinct s is $\sim (|\Omega|)/((\lambda/\rho)L)$, which of course grows large with Ω . A negligible part of Ω near $\partial\Omega$ may fall to be covered by the boxes Q_j^s .

Now for fixed $E \subset R^3$ and fixed τ, \bar{M}, s , and for fixed sets J_1, J_2, J_3 partitioning $\{1, \dots, L\}$, we define an event $\mathcal{E}_s = \mathcal{E}_s(\tau, \bar{M}, E, J_1, J_2, J_3)$ as follows.

$$\text{Let } \mathcal{Q}_j^s = \{D \in \mathcal{Q} \mid (D + \tau) \subset Q_j^s\}, \quad \text{and} \quad \mathcal{Q}^s = \bigcup_{j=1}^L \mathcal{Q}_j^s.$$

Then \mathcal{E}_s means that:

$$\begin{aligned} \mathcal{Q}_j^s &\text{ is monotonic with displacement vector } \vec{r}(\mathcal{Q}_j^s) \in E \quad \text{for } j \in J_1 \\ \mathcal{Q}_j^s &\text{ is monotonic with displacement vector } \vec{r}(\mathcal{Q}_j^s) \notin E \quad \text{for } j \in J_2 \\ \mathcal{Q}_j^s &\text{ is not monotonic} \quad \text{for } j \in J_3. \end{aligned}$$

Finally, we set $A_{ex}^s(\tau, \bar{M}) = \chi_{\mathcal{E}_s}$ and $A_{ex}(\tau, \bar{M}) = \sum_s A_{ex}^s(\tau, \bar{M})$. For fixed τ, \bar{M}, s , we compute $\iota^* A_{ex}^s \iota$. To do so, look first at an arbitrary potential $\hat{V}(\hat{z}_1 \dots \hat{z}_{N+N'})$ defined on $(\Omega_{ex})^{N+N'}$. By definition of $\iota = \iota_\tau^M$ we have

$$\langle \hat{V} \iota \psi, \iota \psi \rangle = \langle V \psi, \psi \rangle \quad \text{for } \psi \in L_{N, N'}^2(\Omega), \quad (11.2)$$

with

$$\begin{aligned} V(z_1 \dots z_{N+N'}) &= \sum_{D_1 \dots D_{N+N'} \in \mathcal{Q}} \prod_{l=1}^{N+N'} \theta^2(z_l - \tau, D_l) \cdot \\ &\quad \cdot \hat{V}(z_1 + \xi(D_1), \dots, z_{N+N'} + \xi(D_{N+N'})). \end{aligned} \quad (11.3)$$

Assume now \hat{V} has the special form

$$\hat{V}(\hat{z}_1 \dots \hat{z}_{N+N'}) = \prod_{j \notin \mathcal{J}} \chi_{\bigcup_{D \in \mathcal{S}} D}(\hat{z}_j) \cdot \prod_{j \in \mathcal{J}} \chi_{c(\bigcup_{D \in \mathcal{S}} D)}(\hat{z}_j) \cdot \hat{W}(\hat{z}_j, j \in \mathcal{J}) \quad (11.4)$$

for a collection $\mathcal{S} \subset \mathcal{Q}$ and $\mathcal{J} \subset \{1, 2, \dots, N+N'\}$. Then in (11.3) we can carry out the sum over the D_l for $l \notin \mathcal{J}$, obtaining

$$\begin{aligned} V(z_1 \dots z_N) &= \left[\sum_{D_j \in \mathcal{S}} \prod_{\text{for } j \in \mathcal{J}} \theta^2(z_j - \tau, D_j) \hat{W}(z_j + \xi(D_j); j \in \mathcal{J}) \right] \cdot \\ &\quad \cdot \prod_{l \notin \mathcal{J}} \left(\sum_{D \notin \mathcal{S}} \theta^2(z_l - \tau, D) \right). \end{aligned} \quad (11.5)$$

$$\text{Let } F = F(\tau, \bar{M}, \mathcal{S}) = \left[\bigcup_{\bar{Q}_\alpha \in \mathcal{S}} (\bar{Q}_\alpha + \tau) \right] \cup \left[\bigcup_{B_{k_\alpha} \in \mathcal{S}} \{x \mid \text{dist}(x, \partial B_{k_\alpha} + \tau) < e^{\bar{c}\beta}\} \right]$$

for \bar{c} smaller than the constants c_1, c_2 for our Swiss cheese. Later we will use the observation

$$Av_\tau \chi_{F(\tau, \bar{M}, \mathcal{S})}(x) \leq e^{-c\beta} \quad \text{for any } x. \quad (11.6)$$

For now, we continue to fix τ . Assume that none of the particles z_j lies in F . Then one checks easily that for $z \notin F$,

$$\sum_{D \notin \mathfrak{S}} \theta^2(z - \tau, D) = 1 - \chi_{G(\mathfrak{S})}(z) \quad \text{with} \quad G(\mathfrak{S}) = \bigcup_{D \in \mathfrak{S}} (D + \tau).$$

Moreover, if $z \notin F$ then we have $z - \tau \in D_z$ for a *unique* $D_z \in \mathcal{Q}$, and we have $\theta(z - \tau, D) = 1$ if $D = D_z$, 0 otherwise.

Setting $\gamma(z) = z + \xi(D_z)$ for $z \notin F$, and putting the above remarks into (11.5), we obtain

$$V(z_1 \dots z_{N+N'}) = \prod_{l \in \mathfrak{G}} \chi_{G(\mathfrak{S})}(z_l) \cdot \prod_{l \notin \mathfrak{G}} (1 - \chi_{G(\mathfrak{S})}(z_l)) \cdot \widehat{W}(\gamma(z_j); j \in \mathfrak{G}) \quad (11.7)$$

when $z_1 \dots z_{N+N'} \notin F$.

Now specialize to the case

$$\mathfrak{S} = \mathcal{Q}^s = \bigcup_{j=1}^L \mathcal{Q}_j^s,$$

$\widehat{W}(\hat{z}_j; j \in \mathfrak{G}) =$ characteristic function of the following event: After deleting all the particles \hat{z}_l with $l \notin \mathfrak{G}$, we find that

- (\cdot) \mathcal{Q}_j^s is monotonic with displacement vector in E for $j \in J_1$
- (\cdot) \mathcal{Q}_j^s is monotonic with displacement vector not in E for $j \in J_2$
- (\cdot) \mathcal{Q}_j^s is not monotonic for $j \in J_3$.

Thus \widehat{V} defined by (11.4) is the characteristic function of the event $\mathcal{E}_s \cap \{\hat{z}_j \in (\bigcup_{D \in \mathfrak{S}} \widehat{D}) \text{ precisely for those } j \in \mathfrak{G}\}$, while for $z_1 \dots z_{N+N'} \notin F = F(\tau, \overline{M}, \mathcal{Q}^s)$, equation (11.7) shows that V is the characteristic function of the following event:

- (a) $z_j \in G(\mathcal{Q}^s)$ exactly for $j \in \mathfrak{G}$.
- (b) For $j \in J_1$, in \mathcal{Q}_j^s there is a unique D with $D + \tau$ containing some particles; that D is a ball $B_{k\alpha}$, $D + \tau$ contains a single electron x_μ and a single proton y_ν ; and $x_\mu - y_\nu \in E$.
- (c) For $j \in J_2$, in \mathcal{Q}_j^s there is a unique D with $D + \tau$ containing some particles; that D is a ball $B_{k\alpha}$, $D + \tau$ contains a single electron x_μ and a single proton y_ν ; and $x_\mu - y_\nu \notin E$.
- (d) For $j \in J_3$, it is *not* true that in \mathcal{Q}_j^s there is a unique D with $D + \tau$ containing some particles, that D being a ball $B_{k\alpha}$ with $D + \tau$ containing a single electron and a single proton.

Sum this information over all subsets $\mathfrak{G} \subset \{1, 2, \dots, N + N'\}$. Thus for fixed τ, \overline{M}, s we see that

$$\text{For } z_1 \dots z_{N+N'} \notin F(\tau, \overline{M}, \mathcal{Q}^s) \quad (11.8)$$

we have $\iota^* A_{ex}^s(\tau, \bar{M}) \iota = V =$ characteristic function of the event defined by (b), (c), (d) above.

To clarify the meaning of this event, pick two small constants $0 < c' < c''$, and assume all the particles in $\bigcup_{j=1}^L Q_j^s$ belong to atoms of type (c', c'') in the sense of Section 9. We can pick c', c'' so that $0 < c' < \bar{c} < c_2 < c_1 < c'' \ll 1$, where \bar{c} is the constant in the definition of F above, and c_1, c_2 are the constants related to the radii of the balls in the Swiss cheese ($e^{c_2 \beta} < \text{radius}(B_{k\alpha}) < e^{c_1 \beta}$).

Assume also that there are no particles within distance $e^{2c''\beta}$ of ∂Q_j^s for $j = 1, \dots, L$. Under our assumptions, (b), (c), (d) above are equivalent to

- (b)' For $j \in J_1$, Q_j^s contains exactly one atom, and its displacement vector lies in E .
- (c)' For $j \in J_2$, Q_j^s contains exactly one atom, and its displacement vector does not lie in E .
- (d)' For $j \in J_3$, Q_j^s fails to contain a unique atom.

Call this event \mathcal{E}_s^s . Here, "atom" means "atom of type (c', c'') "; and (b), (c), (d) are equivalent to (b)', (c)', (d)' provided:

- (·) No particles lie in $F(\tau, \bar{M}, \mathcal{Q}^s)$.
- (·) All particles in $\bigcup_{j=1}^L Q_j^s$ belong to atoms of type (c', c'') .
- (·) No particles lie in $E_s = \bigcup_{j=1}^L \{\text{dist}(x, \partial Q_j^s) < e^{2c''\beta}\}$.

So for a fixed τ, \bar{M}, s , we know that $(\iota_{\tau}^{\bar{M}})^* A_{ex}^s(\tau, \bar{M}) \iota_{\tau}^{\bar{M}} = V$, where $V = \chi_{\mathcal{E}_s^s}$ under the three assumptions just given.

Even without any assumptions, (11.2) and (11.3) show that $0 \leq V \leq 1$ always, since $A_{ex}^s(\tau, \bar{M})$ has the form $\hat{V} =$ characteristic function of an event. Consequently, we know that $|(\iota_{\tau}^{\bar{M}})^* A_{ex}^s(\tau, \bar{M}) \iota_{\tau}^{\bar{M}} - \chi_{\mathcal{E}_s^s}| \leq \sum_{j=1}^L (\text{Number of particles in } Q_j^s \text{ not belonging to atoms of type } (c', c'')) + (\text{Number of particles belonging to } F(\tau, \bar{M}, \mathcal{Q}^s)) + (\text{Number of particles in } E_s)$.

Average this over translates τ , and use estimate (11.6) with $\mathcal{S} = \mathcal{Q}^s$. The result is $|Av_{\tau}[(\iota_{\tau}^{\bar{M}})^* A_{ex}^s(\tau, \bar{M}) \iota_{\tau}^{\bar{M}}] - \chi_{\mathcal{E}_s^s}| \leq \sum_{j=1}^L (\text{Number of particles in } Q_j^s \text{ not belonging to atoms of type } (c', c'')) + e^{-c\beta} \cdot (\text{Number of particles in } \bigcup_{j=1}^L Q_j^s) + (\text{Number of particles in } E_s)$. (Here we used $\chi_{F(\tau, \bar{M}, \mathcal{Q}^s)}(x) = 0$ for $x \notin \bigcup_{j=1}^L Q_j^s$).

Summing this over s and averaging in \bar{M} , we have for

$$\bar{\mathcal{Q}} = Av_{\tau, \bar{M}}[(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, M) \iota_{\tau}^{\bar{M}}]$$

the estimate $|\bar{\mathcal{Q}} - \sum_s \chi_{\mathcal{E}_s^s}| \leq (\text{Number of particles not in atoms of type } (c', c'')) + (\text{Number of particles in } \bigcup_s E_s) + e^{-c\beta}(N + N')$.

Since $|\cup_s E_s| \leq e^{-c\beta}|\Omega|$, estimates (9.3), (9.5), (10.10) imply

$$|\langle \mathcal{Q} \rangle - \langle \sum_s \chi_{E_s} \rangle| \leq \frac{C}{\beta} \rho |\Omega| \quad \text{for } \mathcal{Q} = Av_{\tau\bar{M}}[(\iota_{\tau}^{\bar{M}})^* A_{ex}(\tau, \bar{M})(\iota_{\tau}^{\bar{M}})]. \quad (11.9)$$

Recalling that \mathcal{E}'_s is the event described by (b)', (c)', (d)' above, we see that $\langle \sum_s \chi_{\mathcal{E}'_s} \rangle$ carries a lot of information.

12. The Expected Value of the Special Observable

In this section we fix τ, \bar{M} and compute $Tr \exp\{tA_{ex}(\tau, \bar{M}) + \mu(N + N') - \beta H^{ex\bar{M}}\}$ for $|t| \ll 1$ and $A_{ex}(\tau, \bar{M})$ as in Section 11.

Recall the definitions of \mathcal{Q}_i^s and \mathcal{Q}^s , and define

$$\mathcal{Q}_{extra} = \mathcal{Q} \setminus \bigcup_{s,l} \mathcal{Q}_i^s = \{D \in \mathcal{Q} \mid D + \tau \text{ meets some } \partial Q_i^s \text{ or lies within } \text{diam}(Q_i^s) \text{ of } \partial\Omega\}.$$

Let

$$\Omega_{ex}^s = \bigcup_{l=1}^L \left(\bigcup_{D \in \mathcal{Q}_i^s} \hat{D} \right) \equiv \bigcup_{l=1}^L \Omega_{exl}^s.$$

We first note that H^{ex} and $A_{ex}(\tau, \bar{M})$ both break up as sums $H^{ex} = \sum_s H_{ex}^s + H_{ex}^{extra}$

$$A_{ex}(\tau, \bar{M}) = \sum_s A_{ex}^s,$$

with A_{ex}^s, H_{ex}^s acting on $L_*^2(\Omega_{ex}^s)$ and H_{ex}^{extra} acting on

$$L_*^2 \left(\bigcup_{D \in \mathcal{Q}_{extra}} \hat{D} \right).$$

Consequently,

$$\begin{aligned} Tr \exp\{tA_{ex}(\tau, \bar{M}) + \mu(N + N') - \beta H^{ex}\} &= \\ &= \prod_s Tr \exp\{tA_{ex}^s + \mu(N + N') - \beta H_{ex}^s \mid L_*^2(\Omega_{ex}^s)\} \cdot \\ &\cdot \prod_{B_{k\alpha} \in \mathcal{Q}_{extra}} Z(\mu, \beta, B_{k\alpha}) \cdot \prod_{\tilde{Q}_\alpha \in \mathcal{Q}_{extra}} Z_0(\mu, \beta, \tilde{Q}_\alpha). \end{aligned} \quad (12.1)$$

From Section 3, we know that the terms from \mathcal{Q}_{extra} contribute a factor

$$\exp \left[O \left(\rho \sum_{D \in \mathcal{Q}_{extra}} |D| \right) \right] = \exp \left[O \left(\frac{\rho |\Omega|}{\beta} \right) \right]$$

for large β, Ω .

Fix s . We shall introduce some definitions to help us compute the right-hand side of (12.1).

$N(D)$, $N'(D)$ denote arbitrary assignments of a non-negative integer to each $D \in \mathcal{Q}^s$.

$N_l(D)$, $N'_l(D)$ denote arbitrary assignments of a non-negative integer to each $D \in \mathcal{Q}_l^s$.

Evidently, each $N(D)$, $N'(D)$ induces $N_l(D)$, $N'_l(D)$ for each l . We say that $N(D)$, $N'(D)$ is *monatomic* for \mathcal{Q}_l^s , or equivalently that $N_l(D)$, $N'_l(D)$ is monatomic, if $N_l(D) = N'_l(D) = 0$ for all $D \in \mathcal{Q}_l^s$ except for a single ball $B_{k\alpha}$ (called the *active ball* in \mathcal{Q}_l^s) with $N_l(B_{k\alpha}) = N'_l(B_{k\alpha}) = 1$.

\mathcal{B} denotes an arbitrary assignment of a ball $B \in \mathcal{Q}_l^s$ to each $l \in J_1 \cup J_2$. Define a set $\mathcal{E}(N(D), N'(D)) = \{(z_1 \dots z_{N+N'}) \mid \text{Each } z_j \in \Omega_{ex}^s \text{ and each } \tilde{D} \text{ contains } N(D) \text{ electrons and } N'(D) \text{ protons, } D \in \mathcal{Q}^s\}$. Given a \mathcal{B} and given $(N_l(D), N'_l(D))$ for $l \in J_3$, there is an induced

$$N(D), N'(D) = \begin{cases} N_l(D), N'_l(D) & \text{if } D \in \mathcal{Q}_l^s \text{ with } l \in J_3 \\ D \in \mathcal{Q}_l^s \text{ with } l \in J_1 \cup J_2 \text{ and } D \text{ is the} & \\ \text{ball assigned to } l \text{ by } \mathcal{B}; & 0, 0 \text{ otherwise.} \end{cases} \quad (12.2)$$

We give the resulting set $\mathcal{E}(N(D), N'(D))$ the name $\mathcal{E}(\mathcal{B}, (N_l(D), N'_l(D))_{l \in J_3})$.

Note that (12.2) is the most general $N(D)$, $N'(D)$ which is monatomic for all $l \in J_1 \cup J_2$.

Now define subspaces of $L_*^2(\Omega_{ex}^s)$: $X(N(D), N'(D)) = \text{space of } \psi \in L_*^2(\Omega_{ex}^s) \text{ supported in } \mathcal{E}(N(D), N'(D))$ $X(\mathcal{B}, (N_l(D), N'_l(D))_{l \in J_3}) = X(N(D), N'(D))$ with N, N' defined by (12.2).

We have

$$L_*^2(\Omega_{ex}^s) = \sum_{N(D), N'(D)} X(N(D), N'(D)),$$

and therefore

$$\begin{aligned} \Phi &= \text{Tr exp}\{tA_{ex}^s + \mu(N + N') - \beta H_{ex}^s \mid L_*^2(\Omega_{ex}^s)\} - \text{Tr exp}\{\mu(N + N') - \\ &\quad - \beta H_{ex}^s \mid L_*^2(\Omega_{ex}^s)\} = \\ &= \sum_{N(D), N'(D)} [\text{Tr exp}\{tA_{ex}^s + \mu(N + N') - \beta H_{ex}^s \mid X(N(D), N'(D))\} - \\ &\quad - \text{Tr exp}\{\mu(N + N') - \beta H_{ex}^s \mid X(N(D), N'(D))\}] = \\ &= \sum_{N(D), N'(D)} \phi(N(D), N'(D)). \end{aligned}$$

Let us recall how A_{ex}^s behaves. For $(z_1 \dots z_{N+N'}) \in \mathcal{E}(N(D), N'(D))$, we note that \mathcal{Q}_l^s is monatomic if and only if $N_l(D)$, $N'_l(D)$ is monatomic. Therefore, $A_{ex}^s = 0$ and so $\Phi(N(D), N'(D)) = 0$ unless $N_l(D)$, $N'_l(D)$ is monatomic precisely for $l \in J_1 \cup J_2$. Such $N(D)$, $N'(D)$ are given by (12.2), with

$(N_l(D), N'_l(D))$ not monotonic for any $l \in J_3$. If $N(D), N'(D)$ are given by (12.2), we write $\Phi(\mathfrak{B}, (N_l(D), N'_l(D))_{l \in J_3})$ for $\Phi(N(D), N'(D))$.

Now fix \mathfrak{B} and $(N_l(D), N'_l(D))_{l \in J_3}$, with none of the $(N_l(D), N'_l(D))$ monotonic. Let $B_1 \dots B_{L_0}$ be the balls assigned to $l \in J_1 \cup J_2$ by \mathfrak{B} , with $B_1 \dots B_{s_0}$ coming from J_1 and $B_{s_0+1} \dots B_{L_0}$ coming from J_2 . We can compute $\Phi(\mathfrak{B}, (N_l(D), N'_l(D))_{l \in J_3})$ using Lemma 4.1. For, A_{ex}^s and H_{ex}^s restricted to $X(\mathfrak{B}, (N_l(D), N'_l(D))_{l \in J_3})$ are observables on a system composed of two non-interacting parts, namely $B_1 \dots B_{L_0}$ and

$$\Omega_{ex}^{J_3} = \left(\bigcup_{l \in J_3} \bigcup_{D \in \mathcal{Q}_l^s} \partial \hat{D} \right).$$

The Hamiltonian breaks up as a sum of the Hamiltonian of Lemma 4.1 acting on $B_1 \dots B_{L_0}$, and an exploded Hamiltonian on $\Omega_{ex}^{J_3}$. The observable A_{ex}^s refers entirely to $B_1 \dots B_{L_0}$ and in fact agrees with G in Lemma 4.1. Therefore, we can write

$$\begin{aligned} & \text{Tr} \exp\{tA_{ex}^s + \mu(N + N') - \beta H_{ex}^s \mid X(\mathfrak{B}, (N_l(D), N'_l(D))_{l \in J_3})\} = \\ & = \text{Tr} \exp\{tG + 2L_0\mu - \beta \mathring{H} \mid L_{1,1}^2(B_1 \dots B_{L_0})\} \cdot \\ & \quad \cdot \prod_{l \in J_3} \left[\prod_{B_{k\alpha} \in \mathcal{Q}_l^s} Z(m, \beta, B_{k\alpha}, N_l(B_{k\alpha}), N'_l(B_{k\alpha})) \cdot \right. \\ & \quad \left. \cdot \prod_{\tilde{Q}_\alpha \in \mathcal{Q}_l^s} Z_0(\mu, \beta, \tilde{Q}_\alpha, N_l(\tilde{Q}_\alpha), N'_l(\tilde{Q}_\alpha)) \right], \end{aligned} \quad (12.4)$$

and the first term on the right can be evaluated using Lemma 4.1. In fact, we have from Lemma 4.1 that

$$\begin{aligned} & \text{Tr} \exp\{tG + 2L_0\mu - \beta \mathring{H} \mid L_{1,1}(B_1 \dots B_{L_0})\} = \\ & = \text{Tr} \exp\{2L_0\mu - \beta \mathring{H} \mid L_{1,1}(B_1 \dots B_{L_0})\} e^{tG_0} (1 + O(t^2 + \beta^{-1})), \end{aligned}$$

with

$$G_0 = (c \int_E e^{-|x|} dx)^{s_0} (c \int_{cE} e^{-|x|} dx)^{L_0 - s_0}, \quad s_0 = |J_1|, \quad L_0 - s_0 = |J_2|.$$

Substituting this into (12.4), then taking $t = 0$ in (12.4) and subtracting, we obtain

$$\begin{aligned} \Phi(N(D), N'(D)) &= (tG_0 + O(t^2 + \beta^{-1})) \cdot \text{Tr}\{\mu(N + N') - \\ & \quad - \beta H_{ex}^s \mid X(N(D), N'(D))\} \end{aligned} \quad (12.5)$$

if $(N_l(D), N'_l(D))$ is monotonic precisely for $l \in J_1 \cup J_2$; $\Phi(N(D), N'(D)) = 0$ otherwise;

$$G_0 = (\text{const} \int_E e^{-|x|} dx)^{|J_1|} (\text{const} \int_{cE} e^{-|x|} dx)^{|J_2|}. \quad (12.6)$$

In (12.5) we wrote $tG_0 + O(t^2)$ for $(e^{tG_0} - 1)$.

Now set

$$Z^{atomic}(\mu, \beta, \mathcal{Q}_i^s) = \sum_{N_l(D), N_l(\bar{D})} \prod_{\text{monatomic } B_{k\alpha} \in \mathcal{Q}_i^s} Z(\mu, \beta, B_{k\alpha}, N_l(B_{k\alpha}), N_l(\bar{B}_{k\alpha})) \cdot \prod_{\bar{Q}_\alpha \in \mathcal{Q}_i^s} Z_0(\mu, \beta, \bar{Q}_\alpha, N_l(\bar{Q}_\alpha), N_l(\bar{\bar{Q}}_\alpha)) \quad (12.7)$$

$$Z^{non-atomic}(\mu, \beta, \mathcal{Q}_i^s) = \sum_{N_l(D), N_l(\bar{D})} \prod_{\text{not monatomic}} (\text{same product}). \quad (12.8)$$

Since the trace on the right in (12.5) breaks up as a product of terms corresponding to the different \mathcal{Q}_i^s , we find that when (12.5) is substituted into (12.3), we get

$$\Phi = (tG_0 + O(t^2 + \beta^{-1})) \prod_{l \in J_1 \cup J_2} Z^{atomic}(\mu, \beta, \mathcal{Q}_i^s) \cdot \prod_{l \in J_3} Z^{non-atomic}(\mu, \beta, \mathcal{Q}_i^s). \quad (12.9)$$

It is easy to compute Z^{atomic} and $Z^{non-atomic}$. In fact

$$Z^{atomic}(\mu, \beta, \mathcal{Q}_i^s) = \sum_{B_{k\alpha} \in \mathcal{Q}_i^s} Z(\mu, \beta, B_{k\alpha}, 1, 1) = \sum_{B_{k\alpha} \in \mathcal{Q}_i^s} \rho(1 + O(\beta^{-1})) |B_{k\alpha}|$$

(by Section 4)

$$\begin{aligned} &= \rho |Q_i^s| \cdot (1 + O(\beta^{-1})) \\ &= \lambda(1 + O(\beta^{-1})) \end{aligned}$$

(see equation (11.1)).

On the other hand,

$$\begin{aligned} Z^{atomic}(\mu, \beta, \mathcal{Q}_i^s) + Z^{non-atomic}(\mu, \beta, \mathcal{Q}_i^s) &= \\ &= \prod_{B_{k\alpha} \in \mathcal{Q}_i^s} Z(\mu, \beta, B_{k\alpha}) \cdot \prod_{\bar{Q}_\alpha \in \mathcal{Q}_i^s} Z_0(\mu, \beta, \bar{Q}_\alpha) \end{aligned}$$

(by (12.7), (12.8))

$$= \exp\{\rho |Q_i^s| \cdot (1 + O(\beta^{-1}))\} = \exp(\lambda(1 + O(\beta^{-1}))),$$

by (11.1) and Section 4 again. It follows that

$$\begin{aligned} Z^{non-atomic}(\mu, \beta, \mathcal{Q}_i^s) &= (e^\lambda - \lambda)(1 + O(\beta^{-(1/2)})), \\ &\text{as long as } \beta^{-(1/20)} < \lambda < 100. \end{aligned} \quad (12.10)$$

Substituting our formulas for Z^{atomic} , $Z^{non-atomic}$ into (12.9), we get

$$\Phi = (tG_0 + O(t^2 + \beta^{-1/2})) \cdot \lambda^{|J_1 \cup J_2|} (e^\lambda - \lambda)^{|J_3|}. \quad (12.11)$$

We have also

$$\begin{aligned} \text{Tr exp}\{\mu(N + N') - \beta H_{ex}^s | L_*^2(\Omega_{ex}^s)\} &= \prod_{B_{k\alpha} \in \mathbb{Q}^s} Z(\mu, \beta, B_{k\alpha}) \cdot \\ &\quad \cdot \prod_{\tilde{Q}_\alpha \in \mathbb{Q}^s} Z_0(\mu, \beta, \tilde{Q}_\alpha) = \\ &= \exp\left\{\rho \sum_{B_{k\alpha} \in \mathbb{Q}^s} |B_{k\alpha}| \cdot (1 + O(\beta^{-1}))\right\} \cdot \exp\left\{O\left(\beta^{-1}\rho \sum_{l=1}^L |Q_l^L|\right)\right\} \end{aligned}$$

(by Section 4)

$$= \exp\left\{\rho \sum_{l=1}^L |Q_l^s| (1 + O(\beta^{-1}))\right\} = e^{\lambda L} (1 + O(\beta^{-1/2})),$$

provided (12.10) holds and β is large enough, depending on L . Combining this and (12.11) with (12.13), we get

$$\begin{aligned} \text{Tr exp}\{tA_{ex}^s + \mu(N + N') - \beta H_{ex}^s | L_*^2(\Omega_{ex}^s)\} &= \\ &= \left(1 + tG_0\left(\frac{\lambda}{e^\lambda}\right)^{|J_1 \cup J_2|} \left(\frac{e^\lambda - \lambda}{e^\lambda}\right)^{|J_3|} + O(t^2 + \beta^{-1/2})\right) \cdot \\ &\quad \cdot \text{Tr exp}\{\mu(N + N') - \beta H_{ex}^s | L_*^2(\Omega_{ex}^s)\}, \end{aligned} \quad (12.12)$$

where $O(t^2 + \beta^{-1/2})$ means less than $\text{Const}(L) \cdot (t^2 + \beta^{-1/2})$ in absolute value. Substituting (12.12) into (12.1) now gives

$$\text{Tr exp}\{tA_{ex}(\tau, \bar{M}) + \mu(N + N') - \beta H^{ex}\} \leq e^S \text{Tr exp}\{\mu(N + N') - \beta H^{ex}\} \quad (12.13)$$

with

$$S = (\text{Number of different } s)[tG_0(\lambda e^{-\lambda})^{|J_1 \cup J_2|} (1 - \lambda e^{-\lambda})^{|J_3|} + O(t^2 + \beta^{-1/2})].$$

Here, the number of different s is

$$\frac{|\Omega|}{\binom{\lambda}{\rho} L} + \text{error tending to zero as } \Omega \text{ gets big} = \frac{\rho|\Omega|}{\lambda L} (1 + O(\beta^{-1})), \text{ say.}$$

Applying (8.1) and (9.4) with $A_{ex}(\tau, \bar{M})$ replaced by $tA_{ex}(\tau, \bar{M})$, we see that (12.13) yields

$$\begin{aligned} t\langle \mathcal{Q} \rangle &\leq t(\text{Number of different } s)G_0(\lambda e^{-\lambda})^{|J_1 \cup J_2|} (1 - \lambda e^{-\lambda})^{|J_3|} + \\ &\quad + \frac{\rho|\Omega|}{\lambda L} O(t^2 + \beta^{-1/2}) + O(\beta^{-1}\rho|\Omega|). \end{aligned}$$

Taking $t = \pm\beta^{-1/20}$, and comparing with (11.9), we obtain

$$\langle \sum_s \chi_{\mathcal{E}'_s} \rangle = (\text{Number of different } s)[G_0(\lambda e^{-\lambda})^{|J_1 \cup J_2|}(1 - \lambda e^{-\lambda})^{|J_3|} + O(\beta^{-1/20})] \quad (12.14)$$

with G_0 given by (12.6), and \mathcal{E}'_s defined by (b)', (c)', (d)' in Section 11.

13. Proof of the Theorem

The idea is to use (12.14), together with a simple quantitative form of the law of large numbers, which we now set down. Suppose we have independent random variables $X_1 \dots X_L$, with $X_j = 1$ with probability p , $X_j = 0$ with probability $1 - p$. Then $E(e^{tX_j}) = e^{tp} + (1 - p) = \exp(pt + O(t^2))$, uniformly in $p \in [0, 1]$. Consequently, $E(e^{t(X_1 + \dots + X_L)}) = \exp(Lpt + O(Lt^2))$, so that

$$\text{Prob}\left\{\frac{X_1 + \dots + X_L}{L} \geq p + \delta\right\} \leq \exp(Lpt + O(Lt^2) - tL(p + \delta)).$$

Picking $t = (\text{small const})\delta$, we obtain

$$\text{Prob}\left\{\frac{X_1 + \dots + X_L}{L} \geq p + \delta\right\} \leq \exp(-c\delta^2 L).$$

Applying this also to $X_j = 1 - X_j$, $p' = 1 - p$ we obtain

$$\text{Prob}\left\{\left|\frac{X_1 + \dots + X_L}{L} - p\right| \geq \delta\right\} < \exp(-c\delta^2 L). \quad (13.1)$$

We apply this to a probability space defined as follows.

The points of the space are functions $f: \{1 \dots L\} \rightarrow \{1, 2, 3\}$. Thus, each f gives rise to subsets $J_1 = \{l \mid f(l) = 1\}$, $J_2 = \{l \mid f(l) = 2\}$, $J_3 = \{l \mid f(l) = 3\}$. We fix $E \subset \mathcal{R}^3$, and define the probability of f as $\text{Prob}(f) = \langle \sum_s \chi_{\mathcal{E}'_s} \rangle / (\text{Number of } s)$, where \mathcal{E}'_s is the event defined by (b)', (c)', (d)' in Section 10.

Formula (12.14) shows that $\text{Prob}(f)$ differs by at most $C(L)/\beta^{1/20}$ from $\text{Prob}'(f)$, defined by picking each $f(l)$ independently with probabilities

$$\text{Prob}'(f(l) = 1) = (\text{const}) \int_E e^{-|x|} dx (\lambda e^{-\lambda}) = p_1$$

$$\text{Prob}'(f(l) = 2) = (\text{const}) \int_{cE} e^{-|x|} dx (\lambda e^{-\lambda}) = p_2$$

$$\text{Prob}'(f(l) = 3) = (1 - \lambda e^{-\lambda}) = p_3.$$

Since the probability space contains only 3^L points, it follows that

$$|\text{Prob}(\mathcal{E}) - \text{Prob}'(\mathcal{E})| < \frac{C'(L)}{\beta^{1/20}} \quad (13.2)$$

for any event \mathcal{E} in the probability space. We apply this to the event

$$\mathcal{E} = \left\{ \left| \left(\frac{\text{Number of } l \text{ for which } f(l) = 1}{L} \right) - p_1 \right| > \delta \right\}.$$

From (13.2), and (13.1) applied to Prob', we conclude that

$$\text{Prob}(\mathcal{E}) \leq \exp(-c\delta^2 L) + \frac{C(L)}{\beta^{1/20}}.$$

Now $\text{Prob}(\mathcal{E})$ has a simple interpretation.

We define

$$X_l^s = \begin{cases} 1 & \text{if } Q_l^s \text{ contains an atom of type } (c', c'') \text{ and no other particles, and that atom has displacement vector in } E \\ 0 & \text{otherwise} \end{cases}$$

Then

$$\text{Prob}(\mathcal{E}) = \frac{\langle \text{Number of } s \text{ with } \left| \sum_{l=1}^L X_l^s - p_1 L \right| > \delta L \rangle}{(\text{Number of } s)}$$

Hence,

$$\left\langle \text{Number of } s \text{ with } \left| \sum_{l=1}^L X_l^s - p_1 L \right| > \delta L \right\rangle \leq \left(\exp(-c\delta^2 L) + \frac{C(L)}{\beta^{1/20}} \right) \cdot (\text{Number of } s)$$

Since

$$\left\langle \left| \sum_{s,l} X_l^s - p_1 L (\text{Number of } s) \right| \right\rangle \leq (\delta L)(\text{Number of } s) + L \left\langle \text{Number of } s \text{ with } \left| \sum_l X_l^s - p_1 L \right| > \delta L \right\rangle,$$

it follows that

$$\left\langle \left| \sum_s X_l^s - p_1 L (\text{Number of } s) \right| \right\rangle \leq (\text{Number of } s) \left(\delta L + L \exp(-c\delta^2 L) + \frac{C(L)}{\beta^{1/20}} \right)$$

or, since $L(\text{Number of } s) = (\text{Number of boxes } Q_l^s) \equiv N_0$,

$$\left\langle \left| \sum_{l,s} X_l^s - p_1 N_0 \right| \right\rangle \leq N_0 (\delta + \exp(-c\delta^2 L) + C(L)\beta^{-1/20}). \quad (13.3)$$

Now take δ small first, then pick L so large that $\exp(-c\delta^2 L) < \delta$, then pick

β so large that $C(L)\beta^{-1/20} < \delta$, and finally pick Ω so large that all our estimates are valid for the β we picked. In that case, (13.3) becomes

$$\left\langle \left| \frac{\sum_{l,s} X_l^s}{(\text{Number of } l, s)} - p_1 \right| \right\rangle \leq 3\delta, \quad (13.4)$$

β large enough and Ω large depending on β .

Taking $E = R^3$ in (13.4), we find that the number of boxes Q_i^s containing exactly an atom of type (c', c'') is $(p_1 + O(\delta^{1/2})) \cdot N_0$ with probability $> 1 - \delta^{1/2}$. For $E = R^3$ and $\lambda \ll 1$, our defining formula for p_1 becomes $P_1 = \lambda + O(\lambda^2)$, while $N_0 = \text{Number of } s, l = (|\Omega|/(\lambda/\rho)) + (\text{error tending to zero with large } \Omega) = (\rho|\Omega|/\lambda) \cdot (1 + O(\lambda^{10}))$ certainly. So (13.4) in this special case gives $\langle |(\text{Number of } Q_i^s \text{ containing exactly an atom of type } (c', c'')) - \rho|\Omega|(1 + O(\lambda^2))| \rangle \leq (3\delta/\lambda)\rho|\Omega|$.

So if we take $\lambda < \epsilon^{10}$ and $\delta < \lambda^2$, then we find with probability at least $(1 - \epsilon)$ that the number of Q_i^s containing exactly an atom of type (c', c'') is $\rho|\Omega|(1 + O(\epsilon))$. However, we already know that with probability $> 1 - \epsilon$, all but at most $\epsilon\rho|\Omega|$ of the particles belong to atoms of type (c', c'') and the total number of particles is $2\rho|\Omega|(1 + O(\epsilon))$. So with probability $> 1 - O(\epsilon)$, we know that all but $O(\epsilon)$ fraction of the particles come from atoms of type (c', c'') which form the sole contents of one of the Q_i^s . Returning to the general case of $E \subset R^3$, we look at (13.4) and realize that with probability $> 1 - O(\epsilon)$, $\sum_{l,s} X_l^s = (\text{Number of atoms with displacement vectors in } E) + O(\epsilon \cdot \text{Number of atoms})$, while

$$p_1 \cdot (\text{Number of } s, l) = (\text{const} \int_E e^{-|x|} dx)(\text{Number of atoms}) + O(\epsilon \cdot \text{Number of atoms}).$$

Therefore, (13.4) implies that with probability $> 1 - O(\epsilon)$, the fraction of atoms having displacement vectors in E is within $O(\epsilon)$ of $(\text{const} \int_E e^{-|x|} dx)$. So we know (2.1) and (2.2).

The same technique also proves (2.3). We simply pair up the boxes Q_i^s into, say Q_{2j-1}^s, Q_{2j}^s , and define random variables

$$Y_j^s = \begin{cases} 1 & \text{if both } Q_{2j-1}^s, Q_{2j}^s \text{ contain exactly a } (c', c'')\text{-atom, and the} \\ & \text{displacement vectors of both atoms lie in } E, \\ 0 & \text{otherwise.} \end{cases}$$

Using Y_j^s in place of the X_l^s , we obtain in the notation of (2.3) that

$$p^* = [(\text{const} \int_E e^{-|x|} dx)\lambda e^{-\lambda}]^2 + O(\epsilon)$$

$$p', p'' = [(\text{const} \int_E e^{-|x|} dx)\lambda e^{-\lambda}] + O(\epsilon),$$

all with probability $> 1 - \epsilon$. This time, we need not take λ small. These last equations imply (2.3). The proof of our theorem is complete.

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Supported in part by NSF Grant N.^o MCS 80-03072.