J. Math. Sci. Univ. Tokyo
3 (1996), 713–722.

The Thermodynamic Limit of the Magnetic Thomas-Fermi Energy

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Abstract. We prove the existence of the thermodynamic limit of the magnetic Thomas-Fermi energy and its density functions.

§1. Introduction

In [LS1], where the Thomas-Fermi theory is studied, Lieb and Simon proved the existence and property of the thermodynamic limit (namely, the energy per volume of solids) of the Thomas-Fermi energy and discussed its application to the screening problem. In this paper, we will study the analog of this in the magnetic Thomas-Fermi(MTF) theory.

Let us recall about MTF energy[FGPY, LSY2, Y]. This comes from seeking the ground state energy of the atomic Hamiltonian in a magnetic field:

$$H_N := \sum_{i=1}^{N} \left\{ (\mathbf{p}^i + \mathbf{A}(x^i))^2 + \sigma^i \cdot \mathbf{B} - Z\,|x^i|^{-1} \right\} + \sum_{1 \le i < j \le N} |x^i - x^j|^{-1}, \tag{1.1}$$

on $\mathcal{H}_N := \bigwedge^N L^2(\mathbf{R}^3; \mathbf{C}^2)$ (the anti-symmetric spinor valued functions).

$$E^Q(N, Z, B) := \inf\{(\Psi, H_N\Psi) : \Psi \in \text{ domain of } H_N,\ (\Psi, \Psi) = 1\}, \tag{1.2}$$

1991 *Mathematics Subject Classification.* Primary 35J10; Secondary 81V70, 35P15, 30V20.

where x^i(resp. $\mathbf{p}^i$) is the position(resp. momentum) operator of the i-th particle, $\mathbf{A} := \frac{1}{2}\mathbf{B} \times \mathbf{x}$ is a vector potential corresponding to the constant magnetic field $\mathbf{B} = (0, 0, B)$ $(B > 0)$, σ is the Pauli spin matrix and $Z > 0$ is the charge of nucleus.

We approximate $E^Q(N, Z, B)$ by the infimum of a density functional (called MTF functional):

$$(1.3) \qquad E^{MTF}(N, Z, B) := \inf\{\mathcal{E}^{MTF}[\rho] : \rho \in \mathcal{C}_B, \int \rho(x)dx = N\},$$

$$(1.4) \quad \text{where} \quad \mathcal{E}^{MTF}[\rho] := \int \tau_B(\rho(x))dx - Z\int \rho(x)\ |x|^{-1}dx + D(\rho, \rho),$$

($\int = \int_{\mathbf{R}^3}$ unless stated otherwise). We need the definitions of notations. $\tau_B(\rho(x))$ represents the kinetic energy per volume defined as

$$(1.5) \qquad \tau_B(\rho(x)) := \sup_\omega \left(\rho\,\omega - P_B(\omega)\right),$$

which is the Legendre transform of $P_B(\omega)$, where $P_B(\omega)$ is the pressure of the free Landau gas, as a function of the chemical potential, ω:

$$(1.6) \qquad P_B(\omega) := \frac{B}{3\pi^2}(\omega^{3/2} + 2\sum_{\nu=1}^{\infty} |\omega - 2\nu B|_+^{3/2}),$$

where $|f|_+$ is the positive part of f. $D(\rho, \rho)$ is the repulsion energy of particles:

$$(1.7) \qquad D(f, g) := \frac{1}{2}\iint f(x)g(y)\ |x-y|^{-1}dxdy.$$

$\mathcal{C}_B$ is the natural domain of $\mathcal{E}^{MTF}[\rho]$:

$$(1.8) \quad \mathcal{C}_B := \{\rho \in L^1(\mathbf{R}^3),\ \rho(x) \geq 0\ a.e., \int \tau_B(\rho(x)) < \infty,\ D(\rho, \rho) < \infty\}.$$

In this case, $\mathcal{C}_B$ is written explicitly as [LSY2]

$$\mathcal{C}_B = \{\rho \in L^1(\mathbf{R}^3) \cap L^{5/3}(\mathbf{R}^3),\ \rho(x) \geq 0\ a.e.\}.$$

The existence and uniqueness of the minimizer of (1.3) are proved in [LSY2]. Moreover,

FACT. ([LSY2])

(1) *Let ρ^{MTF} be the minimizer of (1.3). If we set*

$$\phi(x) := Z|x|^{-1} - \rho^{MTF} * |x|^{-1}, \tag{1.9}$$

(which is -(effective potential)) then it satisfies the MTF equation:

$$\tau_B'(\rho^{MTF}(x)) = |\phi(x) - \mu|_+, \tag{1.10}$$

for a constant μ(the chemical potential)> 0 . It is equivalent to

$$\rho^{MTF}(x) = P_B'(|\phi(x) - \mu|_+), \tag{1.11}$$

since τ_B' is the inverse of P_B'.

(2) *ρ^{MTF} has compact support, that is, if we set $R_{max} := \inf\{R : \rho(x) = 0$ a.e. for $|x| \geq R\}$, R_{max} obeys the following bound:*

$$R_{max} \leq \max\{\frac{5}{2} Z B^{-1}, 3.3\pi^{2/5} Z^{1/5} B^{-2/5}\}. \tag{1.12}$$

(3) *If $\lambda := N/Z > 0$ fixed and $B/Z^3 \to 0$ as $Z \to \infty$,*

$$E^Q(N, Z, B)/E^{MTF}(N, Z, B) \to 1. \tag{1.13}$$

The motivation to study the large field asymptotics in (1.13) is to investigate the surface structure of neutron star([LSY1, 2] and references therein). In [LSY1, 2], molecule of finite nuclei is considered. But on the other hand, in $B = 0$ case, Lieb and Simon proved that the Thomas-Fermi energy has the thermodynamic limit. Hence our problem is related to consider the same problem of [LSY1, 2] in solids. We should remark that the numerical calculation using the Hartree-Fock approximation of infinite nuclei(called the "molecular chain") has done[NKL] to study whether the molecular binding occurs.

To state the results, we shall define the notation. We define Λ to be a finite subset of $\mathbf{Z}^3$ and for any $y \in \Lambda$, we set the elementary cube:

$$\Gamma_y := \{x \in \mathbf{R}^3 : -\frac{1}{2} \le x_i - y_i \le \frac{1}{2},\ i = 1, 2, 3\}. \tag{1.14}$$

And we let $\Gamma(\Lambda) := \cup_{y \in \Lambda} \Gamma_y$. We define V_Λ to be the potential made by nuclei put on each point of Λ:

$$V_\Lambda(x) := -Z \sum_{y \in \Lambda} |x - y|^{-1}. \tag{1.15}$$

Let E_Λ^{MTF} be the MTF energy when the attraction energy $-Z|x|^{-1}$ in (1.3) is replaced by V_Λ and plus the repulsion energy between nuclei ($|\Lambda| := \sharp \Lambda$):

$$E_\Lambda^{MTF} := \inf\{\mathcal{E}_\Lambda^{MTF} : \rho \in \mathcal{C}_B,\ \int \rho(x) dx = Z|\Lambda|\ \}, \tag{1.16}$$

$$\mathcal{E}_\Lambda^{MTF}[\rho] := \int \tau_B(\rho(x))\, dx + \int V_\Lambda(x)\, \rho(x)\, dx + D(\rho, \rho) + \frac{Z^2}{2} \sum_{\substack{y,z \in \Lambda \\ y \ne z}} |y - z|^{-1}. \tag{1.17}$$

On the above setting, only the neutral molecules are considered and we have put $N = Z|\Lambda|$. Next, we want to let Λ to be large. To clarify it, we recall the definition used in [LS1].

DEFINITION. Let $\{\Lambda_i\}_{i=1}^\infty$ be a sequence of finite subsets of $\mathbf{Z}^3$. We define $\Lambda_i \to \infty$ if and only if

(1) $\cup_{i=1}^\infty \Gamma(\Lambda_i) = \mathbf{R}^3$.
(2) $\Gamma(\Lambda_i) \subset \Gamma(\Lambda_{i+1})$.
(3) If Λ^h denotes the subset of Λ whose distance to $\partial\Lambda$ is less than h, then

$$\lim_{i \to \infty} \frac{|\Lambda_i^h|}{|\Lambda_i|} = 0 \quad \text{for arbitrary } h > 0.$$

As an analog to (1.9), we set

$$\phi_\Lambda(x) := -V_\Lambda(x) - \rho_\Lambda^{MTF} * |x|^{-1}, \tag{1.18}$$

where ρ_Λ^{MTF} is the minimizer of (1.16). The main theorem describes the limit of $\phi_\Lambda(x)$ and $\rho_\Lambda^{MTF}(x)$.

THEOREM 1.1.

(1) *There exists* $\phi(x) := \lim_{\Lambda\to\infty} \phi_\Lambda(x)$, $x \in \mathbf{R}^3 \setminus \mathbf{Z}^3$ *and it does not depend on the choice of the form of* $\{\Lambda_i\}_{i=1}^\infty$. *This convergence is monotone and uniform on the compact set of* $\mathbf{R}^3 \setminus \mathbf{Z}^3$.

(2) *More generally, if* K *is a compact set of* $\mathbf{R}^3$,

$$\phi_\Lambda(x) - \sum_{y\in K\cap\mathbf{Z}^3} Z\,|x-y|^{-1} \;\to\; \phi(x) - \sum_{y\in K\cap\mathbf{Z}^3} Z\,|x-y|^{-1}$$

uniformly on K.

(3) $\phi(x)$ *is periodic of period* 1, *and* $\rho^{MTF}(x)(:= P_B'(|\phi(x)|_+))$ *satisfies*

$$\int_{\Gamma_0} \rho^{MTF}(x)\,dx = \lim_{\Lambda\to\infty} \int_{\Gamma_0} \rho_\Lambda^{MTF}(x)\,dx = Z, \tag{1.19}$$

$$\int_{\Gamma_0} \tau_B(\rho^{MTF}(x))\,dx = \lim_{\Lambda\to\infty} |\Lambda|^{-1} \int \tau_B(\rho_\Lambda^{MTF}(x))\,dx, \tag{1.20}$$

$$\int_{\Gamma_0} \phi(x)\,\rho^{MTF}(x)\,dx = \lim_{\Lambda\to\infty} |\Lambda|^{-1} \int \phi_\Lambda(x)\,\rho_\Lambda^{MTF}(x)\,dx. \tag{1.21}$$

(4)

$$\phi(x) = \lim_{\Lambda\to\infty} |\Lambda|^{-1} \sum_{y\in\Lambda} \phi_\Lambda(x+y), \tag{1.22}$$

and the following limit exists and satisfies:

$$\lim_{x\to 0}\{\phi(x) - Z|x|^{-1}\} = \lim_{\Lambda\to\infty} |\Lambda|^{-1} \sum_{y\in\Lambda} \lim_{x\to y}\{\phi_\Lambda(x) - Z\,|x-y|^{-1}\}. \tag{1.23}$$

Using this theorem, we obtain the existence of the thermodynamic limit:

THEOREM 1.2. *There exists* $\lim_{\Lambda\to\infty} E_{\Lambda}^{MTF}/|\Lambda| =: E^{MTF}$ *and it satisfies*

$$E^{MTF} = \int_{\Gamma_0} \tau_B(\rho^{MTF}(x))\, dx - -\frac{1}{2}\int_{\Gamma_0} \rho^{MTF}(x)\, \phi(x)\, dx + \frac{Z}{2}\lim_{x\to 0}\{\phi(x) - Z\,|x|^{-1}\}. \tag{1.24}$$

The above theorems state that almost the same results as [LS1] hold. Instead of $\mathbf{Z}^3$, we can consider more general lattice, Λ^a which is a finite subset of $\mathbf{Z}(a)$, where

$$\mathbf{Z}(a) := \{(na, na, na) \in \mathbf{R}^3 : n \in \mathbf{Z}\},\ a \in \mathbf{R}^3. \tag{1.25}$$

And corresponding elementary cube is:

$$\Gamma_y^a := \{x \in \mathbf{R}^3 : -\frac{a}{2} \le x_i - y_i \le \frac{a}{2},\ i = 1, 2, 3\},\ y \in \mathbf{R}^3. \tag{1.26}$$

We define $V_{\Lambda^a}(x)$, $\phi_{\Lambda^a}(x)$, $\rho_{\Lambda^a}^{MTF}(x)$ and $E_{\Lambda^a}^{MTF}$ similarly. Theorem 1.1,1.2 are still applicable in this case and we denote $\phi_a(x)$ by the thermodynamic limit of $\phi_{\Lambda^a}(x)$ and we define $\rho_a^{MTF}(x)$ and E_a^{MTF} similarly. Then, we can easily confirm from (1.12) and Lemma 2.4 in the next section that ρ_a^{MTF} is a sum of compactly supported functions:

PROPOSITION 1.3. *If* $a \ge 2R_{max}$, *then there exists a compactly supported function* $\rho(x)$ *such that*

$$\rho_a^{MTF}(x) = \sum_{y\in\mathbf{Z}(a)} \rho(x - y) \tag{1.27}$$

And if $y, z \in \mathbf{Z}(a)$, $y \ne z$, *then supp* $\rho(x - y) \cap$ *supp* $\rho(x - z) = \emptyset$.

In ordinary Thomas-Fermi theory(in the case of $\mathbf{B} = 0$), the TF-minimizer $\rho^{TF}(x)$ of a single atom(the Hamiltonian is (1.1) with $\mathbf{B} = 0$) satisfies $\rho^{TF}(x) \ge (\text{const.})|x|^{-6}$ for $|x|$ large[LS1] which is never compactly supported. Hence Proposition 1.3 implies that, when the magnetic field is turned on, the matter would vary from metal to insulator.

The next section is devoted to prove the above theorems.

§2. Proof of theorems

To prove above theorems, we show some properties about MTF equations. At first we notice that, in the neutral case ($N = Z|\Lambda|$), the chemical potential $\mu = 0$ in (1.10).

Lemma 2.1. *$\phi_\Lambda(x) \geq 0$ on $x \in \mathbf{R}^3 \setminus \Lambda$.*

Proof. From Lemma II. 25 of [LS1], $\rho_\Lambda^{MTF} * |x|^{-1}$ is bounded, continuous and vanishes at infinity. Let $A := \{x \in \mathbf{R}^3 : \phi_\Lambda < 0\}$.

It is open and disjoint from Λ. $\phi_\Lambda(x)$ and $\rho_\Lambda^{MTF}(x)$ satisfy the MTF equation:

$$\rho_\Lambda^{MTF}(x) = P_B'(|\phi_\Lambda(x)|_+), \tag{2.1}$$

where

$$P_B'(\omega) = \frac{B}{2\pi^2}(\omega^{1/2} + 2\sum_{\nu=1}^{\infty} |\omega - 2\nu B|_+^{1/2}). \tag{2.2}$$

It follows that $\rho_\Lambda^{MTF}(x) = 0$ on A. From the definition of $\phi_\Lambda(x)$(1.18), it implies $\phi_\Lambda(x)$ is harmonic on A. Since $\phi_\Lambda(x) = 0$ on ∂A and at infinity, $\phi_\Lambda(x) \equiv 0$ on A. □

The following lemma is called the "Teller's Lemma" which follows from the superharmonic argument. It imply that if $\Lambda \subset \Lambda'$, then $\phi_\Lambda(x) \leq \phi_{\Lambda'}(x)$ on $x \in \mathbf{R}^3 \setminus \mathbf{Z}^3$.

Lemma 2.2. *Let $\phi_1(x)$, $\rho_1(x)$ be the -(effective potential) defined in (1.9) and the MTF minimizer corresponding to $V_1(x) = \sum_{i=1}^K a_i\ |x - R_i|^{-1}$ respectively. And we let $\phi_2(x)$, $\rho_2(x)$ similarly corresponding to $V_2(x) = \sum_{i=1}^K b_i\ |x - R_i|^{-1}$. We assume $b_i \geq a_i \geq 0$ for $i = 1, \cdots, K$. Then $\phi_2(x) \geq \phi_1(x)$ on $\mathbf{R}^3 \setminus \{R_i\}_{i=1}^K$.*

Proof. Let $S := \{x \in \mathbf{R}^3 : \phi_2(x) < \phi_1(x)\}$. Since $\phi_1(x)\ |x - R_i|^{-1} \to a_i$ and $\phi_2(x)\ |x - R_i|^{-1} \to b_i$ as $x \to R_i$, S is disjoint from the neighborhoods of each R_i. Since $\phi_1(x)$, $\phi_2(x)$ are bounded and continuous away from

$\{R_i\}_{i=1}^K$, S is open. Let $\psi(x) := \phi_2(x) - \phi_1(x)(< 0$ on $S)$. From the definition of $\phi(x)$ (1.9) and the MTF equation,

$$(4\pi)^{-1}\triangle\psi = P_B'(|\phi_2|_+) - P_B'(|\phi_1|_+). \tag{2.3}$$

Since $P_B'(\omega)$ is monotone, $\triangle\psi < 0$ on S which implies ψ is superharmonic on S. Hence ψ takes its minimum on ∂S which contradicts the definition of S since $\psi \equiv 0$ on ∂S and at infinity. □

The next lemma is a important step of Lemma 2.4.

LEMMA 2.3. *If* $0 \le a + b \le c$, *then*

$$P_B'(a) + P_B'(b) \le 2P_B'(c). \tag{2.4}$$

PROOF. We first fix c and vary a, b under the condition $0 \le a + b \le c$. Since $P_B'(\cdot) \ge 0$ is monotone increasing and $f(t) := t^{1/2} + (c-t)^{1/2}$ achieves its maximum at $t = c/2$, we may assume $a = b$, $c = 2a$. We consider several cases.

(1) if $a \le 2B$

Then, $P_B'(a) = \frac{B}{2\pi^2}a^{1/2}$ and we can easily confirm (2.4).

(2) if $2B \le a \le 4B$

Then, $P_B'(a) = \frac{B}{2\pi^2}\{a^{1/2} + 2(a - 2B)^{1/2}\}$, and $P_B'(2a) = \frac{B}{2\pi^2}\{(2a)^{1/2} + 2\sum_{\nu=1}^2(2a - 2\nu B)^{1/2}\}$. We estimate $P_B'(2a) - 2P_B'(a)$ and obtain (2.4).

(3) Otherwise

The number of terms of $\sum_{\nu=1}^\infty$ increases. But the increase of $P_B'(2a)$ is always more than that of $2P_B'(a)$. □

The above lemma enables us to prove another type of the Teller's lemma. It will imply that $\phi_\Lambda \le \sum_{y\in\Lambda}\phi(x-y)$, and it and (1.12) guarantee the uniform boundedness(with respect to Λ) and the uniform convergence of $\phi_\Lambda(x)$.

Lemma 2.4. *Let $\phi_i(x)$, $\rho_i(x)(i=1,2)$ be the same as Lemma 2.2 and $\tilde{\phi}(x)$, $\tilde{\rho}(x)$ be the -(effective potential) and the MTF minimizer corresponding to $V_1(x)+V_2(x)$ respectively. Then it follows that*

$$\tilde{\phi}(x) \leq \phi_1(x)+\phi_2(x), \quad x \in \mathbf{R}^3 \setminus \mathbf{Z}^3. \tag{2.5}$$

Proof. Let $S := \{x \in \mathbf{R}^3 : \psi := 2\tilde{\phi}(x) - \phi_1(x) - \phi_2(x) > 0\}$. As before, it is open and $\psi = 0$ on ∂S. From Lemma 2.3, $\triangle\psi = 2P'_B(|\tilde{\phi}|_+) - P'_B(|\phi_1|_+) - -P'_B(|\phi_2|_+) > 0$, and it implies ψ is subharmonic on S and thus achieves its maximum on ∂S. It is a contradiction. Using Lemma 2.1, we obtain (2.5). □

The above lemmas imply the Theorem 1.1 (it is the same argument as the proof of Theorem VI.2 in [LS1]). We turn to prove Theorem 1.2.

Proof of Theorem 1.2. We write:

$$\begin{aligned} E_\Lambda^{MTF} = &\int \tau_B(\rho_\Lambda^{MTF}(x))dx + \frac{1}{2}\int V_\Lambda(x)\,\rho_\Lambda^{MTF}(x)\,dx \\ &+ \frac{1}{2}\int V_\Lambda(x)\,\rho_\Lambda^{MTF}(x)\,dx \\ &+ D(\rho_\Lambda^{MTF},\rho_\Lambda^{MTF}) + \frac{Z^2}{2}\sum_{\substack{y,z\in\Lambda \\ y\neq z}} |y-z|^{-1}. \end{aligned} \tag{2.6}$$

By direct calculation:

$$\frac{1}{2}\int V_\Lambda(x)\,\rho_\Lambda^{MTF}(x)\,dx + D(\rho_\Lambda^{MTF},\rho_\Lambda^{MTF}) = -\frac{1}{2}\int \phi_\Lambda(x)\,\rho_\Lambda^{MTF}(x)\,dx.$$

On the other hand,

$$\begin{aligned} &\frac{1}{2}\int V_\Lambda(x)\,\rho_\Lambda^{MTF}(x)\,dx + \frac{Z^2}{2}\sum_{y\in\Lambda}\sum_{\substack{z\in\Lambda \\ z\neq y}} |z-y|^{-1} \\ &= \frac{Z}{2}\sum_{y\in\Lambda}\left(\sum_{\substack{x\in\Lambda \\ x\neq y}} Z\,|x-y|^{-1} - -\int \rho_\Lambda^{MTF}(x)\,|x-y|^{-1}\,dx\right) \\ &= \frac{Z}{2}\sum_{y\in\Lambda}\lim_{y'\to y}(\phi_\Lambda^{MTF}(y') - -Z|y'-y|^{-1}). \end{aligned}$$

Together with Theorem 1.1, we obtain Theorem 1.2. □

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(Received February 16, 1996)

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