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Ionization Equilibrium in the Electron–Proton Gas

N. Macris[1] **and Ph. A. Martin**[1]

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Using Fefferman's analysis of the quantum electron–proton gas, we give a rigorous proof of ionization equilibrium in this system. Ionization equilibrium phases are obtained as low-density and low-temperature limits, letting the chemical potential $\mu(T)$ approach the ground-state energy of the hydrogen atom as the temperature T tends to zero. The rate of ionization is determined by the slope of $\mu(T)$ at $T=0$ and is correctly given by the Saha formula. We also discuss a simpler model where a single quantum particle interacts with a classical gas of hard spheres.

KEY WORDS: Ionization equilibrium; Saha formula; Coulomb systems; dilute gases.

1. INTRODUCTION AND STATEMENT OF RESULTS

In a beautiful piece of work, Fefferman$^{(1,2)}$ has shown that a system of protons and electrons behaves as a gas of independent hydrogen atoms in a suitable low-density and low-temperature regime provided that an optimal form of the lower bound for the stability of matter holds. Let μ be the chemical potential associated with the total number density ρ and $-E_a$ ($E_a>0$) the ground-state energy of the hydrogen atom. Fefferman proves that if μ is fixed slightly above $-E_a$, the equation of state is that of a perfect gas of hydrogen atoms in their ground state when the temperature is small enough. On the other hand, if μ is chosen strictly less than $-E_a$ and $T\to 0$, the system will behave as a free gas of noninteracting protons and electrons.[2] This paper is concerned with the behavior of the Coulomb gas at the borderline between these two situations: we show that if one

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[1] Institut de Physique Théorique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

[2] Lebowitz and Penna$^{(3)}$ (and Hughes$^{(4)}$) establish that this is the case when $\mu\to -\infty$ and T is fixed.

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lets μ tend to $-E_a$ in the (μ, T) plane linearly with T [i.e., $\mu(T) = -E_a + \sigma T + o(T)$], one obtains a number of other equilibrium phases, the ionization equilibrium phases, which interpolate continuously between the free proton–electron gas and the pure atomic phase as σ ranges from $-\infty$ to $+\infty$.

In the standard thermodynamic treatment of equilibrium ionization,⁽⁵⁾ one uses a chemical picture where the unbound electrons (e) and protons (p) and the atoms (a) are considered as different species with number densities ρ_e, ρ_p, and ρ_a ($\rho_p = \rho_e$ by neutrality). Then the ionization equilibrum phases are characterized by their degree of ionization

$$\alpha = \frac{\rho_e}{\rho_e + \rho_a}, \qquad 0 \leqslant \alpha \leqslant 1 \tag{1.1}$$

Assuming that each species behaves as a perfect gas, one has for the equation of state

$$\frac{P}{k_B T} = \rho_e + \rho_p + \rho_a = \left(\frac{1+\alpha}{2}\right)\rho \tag{1.2}$$

where P is the pressure and $\rho = \rho_e + \rho_p + 2\rho_a$ is the total number density of protons and electrons. Applying the law of mass action to the reaction $e + p \leftrightarrow a$, one derives the Saha equation for thermal ionization expressing α in terms of pressure and temperature:

$$\alpha(P, T) = \left[1 + \frac{P}{k_B T}\left(\frac{2\pi\hbar^2}{\bar{m} k_B T}\right)^{3/2} \exp\left(\frac{E_a}{k_B T}\right)\right]^{-1/2} \tag{1.3}$$

where $\bar{m}$ is the reduced mass of the hydrogen atom.

Let H^{Ω}_{NM} be the Hamiltonian of N electrons and M protons in a region Ω with Dirichlet conditions at the boundary of Ω. The electrons and the protons have, respectively, charges $(e, -e)$ and masses (m_e, m_p), and they obey Fermi statistics. Here we neglect the spin of the electron, since it will play no role in the present situation. The corresponding grand-canonical partition function with chemical potentials $(\mu_e, \mu_p) = (\mu + \nu, \mu - \nu)$ and inverse temperature $\beta = (k_B T)^{-1}$ is

$$Z(\mu, \nu, \beta, \Omega) = \sum_{N, M=0}^{\infty} Z_{N,M}(\mu, \nu, \beta, \Omega) \tag{1.4}$$

$$Z_{N,M}(\mu, \nu, \beta, \Omega) = e^{\beta[\mu(N+M) + \nu(N-M)]} \operatorname{Tr} e^{-\beta H^{\Omega}_{NM}} \tag{1.5}$$

where the trace is taken on the space $L^2_{NM}(\Omega)$ of square-integrable functions antisymetric in the electron and proton coordinates $[Z_{0,0}(\mu, \nu, \beta, \Omega) = 1]$.

The theorems on the thermodynamic limit$^{(6)}$ ensure that the infinite-volume pressure and number density

$$\beta P(\mu, \beta) = \lim_{|\Omega| \to \infty} \frac{1}{|\Omega|} \ln Z(\mu, \nu, \beta, \Omega) \tag{1.6}$$

$$\rho(\mu, \beta) = \lim_{|\Omega| \to \infty} \frac{1}{|\Omega|} \langle N + M \rangle(\mu, \nu, \beta, \Omega) \tag{1.7}$$

exist and are independent of the projection ν of the chemical potential (μ_e, μ_p) on the charge vector $(e, -e)$. In (1.7), $\langle \cdots \rangle(\mu, \nu, \beta, \Omega)$ is the grand-canonical average with respect to H^{Ω}_{NM}.

The stability assumption of Fefferman is

$$H^{\Omega}_{NM} \geqslant -K(N + M - 1) \tag{1.8}$$

with $0 < K < E_a$ for $N + M > 2$ [see ref. 2 for a discussion of the validity of (1.8)]. Our result is formulated in the following theorem.

Theorem 1. Set

$$\mu(\beta) = -E_a + \sigma\beta^{-1} + o(\beta^{-1}), \qquad -\infty < \sigma < \infty \tag{1.9}$$

and assume that (1.8) holds; then

$$\lim_{\beta \to \infty} \frac{\beta P(\mu(\beta), \beta)}{\rho(\mu(\beta), \beta)} = \frac{1 + \alpha}{2} \tag{1.10}$$

with

$$\alpha = \left[\frac{(m_e m_p)^{3/4}}{(m_e + m_p)^{3/2}} e^{\sigma} + 1 \right]^{-1} \tag{1.11}$$

We add that the case where $\mu(\beta) = -E_a + g(\beta)$ with $g(\beta) \to 0$ but $\beta g(\beta) \to +\infty$ (resp. $-\infty$) as $\beta \to +\infty$ gives the value 1/2 (resp. 1) for the limit (1.10). This means that $\alpha = 0$, full binding (resp. $\alpha = 1$, full dissociation), and corresponds to $\sigma = \infty$ (resp. $\sigma = -\infty$) in (1.11).

As in Fefferman's work, one calculates explicit lower and upper bounds for the partition function (1.4), which have the structure of that of a mixture of three perfect gases of electrons, protons, and hydrogen atoms with number densities

$$\begin{aligned} \rho_e &= \left(\frac{m_e}{2\pi\beta\hbar^2} \right)^{3/2} e^{\beta(\mu + \nu)} \\ \rho_p &= \left(\frac{m_p}{2\pi\beta\hbar^2} \right)^{3/2} e^{\beta(\mu - \nu)} \\ \rho_a &= \left(\frac{m_e + m_p}{2\pi\beta\hbar^2} \right)^{3/2} e^{\beta(2\mu + E_a)} \end{aligned} \tag{1.12}$$

In (1.12), $\mu=\mu(\beta)$ is given by (1.9) and ν is set equal to

$$\nu(\beta)=\frac{3}{4\beta}\ln\frac{m_p}{m_e} \tag{1.13}$$

to ensure the neutrality $\rho_e=\rho_p$.

The lower bound (Section 2) is a modification of the subdomains inequality of Lieb and Lebowitz including nonneutral balls, while the upper bound (Section 3) is essentially that proven by Fefferman. With the help of these bounds, one finds that the pressure (1.6) and the number density (1.7) are asymptotically of the form

$$\beta P(\mu(\beta),\beta)=(\rho_e+\rho_p+\rho_a)\left[1+O\left(\frac{1}{\beta}\right)\right] \tag{1.14}$$

$$\rho(\mu(\beta),\beta)=(\rho_e+\rho_p+2\rho_a)\left[1+O\left(\frac{1}{\sqrt{\beta}}\right)\right] \tag{1.15}$$

as $\beta\to\infty$.

The result of the theorem follows immediately if one inserts the explicit formulas (1.12), (1.9), and (1.13) in (1.14) and (1.15). Moreover, one checks that the coefficient α in (1.11) is also expressed by the limit

$$\alpha=\lim_{\beta\to\infty}\left[1+\beta P(\mu(\beta),\beta)\left(\frac{2\pi\beta\hbar^2}{\bar{m}}\right)^{3/2}e^{\beta E_a}\right]^{-1/2} \tag{1.16}$$

so justifying the Saha equation (1.3) in the asymptotic regime (1.9).

During the completion of this work, Conlon *et al.*$^{(7)}$ published an article generalizing the results of Fefferman by different methods. They show that for fixed, negative $\boldsymbol{\mu}$ and $\beta\to\infty$, a system of nuclei end electrons behaves as a dilute gas of atoms or molecules of various kinds, depending on the choice of $\boldsymbol{\mu}$. The function defined by

$$y(\boldsymbol{\mu})=\lim_{\beta\to\infty}\frac{\beta P(\boldsymbol{\mu},\beta)}{\rho(\boldsymbol{\mu},\beta)} \tag{1.17}$$

is in general discontinuous when $\boldsymbol{\mu}$ is varied from a value selecting certain types of complexes to values corresponding to other types. In (1.17), for several species of charged particles, $\rho(\boldsymbol{\mu},\beta)$ is the total number density of nuclei and electrons, and $\boldsymbol{\mu}$ is the component of the chemical potential vector orthogonal to the charge vector. For instance, in the present case, $y(\mu)=1$ if $\mu<-E_a$ (fully dissociated phase) and $y(\mu)=1/2$ if μ is slightly above $-E_a$ (atomic phase). However, Theorem 1 shows that the ionization equilibrium phases interpolate continuously between these two situations by letting μ approach $-E_a$ in various directions in the (μ, T) plane. In the general case, one can expect a similar description of the phase coexistence between different sets of atomic or molecular complexes when one lets $\boldsymbol{\mu}$ tend to a point of discontinuity of $y(\boldsymbol{\mu})$ in various directions in the $(\boldsymbol{\mu}, T)$ space as $T \to 0$. The algebraic error terms in (1.14) and (1.15) could probably be improved to exponentially small ones with the techniques of ref. 7.

In Section 6, we present results on ionization equilibrium obtained in a simpler model.$^{(8)}$ The model consists of a single quantum particle interacting with a gas of classical hard spheres by means of an attractive short-range potential. One can then investgate the low-density and low-temperature behavior of the system by activity expansions. In the same regime as in (1.9), we show that, when a stability condition analogous to (1.8) is satisfied, the ionization probability for the quantum particle approaches a well-defined limit α, $0 < \alpha < 1$ (the Saha coefficient). This particle is found to be in a statistical mixture of a free state and a bound state with weights respectively equal to α and $1-\alpha$. While this model is oversimplified with respect to the real electron–proton gas, the main features are qualitatively the same in the two situations. Moreover, this simpler model may be of interest to treat more difficult questions, such as the first low-density corrections and the broadening of spectral lines. Details and proofs can be found in ref. 8.

2. THE PARTITION FUNCTION FOR A SINGLE BALL

Here and in the next sections, we follow Fefferman's analysis$^{(1)}$ very closely and only indicate places where modifications of his proof occur. We keep the same notation as in ref. 1. More details can be found in ref. 9.

The general strategy is to decompose the region Ω into subdomains, mainly balls B of radius R. The balls must have a size, depending on the temperature, such that if they contain anything, this will most likely be one electron, or one proton, or a single hydrogen atom.

Let

$$P_{N,M}(B) = \frac{Z_{N,M}(\mu, \nu, \beta, B)}{Z(\mu, \nu, \beta, B)} \tag{2.1}$$

be the probability of finding N electrons and M protons in B. We will make a choice of μ, ν, and B such that for β large

$$P_{0,0}(B) \gg P_{1,0}(B) \cong P_{0,1}(B) \cong P_{1,1}(B) \gg P_{N,M}(B) \tag{2.2}$$

for all $(N, M) \neq (0, 0)$, $(1, 0)$, $(0, 1)$, and $(1, 1)$.

One has the following estimates. There exist (small) positive numbers c, c_1, and c_2, with $c_1 > c_2$, such that for any R with

$$e^{\beta c_2} \leqslant R \leqslant e^{\beta c_1} \tag{2.3}$$

and β large,

$$\begin{aligned} Z_{1,0}(\mu, \nu, \beta, B) &= \rho_e\, |B| \left\{1 - \frac{3}{4}(2\pi)^{1/2} \frac{\lambda_e}{R}\,[1 + o(1)]\right\} && (2.4)\\ &= \rho_e\, |B|\,[1 + O(e^{-c\beta})] \\ Z_{0,1}(\mu, \nu, \beta, B) &= \rho_p\, |B| \left\{1 - \frac{3}{4}(2\pi)^{1/2} \frac{\lambda_p}{R}\,[1 + o(1)]\right\} && (2.5)\\ &= \rho_p\, |B|\,[1 + O(e^{-c\beta})] \\ Z_{1,1}(\mu, \nu, \beta, B) &= \rho_a\, |B|\,[1 + O(e^{-c\beta})] && (2.6) \end{aligned}$$

The densities ρ_e, ρ_p, and ρ_a are defined as in (1.3) for general values of μ and ν, and $\lambda_s = (\beta\hbar^2/m_s)^{1/2}$, $s = e, p$, are the thermal wavelengths.

Equation (2.6) is established in Section 4 of ref. 1 (at this point, the error term is indeed exponential). Equations (2.4) and (2.5) follow from the asymptotic properties of the eigenvalues of the Dirichlet Laplacian Δ_B,(10)

$$\operatorname{Tr} \exp \frac{\Delta_B}{2} = \left(\frac{1}{2\pi t}\right)^{3/2} |B| - \frac{1}{8\pi t}\,|\partial B| + o\left(\frac{1}{t}\right), \qquad t \to 0 \tag{2.7}$$

By scaling, one has

$$\operatorname{Tr} \exp(-\beta H^B_{1,0}) = \operatorname{Tr} \exp\left[\left(\frac{\lambda_e}{R}\right)^2 \frac{\Delta_{B_1}}{2}\right]$$

with B_1 the sphere of radius 1, and $\lambda_e/R \to 0$ as $\beta \to \infty$ when (2.3) holds. Thus, (2.7) can be written as

$$\operatorname{Tr} \exp(-\beta H^B_{1,0}) = \frac{1}{(2\pi)^{3/2}} \frac{|B|}{\lambda_e^3} \left\{1 - \frac{3}{4}(2\pi)^{1/2} \frac{\lambda_e}{R}\,[1 + o(1)]\right\} \tag{2.8}$$

Taking (1.5) and (1.12) into account, this leads to (2.4), and (2.5) is obtained in the same way.

The reason for keeping explicitly the surface term in (2.4) and (2.5) is that it shows immediately the inequality (β sufficiently large)

$$\frac{Z_{1,0}(\mu, \nu, \beta, B)}{\rho_e} \leqslant \frac{Z_{0,1}(\mu, \nu, \beta, B)}{\rho_p} \tag{2.9}$$

due to the fact that $m_e < m_p$. The inequality (2.9) holds more generally for an fixed B and all β as a consequence of the monotonicity of the function $t^{3/2}\operatorname{Tr}\exp(t\Delta_B/2)$ (see Appendix).

From now on, we set

$$\nu = \frac{3}{4\beta}\ln\frac{m_p}{m_e} \qquad \text{and} \qquad \mu = -E_a + \sigma\beta^{-1} + o(\beta^{-1})$$

as in (1.13) and (1.9). Hence one has $\rho_e = \rho_p$, giving asymptotically the same probability for finding a proton or an electron in B, and (2.9) reduces to

$$Z_{1,0}(\mu, \nu, \beta, B) \leqslant Z_{0,1}(\mu, \nu, \beta, B) \tag{2.10}$$

Moreover, all terms (2.4)–(2.6) are of the same leading order $\beta^{-3/2}\exp(-\beta E_a) \ll 1$. The establishes the first part of (2.2).

The relations (2.4)–(2.6) imply

$$\begin{aligned} 1 + Z_{1,0}(\mu, \nu, \beta, B) &+ Z_{0,1}(\mu, \nu, \beta, B) + Z_{1,1}(\mu, \nu, \beta, B) \\ &= 1 + (\rho_e + \rho_p + \rho_a)|B|\,[1 + O(e^{-c\beta})] \\ &= \exp\{(\rho_e + \rho_p + \rho_a)|B|\,[1 + O(e^{-c\beta})]\} \end{aligned} \tag{2.11}$$

and since $\rho_e = \rho_p$, we have the same estimate with $Z_{0,1}(\mu, \nu, \beta, B)$ replaced by $Z_{1,0}(\mu, \nu, \beta, B)$ in the left-hand side of (2.11) or vice versa.

The contribution of all terms (N, M) in (1.4) with $N \neq 0, 1$ and $M \neq 0, 1$ is

$$\sum_{N, M \neq 0, 1} Z_{N,M}(\mu, \nu, \beta, B) = Z_{1,1}(\mu, \nu, \beta, B)\, O(e^{-c\beta}) \tag{2.12}$$

This estimate is obtained in Section 4 of ref. 1 with $\nu = 0$ and for all μ less than $-E_0 + \delta$, δ small and positive, as a consequence of the stability condition (1.8). It is easily checked that it holds also with ν given by (1.13) because ν is $O(\beta^{-1})$. So (2.12) is true in the present case. Taking now into account (2.4)–(2.6) and the fact that $Z_{N,M}(\mu, \nu, \beta, B)$, $(N, M) = (1, 0), (0, 1)$, and $(1, 1)$, are of the same order, we conclude from (2.12) that the second part of (2.2) is satisfied. Moreover, we can write (2.12) in the form

$$\sum_{N, M \neq 0, 1} Z_{N,M}(\mu, \nu, \beta, B) = (\rho_e + \rho_p + \rho_a)|B|\, O(e^{-c\beta}) \tag{2.13}$$

This combined with (2.11) gives finally

$$Z(\mu, \nu, \beta, B) = \exp\{(\rho_e + \rho_p + \rho_a)|B|\,[1 + O(e^{-c\beta})]\} \tag{2.14}$$

for any ball satisfying (2.3), ν, μ given by (1.13) and (1.18), and β large enough.

3. LOWER BOUND FOR THE PARTITION FUNCTION

To obtain lower and upper bounds for the partition function (1.4) with an arbitrary large domain Ω (say $|\Omega| \geqslant e^{C\beta}$ for some large, positive constant C), one decomposes it into a disjoint union of balls B_i with radii satisfying the condition (2.3) (a "swiss cheese"), plus a remainder which is $O(e^{-c\beta})|\Omega|$. We refer to Section 6 of ref. 1 for the explicit construction of this "swiss cheese." The method to find a lower bound for $Z(\mu, \nu, \beta, \Omega)$ is adapted from ref. 6 to account for nonneutral balls.

Proposition 1. Let $\mu = \mu(\beta)$ be given by (1.9),

$$\nu = \frac{3}{4\beta} \ln \frac{m_p}{m_e}$$

and take a collection of disjoint balls $B_1, \dots, B_k$, with radii $e^{c_1\beta} < R_i < e^{c_1\beta}$, such that their union is included in Ω. Then, for β sufficiently large, we have

$$Z(\mu, \nu, \beta, \Omega) \geqslant \exp\Big\{(\rho_e + \rho_p + \rho_a) \sum_{i=1}^{k} |B_i| [1 + O(e^{-c\beta})]\Big\} \tag{3.1}$$

The proof of the proposition relies on the inequality

$$\begin{aligned} Z(\mu, \nu, \beta, \Omega) \geqslant \sum_{(N_1, M_1) \cdots (N_k, M_k)} & \left[\prod_{i=1}^{k} Z_{N_i, M_i}(\mu, \nu, \beta, B_i) \right] \\ & \times \exp[-\beta V(N_1, M_1, \dots, N_k, M_k)] \end{aligned} \tag{3.2}$$

where

$$V(N_1, M_1, \dots, N_k, M_k) = e^2 \sum_{l<m}^{k} \frac{(N_l - M_l)(N_m - M_m)}{|\mathbf{r}_l - \mathbf{r}_m|} \tag{3.3}$$

is the interaction between the balls B_i of center $\mathbf{r}_i$, $i = 1, \dots, k$. The inequality (3.2) is the Lieb and Lebowitz subdomains inequality for a collection of balls B_i having total charge $e(N_i - M_i)$.(6)

Proof of Proposition 1. For each set $I \subseteq \{1, \dots, k\}$ of cardinality $|I|$ and complement I^c, we define two sets of sequences. The first one is composed of the sequences of couples (N_i, M_i) with $i \in I^c$ and (N_i, M_i) taking values in $\{(0, 0), (1, 1)\}$. The second one is composed of the sequences of couples (N_i, M_i) with $i \in I$ and (N_i, M_i) taking values in $\{(1,0), (0,1)\}$. These two sets of sequences are denoted, respectively, by $S_0(I^c)$ and $S_1(I)$. If $I^c = \varnothing$ or $I = \varnothing$, then we define $S_0(I^c) = \varnothing$ or $S_1(I) = \varnothing$.

We note that in (3.2) the inequality is preserved if we restrict the sums to the values (0, 0), (1, 0), (0, 1), (1, 1) for (N_i, M_i), $i = 1,..., k$. Thus, by a rearrangement of the restricted sum, we get

$$\begin{aligned}
&Z(\mu, \nu, \beta, \Omega)\\
&\quad \geqslant \sum_{I \subseteq \{1...k\} \text{ or } I = \varnothing} \; \sum_{S_0(I^c)} \sum_{S_1(I)} \left[\prod_{i=1}^{k} Z_{N_i, M_i}(\mu, \nu, \beta, B_i)\right]\\
&\qquad \times \exp[-\beta V(N_1, M_1,..., N_k, M_k)]\\
&\quad = \sum_{I \subseteq \{1...k\} \text{ or } I = \varnothing} \; \sum_{S_0(I^c)} \left[\prod_{i \in I^c} Z_{N_i, M_i}(\mu, \nu, \beta, B_i)\right]\\
&\qquad \times \sum_{S_1(I)} \left[\prod_{i \in I} Z_{N_i, M_i}(\mu, \nu, \beta, B_i)\right] \exp[-\beta V(N_1, M_1,..., N_k, M_k)]
\end{aligned} \tag{3.4}$$

The inequality (3.4) is valid for any β, μ, ν and any collection of disjoint balls included in Ω. Now, we specialize it to the conditions of the proposition and we apply the result (2.10) of Section 2,

$$\begin{aligned}
&Z(\mu, \nu, \beta, \Omega)\\
&\quad \geqslant \sum_{I \subseteq \{1...k\} \text{ or } I = \varnothing} \; \sum_{S_0(I^c)} \left[\prod_{i \in I^c} Z_{N_i, M_i}(\mu, \nu, \beta, B_i)\right] \times \left[\prod_{i \in I} Z_{1,0}(\mu, \nu, \beta, B_i)\right]\\
&\qquad \times \sum_{S_1(I)} \exp[-\beta V(N_1, M_1,..., N_k, M_k)]
\end{aligned} \tag{3.5}$$

Let us remark that for a fixed I and a fixed sequence in $S_0(I^c)$ we have from the formula (3.3)

$$\begin{aligned}
&\sum_{S_1(I)} V(N_1, M_1,..., N_k, M_k)\\
&\quad = \sum_{S_1(I)} e^2 \sum_{(l<m) \in I} \frac{(N_l - M_l)(N_m - M_m)}{|\mathbf{r}_l - \mathbf{r}_m|}\\
&\quad = \sum_{(l<m) \in I} \frac{e^2}{|\mathbf{r}_l - \mathbf{r}_m|} \sum_{S_1(I \backslash (l,m))} \sum_{S_1(l,m)} (N_l - M_l)(N_m - M_m) = 0
\end{aligned} \tag{3.6}$$

The last equality follows from the explicit summation over the four sequences of $S_1(l, m)$. The convexity of the exponential together with (3.6) implies

$$\sum_{S_1(I)} \exp[-\beta V(N_1, M_1,..., N_k, M_k)] \geqslant 2^{|I|} \tag{3.7}$$

From (3.5) and (3.7) we have

$$\begin{aligned} Z(\mu, \nu, \beta, \Omega) \geqslant & \sum_{I \subseteq \{1...k\} \text{ or } I = \varnothing} \ \sum_{S_0(I^c)} \prod_{i \in I^c} Z_{N_i, M_i}(\mu, \nu, \beta, B_i) \\ & \times \sum_{S_1(I)} \prod_{i \in I} Z_{1,0}(\mu, \nu, \beta, B_i) \\ = & \prod_{i=1}^{k} [1 + Z_{1,0}(\mu, \nu, \beta, B_i) + Z_{1,0}(\mu, \nu, \beta, B_i) \\ & + Z_{1,1}(\mu, \nu, \beta, B_i)] \end{aligned} \tag{3.8}$$

Then the result (3.1) of the proposition follows immediately from (2.11) and the remark following (2.11).

Since the balls cover Ω up to a volume $O(e^{-c\beta})|\Omega|$, we get finally

$$Z(\mu, \nu, \beta, \Omega) \geqslant \exp\{(\rho_e + \rho_p + \rho_a)|\Omega| [1 + 0(e^{-c\beta})]\} \tag{3.9}$$

4. UPPER BOUND FOR THE PARTITION FUNCTION

We recall some basic estimates proven in ref. 1. The first one is an inequality between the full Hamiltonian H^{Ω}_{NM} and an effective temperature-dependent hamiltonian $\mathfrak{h}$ essentially obtained by switching off the Coulomb interaction between particles belonging to different balls [Eq. (7.9) of ref. 1]

$$\mathfrak{h} \leqslant (1 + e^{-c\beta}) H^{\Omega} + Ce^{-c\beta}(N + M) + \frac{C}{\beta} V \tag{4.1}$$

In (4.1), c, C are volume and temperature independent constants (which may have different numerical values at different places). V is a potential energy accounting for the missing part of the interaction in $\mathfrak{h}$: it corresponds to a locally regularized Coulomb potential due to smeared charges in the balls. We refer to ref. 1 for a complete description of $\mathfrak{h}$ and V. Since $\mathfrak{h}$ pertains to uncoupled balls, the corresponding partition function can be estimated by a product of partition functions for the balls, up to a small contribution due to the fraction of Ω not covered by the balls. Thus, in the ionization equilibrium regime defined by (1.9) and (1.13), one finds from (2.14)

$$\begin{aligned}
&\operatorname{Tr}\exp[-\beta\mathfrak{h}+\beta\mu(N+M)+\beta\nu(N-M)]\\
&\quad\leqslant\prod_i Z(\mu,\nu,\beta,B_i)\exp[\rho_a\,|\Omega|\,O(e^{-c\beta})]\\
&\quad=\exp\left\{(\rho_e+\rho_p+\rho_a)\sum_i|B_i|[1+O(e^{-c\beta})]\right\}\exp[\rho_a\,|\Omega|\,O(e^{-c\beta})]\\
&\quad=\exp\{(\rho_e+\rho_p+\rho_a)|\Omega|[1+O(e^{-c\beta})]\}
\end{aligned}\tag{4.2}$$

Moreover, the following estimate [Eq. (7.6) of ref. 1] shows that, on the average, V becomes negligible at small temperatures and densities,

$$\langle V\rangle(\mu,\nu,\beta,\Omega)\leqslant\frac{C}{\beta}\langle N+M\rangle(\mu,\nu,\beta,\Omega)+Ce^{-c\beta}(\rho_e+\rho_p+\rho_a)\,|\Omega|\tag{4.3}$$

The proof of (4.2) and (4.3) is exactly as in ref. 1 with the trivial adjunction of the ν component of the chemical potential. Since (4.3) is the estimation of an average (i.e., involving a division by the partition function), it requires also the use of the lower bound in the form (3.9).

We write now (4.1) as

$$\begin{aligned}
&\beta\mathfrak{h}-\beta\mu(N+M)-\beta\nu(N-M)\\
&\qquad\leqslant\bar\beta H^{\Omega}-\bar\beta\bar\mu(N+M)-\bar\beta\bar\nu(N-M)+CV
\end{aligned}\tag{4.4}$$

with $\bar\beta$, $\bar\mu$, and $\bar\nu$ defined by

$$\begin{aligned}
\bar\beta&=\beta(1+e^{-c\beta})\\
\bar\beta\bar\mu&=\beta(\mu-Ce^{-c\beta})\\
\bar\beta\bar\nu&=\beta\nu
\end{aligned}\tag{4.5}$$

Clearly, if $\mu(\beta)$ and $\nu(\beta)$ belong to the class of functions (1.9), (1.13), the same is true for the functions $\bar\mu(\bar\beta)$ and $\bar\nu(\bar\beta)$ given by (4.5). Moreover, denoting by $\bar\rho_s$, $s=e, p, a$, the densities ρ_s in (1.12) written for $\bar\beta$, $\bar\mu$, and $\bar\nu$, one verifies that

$$\rho_s=\bar\rho_s[1+O(e^{-c\beta})]\tag{4.6}$$

Finally, using (4.4), (4.2), (4.6), and the Peierls–Bogoliubov inequality leads to

$$
\begin{aligned}
Z(\bar{\mu}, \bar{\nu}, \bar{\beta}, \Omega) &\leqslant \exp[C\langle V\rangle(\bar{\mu}, \bar{\nu}, \bar{\beta}, \Omega)] \\
&\quad \times \exp\{(\bar{\rho}_e+\bar{\rho}_p+\bar{\rho}_a)\,|\Omega|\,[1+O(e^{-c\beta})]\} \\
&\leqslant \exp\left[\frac{C}{\bar{\beta}} < N+M > (\bar{\mu}, \bar{\nu}, \bar{\beta}, \Omega)\right] \\
&\quad \times \exp\{(\bar{\rho}_e+\bar{\rho}_p+\bar{\rho}_a)\,|\Omega|\,[1+O(e^{-c\beta})]\} \qquad (4.7)
\end{aligned}
$$

where the second inequality (4.7) follows from (4.3) written for $\bar{\beta}$, $\bar{\mu}$, $\bar{\nu}$.

In the next section, we show that the expected value of the total number of particles is

$$
\langle N+M\rangle(\bar{\mu}, \bar{\nu}, \bar{\beta}, \Omega) = (\bar{\rho}_e+\bar{\rho}_p+2\bar{\rho}_a)\,|\Omega|\,[1+O(\bar{\beta}^{-1/2})] \qquad (4.8)
$$

The results (4.7), (4.8), and (3.9) imply the asymptotic expressions (1.14) and (1.15) of the pressure and the number density for the proton–electron system in the thermodynamic limit. This proves Theorem 1.

5. ESTIMATE OF OBSERVABLES

To estimate the average value of an observable A, we use again (4.4) with the term $-tA$ (t small positive or negative) added on each side of the inequality. Then, we apply the Peierls–Bogoliubov inequality to let the average value of $tA - CV$ appear, and use (4.3) together with the lower bound (3.9). This leads to

$$
\begin{aligned}
&\exp[t\langle A\rangle(\bar{\mu}, \bar{\nu}, \bar{\beta}, \Omega) \\
&\quad \leqslant \exp\left[\frac{C}{\bar{\beta}}\langle N+M\rangle(\bar{\mu}, \bar{\nu}, \bar{\beta}, \Omega)\right] \\
&\quad \times \frac{\operatorname{Tr}\exp[-\beta\mathfrak{h} + tA + \beta\mu(N+M) + \beta\nu(N-M)]}{\exp\{(\bar{\rho}_e+\bar{\rho}_p+\bar{\rho}_a)\,|\Omega|\,[1+O(e^{-c\beta})]\}} \qquad (5.1)
\end{aligned}
$$

The choice $A = N+M$ amounts obviously to a shift of the chemical potential μ to $\mu + t/\beta$ in the rhs of the numerator in (5.1). Since this new chemical potential still belongs to the class of function (1.9), we can apply the inequality (4.2) with the appropiate changes in the densities (1.12)

$$
\begin{aligned}
&\operatorname{Tr}\exp[-\beta\mathfrak{h} + t(N+M) + \beta\mu(N+M) + \beta\nu(N-M)] \\
&\quad \leqslant \exp\{(e^t\rho_e + e^t\rho_p + e^{2t}\rho_a)\,|\Omega|\,[1+O(e^{-c\beta})]\} \qquad (5.2)
\end{aligned}
$$

From (5.1), (5.2), and (4.6), we have

$$\exp\left[\left(t-\frac{C}{\bar{\beta}}\right)\langle N+M\rangle(\bar{\beta},\bar{\mu},\bar{\nu},\Omega)\right]$$
$$\leqslant \exp\{t(\bar{\rho}_e+\bar{\rho}_p+\bar{\rho}_a)\,|\Omega|$$
$$\times[1+O(|t|)+O(|t|\,e^{-c\beta})+O(e^{-c\beta})]\} \tag{5.3}$$

Taking successively $t=\pm\bar{\beta}^{-1/2}$ (this is the optimal choice), we obtain the desired result (4.8).

To estimate the total kinetic energy

$$K^{\Omega}=-\frac{\hbar^2}{2m_e}\Delta_e-\frac{\hbar^2}{2m_p}\Delta_p$$

(with Δ_e, Δ_p, the Dirichlet Laplacians for electron and proton coordinates), we note that the modification of the masses

$$m_s\to m_s(t)=(1+t)^{-1}m_s, \qquad s=e,\,p \tag{5.4}$$

corresponds to the addition of a kinetic energy term to the total Hamiltonian

$$H_{NM}^{\Omega}\to H_{NM}^{\Omega}+tK^{\Omega} \tag{5.5}$$

Denoting by $\mathfrak{h}(t)$ the effective Hamiltonian $\mathfrak{h}$ with the masses $m_e(t)$ and $m_p(t)$, the inequality (4.4) becomes

$$\beta\mathfrak{h}(t)-\beta\mu(N+M)-\beta\nu(N-M)$$
$$\leqslant\bar{\beta}(H^{\Omega}+tK^{\Omega})-\bar{\beta}\bar{\mu}(N+M)-\bar{\beta}\bar{\nu}(N-M)+CV \tag{5.6}$$

[the estimate (4.1) is uniform with respect to the masses in a neighborhood of (m_e, m_p)]. In the same way as for (5.1), we deduce with help of the Peierls–Bogoliubov inequality

$$\exp[-\bar{\beta}t\langle K^{\Omega}\rangle(\bar{\mu},\bar{\nu},\bar{\beta},\Omega)]$$
$$\leqslant\exp\left[\frac{C}{\bar{\beta}}<N+M\rangle(\bar{\mu},\bar{\nu},\bar{\beta},\Omega)\right]$$
$$\times\frac{\operatorname{Tr}\exp[-\beta\mathfrak{h}(t)+\beta\mu(N+M)+\beta\nu(N-M)]}{\exp\{(\bar{\rho}_e+\bar{\rho}_p+\bar{\rho}_a)\,|\Omega|[1+O(e^{-c\beta})]\}} \tag{5.7}$$

We can now apply the inequality (4.2) to the numerator in the rhs of (5.7) with the densities $\rho_s(t)$, $s=e,\,p,\,a$, corresponding to the modified masses (5.4)

$$\operatorname{Tr}\exp[-\beta\mathfrak{h}(t)+\beta\mu(N+M)+\beta\nu(N-M)]$$
$$\leqslant\exp\{[\rho_e(t)+\rho_p(t)+\rho_a(t)]\,|\Omega|[1+O(e^{-c\beta})]\} \tag{5.8}$$

Since the ground-state energy E_a of the hydrogen atom is transformed to $E_a(1+t)^{-1}$, one obtains from (1.12)

$$\begin{aligned} \rho_s(t) &= \rho_s[1+O(|t|)], \qquad s=e,\, p \\ \rho_a(t) &= \rho_a \exp\{[-\beta t E_a + O(\beta t^2)][1+O(|t|)]\} \end{aligned} \tag{5.9}$$

Choosing $t = \pm\beta^{-3/2}$ in (5.9) and using (4.6) and the fact that $\langle N+M\rangle$ is of order $\rho_a\,|\Omega|$, we see that (5.7) reduces to

$$\exp[\pm\beta^{-1/2}\langle K^\Omega\rangle] \leqslant \exp\{\pm\beta^{-1/2}\bar{\rho}_a E_a[1+O(\beta^{-1/2})]\} \tag{5.10}$$

Hence

$$\langle K^\Omega\rangle(\mu, \nu, \beta, \Omega) = \rho_a\,|\Omega|\; E_a[1+O(\beta^{-1/2})] \tag{5.11}$$

Moreover, one finds by similar arguments that the total energy is

$$\langle H^\Omega\rangle(\mu, \nu, \beta, \Omega) = -\rho_a\,|\Omega|\; E_a[1+O(\beta^{-1/2})] \tag{5.12}$$

Thus, in the limit $\beta \to \infty$, the total energy is just the ground-state energy of the atoms, as it should be. It is interesting to remark that in the same limit, the total kinetic energy does not vanish, but is the quantum internal kinetic energy of the atoms. It is indeed well known for the hydrogen atom that this quantity is opposite in sign to the ground-state energy.

6. A SIMPLE MODEL

We consider a single quantum mechanical particle of mass m_e (the "electron") in thermal equilibrium with a classical gas of hard spheres with radius d and mass m_p (the "impurities"). The electron interacts with each of the impurities by means of a spherically symmetric attractive potential $V(\mathbf{x})$. The potential $V(\mathbf{x})$ is nonpositive, integrable at infinity, and can have a square integrable singularity at $\mathbf{x} = \mathbf{o}$.

If there are no impurities, the energy of the electron $H^0 = -(\hbar^2/2m_e)\,\Delta$ is purely kinetic, where Δ is the Laplacian. For a configuration of n impurities at $\mathbf{r}_1,\dots, \mathbf{r}_n$, $|\mathbf{r}_i - \mathbf{r}_j| > 2d$, $i \neq j = 1, \dots, n$ and $n \geqslant 1$, the Hamiltonian of the electron

$$H^n(\mathbf{r}_1,\dots, \mathbf{r}_n) = -\frac{\hbar^2}{2m_e}\Delta + \sum_{j=1}^{n} V(\mathbf{r}_j - \mathbf{x}) \tag{6.1}$$

has a finite number of bound states of finite multiplicities with negative energies and an absolutely continuous spectrum on $[0, \infty]$. In particular, the one-impurity Hamiltonian is unitarily equivalent by translation to

$$H^1(\mathbf{o}) = -\frac{\hbar^2}{2m_e}\Delta + V(\mathbf{x}) \tag{6.2}$$

which has a nondegenerate ground state with energy $-E_a$ ($E_a > 0$) and wave function $\psi_a(\mathbf{x})$. In ref. 8, we prove the following stability estimate, which is the analogue of the assumption (1.8) of Fefferman for Coulombic matter.

Proposition 2. For d large enough, there exists K independent of n and $\mathbf{r}_1,..., \mathbf{r}_n$, $n \geqslant 2$, such that

$$0 < K < E_a \tag{6.3}$$

and

$$H^n(\mathbf{r}_1,..., \mathbf{r}_n) \geqslant -Kn \qquad \text{for} \quad n \geqslant 2 \quad \text{and} \quad |\mathbf{r}_i - \mathbf{r}_j| \geqslant 2d, \quad i \neq j \tag{6.4}$$

The important point in this form of the inequality is that the stability constant K can be chosen strictly smaller than the binding energy E_a of the atom. We will come back to this point at the end of this section.

In order to properly define the ionization rate in this model, we introduce the grand canonical average $p_\Lambda(dE, \beta, \mu)$ of the energy distribution of the electron in the volume Λ at temperature β^{-1} and chemical potential μ. It is conveniently defined by its Laplace transform

$$\begin{aligned} g_\Lambda(\lambda, \beta, \mu) &= \int_{-\infty}^{\infty} e^{-\lambda E} p_\Lambda(dE, \beta, \mu) \\ &= \langle \exp(-\lambda H^n) \rangle_\Lambda (\beta, \mu) = \frac{\Xi_\Lambda(\lambda, \beta, \mu)}{\Xi_\Lambda(\lambda = 0, \beta, \mu)} \end{aligned} \tag{6.5}$$

where

$$\begin{aligned} \Xi_\Lambda(\lambda, \beta, \mu) &= \exp[-(\beta + \lambda) H_\Lambda^0] \\ &\quad + \sum_{n=1}^{\infty} \frac{e^{\beta\mu n}}{n!} \left(\frac{m_p}{2\pi\beta\hbar^2}\right)^{3n/2} \int_\Lambda d\mathbf{r}_1 \cdots \int_\Lambda d\mathbf{r}_n \\ &\quad \times \operatorname{Tr} \exp[-(\beta + \lambda) H_\Lambda^n(\mathbf{r}_1,..., \mathbf{r}_n)] \prod_{i<j}^{n} \chi(\mathbf{r}_i - \mathbf{r}_j) \end{aligned} \tag{6.6}$$

and $\Xi_\Lambda(\lambda = 0, \beta, \mu)$ is the grand canonical partition function. In (6.6), $H_\Lambda^n(\mathbf{r}_1,..., \mathbf{r}_n)$ is the Hamiltonian (6.1) with Dirichlet conditions on the boundaries of Λ and $\chi(\mathbf{r}) = 1$, $|\mathbf{r}| \geqslant 2d$; $\chi(\mathbf{r}) = 0$, $|\mathbf{r}| \leqslant 2d$.

Using (6.4), one can show that $g_\Lambda(\lambda, \beta, \mu)$ is represented by low-activity series uniformly convergent with respect to the volume $|\Lambda|$ and that its infinite-volume limit $g(\lambda, \beta, \mu)$ can be computed term by term.

Since in infinite space, quantum states for the Hamiltonian (6.1) with $E \geqslant 0$ (resp. $E < 0$) represent ionized states (resp. bound states), we define the ionization probability $\alpha(\beta, \mu)$ [resp. the binding probability $1 - \alpha(\beta, \mu)$] by the total weight of the positive energy states

$$\alpha(\beta, \mu) = \lim_{\varepsilon > 0, \varepsilon \to 0} \int_{-\varepsilon}^{+\infty} p(dE, \beta, \mu) \tag{6.7}$$

where $p(dE, \beta, \mu)$ is the infinite-volume limit of the energy distribution defined by (6.5).

The main result of ref. 8 is formulated in the following theorem.

Theorem 2. Let $V(\mathbf{x})$ be in the class of potentials described above and the inequalities (6.3) and (6.4) be satisfied; then, for a fixed μ,

(i$_1$) $\lim_{\beta \to \infty} g(\lambda, \beta, \mu) = 1$ when $\mu \in (-\infty, -E_a)$

(i$_2$) $\lim_{\beta \to \infty} g(\lambda, \beta, \mu) = e^{\lambda E_a}$ when $\mu \in (-E_a, -K)$

(ii) If $\mu(\beta) = -E_a + \sigma\beta^{-1} + o(\beta^{-1})$, $-\infty < \sigma < \infty$, then

$$\lim_{\beta \to \infty} g(\lambda, \beta, \mu(\beta)) = \alpha + (1 - \alpha)\, e^{\lambda E_a} \qquad \text{with} \quad \alpha = \left[\left(\frac{m_p}{m_e}\right)^{3/2} e^{\sigma} + 1\right]^{-1}$$

The cases (i$_1$) and (i$_2$) correspond, respectively, to full ionization and full binding. Indeed, in (i$_1$), the energy distribution is concentrated at the edge $E = 0$ of the continuous spectrum, giving $\lim_{\beta \to \infty} \alpha(\beta, \mu) = 1$, while in (i$_2$), the distribution is concentrated at $-E_a$, giving $\lim_{\beta \to \infty} \alpha(\beta, \mu) = 0$. The case (ii) corresponds to partial ionization with $\alpha = \lim_{\beta \to \infty} \alpha(\beta, \mu(\beta))$, $0 < \alpha < 1$. It interpolates continuously between full ionization and full binding as σ is varied from $-\infty$ to $+\infty$.

One obtains also that the momentum distribution of the electron $p(d\mathbf{k}, \beta, \mu)$ tends to

$$\lim_{\beta \to \infty} p(d\mathbf{k}, \beta, \mu(\beta)) = \alpha\delta(\mathbf{k} = \mathbf{o})\, d\mathbf{k} + (1 - \alpha)\, |\tilde{\psi}_a(\mathbf{k})|^2\, d\mathbf{k} \tag{6.8}$$

where $\tilde{\psi}_a(\mathbf{k})$ is the Fourier transform of the ground state $\psi_a(\mathbf{x})$. Thus, when $\alpha \neq 0, 1$, the electron is found in a statistical mixture of a free (zero-momentum) state and a bound state.

We conclude this section with a few remarks. To prove the theorem, we represent the quantities of interest by their low-activity series. The nth order term in these series behaves asymptotically for $\beta \to \infty$ as the Boltzmann weight $\exp[\beta(E_n + \mu n)]$ (up to algebraic functions of β), where

$$E_n = -\inf_{\mathbf{r}_1,\ldots,\mathbf{r}_n} \quad \inf_{|\mathbf{r}_i - \mathbf{r}_j| \geqslant 2d, i \neq j} \operatorname{spec} \quad H^n(\mathbf{r}_1,\ldots,\mathbf{r}_n) \tag{6.9}$$

To obtain a thermodynamic regime where the atom is formed, one must be able to find μ such that the Boltzmann weight corresponding to a single impurity dominates all the others ($E_0 = 0$, $E_1 = E_a$), i.e.,

$$\begin{aligned} &E_1 + \mu > 0 \\ &E_1 + \mu > 0 > E_n + \mu n, \qquad n \geqslant 2 \end{aligned} \tag{6.10}$$

This is possible thanks to the stability estimate (6.3)–(6.4) ($E_n \leqslant Kn$ with $0 < K < E_1$). Indeed, when (6.3) holds, one can choose μ in the interval $(-E_1, -K)$, implying obviously

$$E_n + \mu n \leqslant E_n - Kn < 0 < E_1 + \mu \tag{6.11}$$

So the set of inequalities (6.10) can be satisfied. At this point, it is important to note that a repulsive interaction between the impurities is essential. For example, when $n = 2$, (6.10) holds only if $2E_1 > E_2$. But if one sets $d = 0$ in (6.9), one has

$$E_2 \geqslant -\inf \operatorname{spec} H^2(\mathbf{o}, \mathbf{o}) = -E(2) \tag{6.12}$$

where $E(\gamma)$ is the ground-state energy of the one-impurity Hamiltonian $-(\hbar^2/m_e)\Delta + \gamma V(\mathbf{x})$ with coupling constant γ. Since $E(\gamma)$ is concave, $E(2) \leqslant 2E(1) = -2E_1$. Hence, by (6.12), we find $2E_1 \leqslant E_2$ when $d = 0$. In other words, to observe an atomic phase, the gain in binding energy by adding a second impurity must be less than the binding energy of the atom. The situation is the same as in Coulombic matter, where the additional binding energy to form the hydrogen molecule is less than that of the hydrogen atom. In each case a stability inequality with a not too large constant ensures suitable values of the binding energies to allow for the existence of an atomic phase. This is not possible without repulsive interactions. If the gas of impurities is a free one, one can even show that E_n is a convex function of n, so there is no value of μ such that the Boltzmann weight of any finite aggregate is dominant when $\beta \to \infty$.

The ionization equilibrium case [part (ii) of Theorem 2] occurs when the two first terms of the low-activity series (the free-electron and one-impurity terms) are of the same order as $\beta \to \infty$. The technical problem is to show that the rest of the series is negligible. For this we establish pointwise bounds on the kernels $(\mathbf{x}\,|\exp(-\beta H^n(\mathbf{r}_1,\ldots,\mathbf{r}_n))|\,\mathbf{y})$ that are uniform with respect to the location $\mathbf{r}_1,\ldots,\mathbf{r}_n$ of the impurities by using extensively the theory of Schrödinger semigroups developed by B. Simon. These estimates in conjunction with the standard methods to control the Mayer series enable us to prove the theorem (see ref. 8).

While the physical situations are essentially similar in the model and in the full electron–proton gas, the treatment of the model is clearly much simpler on two main points. First, one does not have to deal with the full quantum mechanical N-body problem. Moreover, since the potentials are short ranged, the infinite-volume limit can be expressed by low-activity expansions, so the detailed configurational analysis of Fefferman required by the Coulombic case is not necessary here.

APPENDIX

Let Ω be a convex set with smooth boundaries in R^3 and Δ_Ω the Dirichlet Laplacian on Ω. Then for all $t_1 \geqslant t_2 > 0$, we have

$$t_1^{3/2}\,\mathrm{Tr}\exp\left(\frac{t_1\Delta_\Omega}{2}\right) \leqslant t_2^{3/2}\,\mathrm{Tr}\exp\left(\frac{t_2\Delta_\Omega}{2}\right) \tag{A.1}$$

This is easily seen with the help of the functional integral representation of $\exp(t\Delta_\Omega/2)$ in terms of the Brownian-bridge process[11]

$$t^{3/2}\,\mathrm{Tr}\exp\left(\frac{t\Delta_\Omega}{2}\right) = \frac{1}{(2\pi)^{3/2}}\int_\Omega d\mathbf{r}\int D\boldsymbol{\alpha}\,\chi_\Omega(\boldsymbol{\alpha},\mathbf{r},t) \tag{A.2}$$

In (A.2), $\boldsymbol{\alpha}(s)$, $0 \leqslant s \leqslant 1$, is the three-dimensional Brownian-bridge process with zero mean and covariance $s_1(1-s_2)$, $s_1 \leqslant s_2$, and the Brownian-bridge measure $D\boldsymbol{\alpha}$ is normalized to one. $\chi_\Omega(\boldsymbol{\alpha},\mathbf{r},t)$ is the characteristic function for the set of paths satisfying $\mathbf{r}+\sqrt{t}\,\boldsymbol{\alpha}(s)\in\Omega$ for all s, $0 \leqslant s \leqslant 1$.

Since Ω is convex, $\mathbf{r}\in\Omega$ and $\mathbf{r}+\sqrt{t_1}\,\boldsymbol{\alpha}(s)\in\Omega$ imply

$$\gamma[\mathbf{r}+\sqrt{t_1}\,\boldsymbol{\alpha}(s)] + (1-\gamma)\,\mathbf{r}\in\Omega, \qquad 0 \leqslant \gamma \leqslant 1 \tag{A.3}$$

Taking $\gamma = \sqrt{t_2}/\sqrt{t_1}$, we obtain $\mathbf{r}+\sqrt{t_2}\,\boldsymbol{\alpha}(s)\in\Omega$, and hence

$$\chi_\Omega(\boldsymbol{\alpha},\mathbf{r},t_1) \leqslant \chi_\Omega(\boldsymbol{\alpha},\mathbf{r},t_2), \qquad t_1 \geqslant t_2 > 0, \quad \mathbf{r}\in\Omega \tag{A.4}$$

The inequality (A.1) follows from (A.4) and (A.2).

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