THE MAXIMAL NEGATIVE ION OF THE TIME-DEPENDENT
THOMAS-FERMI AND THE VLASOV ATOM

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Abstract. We show an atom of atomic number $Z$ described by the time-dependent Thomas-Fermi equation or the Vlasov equation cannot bind more than $4Z$ electrons.

1. Introduction and Statement of the Result

1.1. Known Results on the Excess Charge of Atoms. Experimentally no doubly charged negative ions — or ions that are even more negative — are known (Massey [17, 18]). To prove this simple fact starting from a mathematical model of the atom is called the excess charge problem. Here the excess charge $Q(Z)$ refers to the maximal total number of electron $N$ minus the nuclear charge $Z$. A step in this direction was taken by Hill [9, 10] in the context of the Schrödinger equation showing that the $H$ ion has only one bound state. First results on $Q$ itself were obtained by Ruskai [21, 22] and Sigal [23] showing that atoms cannot be arbitrarily negative; later Lieb et al. [14, 15] showed that the excess charge is asymptotically of lower order than $Z$, i.e., $Q(Z)/Z \to 0$ as $Z \to \infty$. All of these results where obtained for Schrödinger operators and are asymptotic for large $Z$.

For approximate models the results are — not unexpected — stronger. Solovej showed first for the reduced Hartree-Fock model (Hartree-Fock without exchange term) and later for the full Hartree-Fock model that excess charge $Q(Z)$ is uniformly bounded in $Z$ (Solovej [24, 25]). These were big steps forward, however, they are still short of the above mentioned fact, that the observed excess charge is at most one, since no control on the constant is offered.

For density functionals the situation is better. That there are no negative ions in Thomas-Fermi theory is folklore (Gombas [7]). This can be easily shown using a subharmonic estimate (see Lieb and Simon [16]). Benguria and Lieb [2] showed that the Thomas-Fermi-Weizsäcker atom can have an excess charge that does not exceed 0.7335 (where this numeric values holds for the coupling constant of the Weizsäcker term that reproduces the Scott conjecture).

Finally we wish to mention an unpublished discovery of Benguria in Thomas-Fermi theory. He realized that multiplying the Thomas-Fermi equation by $|x|/\rho$ and integrating leads to the inequality

$$Q(Z) < Z$$

on the Thomas-Fermi excess charge. Of course this is of limited value in TF theory, since, as mentioned above, the excess charge is zero. However, the value of the idea is that it can be transferred and extended to other situations. In fact, it was Lieb [13] who realized this for the Schrödinger operator with and without magnetic field and the Chandrasekhar operator. Lieb showed, among other things, that for these operators $Q(Z) < Z + 1$. This bound holds regardless of the symmetry under permutations (Boltzons, Bosons, or Fermions) and is — for large $Z$ worse than the

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asymptotic bounds mentioned above. However, the bound is non-asymptotic and proves the ionization conjecture for \( Z = 1 \) (hydrogen).

Benguria’s idea works also for the Hellmann functional, the Hellmann-Weizsäcker functional [1], the Hartree-Fock functional and others. There are, however, functionals that resisted such a treatment, like the Thomas-Fermi-Dirac-Weizsäcker functional and the Müller functionals and variants thereof which were treated only recently by different means (Frank et al [5, 6], Kehle [11]). Moreover, there are models which are still completely open like the no-pair operators of relativistic quantum mechanics (Sucher [26]) where it is not even known that the excess charge is finite.

The models mentioned so far were all treated in a stationary setting. Although a time-dependent characterization of bound and scattering states exists also in quantum mechanics (see Perry [20, Theorem 2.1]), it took eighty-seven years after the advent of quantum mechanics to approach the problem in a time-dependent way (Lenzmann and Lewin [12]). However, it turns out that this treatment – and therefore also ours since we will follow Lenzmann and Lewin as closely as possible in the non-linear equation treated here – is also a variant of Benguria’s original idea.

An improvement of Lieb’s non-asymptotic result was obtained by Nam [19] who showed

\[
\alpha_N(N - 1) \leq Z(1 + 0.68 N^{-2/3})
\]

with

\[
\alpha_N := \inf_{x_1, \ldots, x_N \in \mathbb{R}^3} \sum_{1 \leq i < j \leq N} \frac{|x_i|^2 + |x_j|^2}{|x_i - x_j|} (N - 1) \sum_{i=1}^N |x_i|.
\]

In this paper, we wish to discuss the excess charge problem of atoms when described by the Vlasov equation [28, 29] and the time-dependent Thomas-Fermi equation [3]. The latter is a hydrodynamic one with a pressure-density relation given by Thomas and Fermi.

1.2. The Vlasov Equation. The Vlasov equation, originally derived in plasma physics, can also be used as an effective equation for the spin summed phase space density

\[
f : \mathbb{R} \times \mathbb{R}^6 \rightarrow \mathbb{R}_+
\]

of fermions. If possible time dependence of the density is indicated by a subscript \( t \), i.e., the functions \( f_t \) are interpreted as the spin-summed phase space density of electrons at time \( t \), at position \( x \) and momentum \( \xi \). The Pauli principle for fermions with \( q \) spin states each (for electrons \( q = 2 \)) is implemented by the requirement

\[
f_t \leq q.\tag{1}
\]

We will work in atomic units in which the rationalized Planck constant \( \hbar \) and the mass \( m \) of the electron are one, in particular we have \( \hbar = 2\pi \). Following Planck one requires that each particle occupies the volume \( h^3 \) in phase space, i.e., we interpret

\[
\rho_t(x) := \int_{\mathbb{R}^3} d\xi f_t(x, \xi)
\]

(with \( d\xi := d\xi / h^3 \)) as the density of electrons at position \( x \) at time \( t \) and

\[
N(t) := \int_{\mathbb{R}^3} dx \rho_t(x),\tag{2}
\]

as the number of particles at time \( t \) which may or may not be finite.
We are interested in the maximal number of electrons which a nucleus of charge \( Z \) can bind. For the moment, though, we allow for arbitrary many nuclei. The electric potential \( \mathcal{V}_{\text{tot}} \) of \( K \) nuclei at positions \( R_1, \ldots, R_K \) with nuclear charges \( Z_1, \ldots, Z_K \) is

\[
\mathcal{V}_{\text{tot}} := V - V_{\text{MF}} := \sum_{k=1}^{K} Z_k \delta_{R_k} \ast | \cdot |^{-1} - \rho \ast | \cdot |^{-1}.
\]

The force \( \mathcal{F} \) is

\[
\mathcal{F}(x) := \nabla \mathcal{V}_{\text{tot}}(x) = -\sum_{k=1}^{K} Z_k \frac{x - R_k}{|x - R_k|^3} + \int_{\mathbb{R}^3} dy \rho_t(y) \frac{x - y}{|x - y|^3}.
\]

Thus the Vlasov equation reads

\[
\partial_t f_t + p \cdot \nabla_x f_t + \mathcal{F} \cdot \nabla_\xi f_t = 0.
\]

For transparency we will assume for our main results that we are in the atomic case, i.e., \( K = 1, \) and \( Z := Z_1, R_1 = 0. \) Using homogeneity in the spirit of Benguria’s idea, it is clear that multiplying by a homogeneous function of degree one might be a hopeful strategy; however, instead of multiplying simply by \( x, \) multiplying by \( x \cdot \xi |x| \) helps in dealing with the derivative with respect to \( \xi. \) Because of the time-dependence, the obvious idea would be to cut-off at an arbitrary distance \( R, \) integrate, and then take \( t \to \infty. \) However because of technical reasons, a sharp cut-off leads to an indefinite term later on. A suitable soft cut-off solves this problem. And instead of taking \( t \) large we will average over all times. We will follow Lenzmann and Lewin \cite{12} and pick as test function

\[
w_R := \nabla g_R \cdot \xi, \quad g_R(x) := R^3 g(|x|/R), \quad g(r) = r - \arctg(r).
\]

We will show that the two potential terms will yield the wanted estimate whereas the other terms of the equation vanish or can be dropped.

**Theorem 1.** Assume \( f_t \) to be a weak solution of the Vlasov equation \( \text{(4)} \) of finite energy \( \text{(12)}, \) assume \( B \subset \mathbb{R}^3 \) bounded and measurable, and set

\[
N_V(t, B) := \int_{\mathbb{R}^3} \int_B dx f_t(x, \xi)
\]

which is the number of electrons in \( B. \) Then in temporal average for large time \( N_V(t, B) \) does not exceeds \( 4Z, \) i.e.,

\[
\limsup_{T \to \infty} \frac{1}{T} \int_0^T dt N_V(t, B) \leq 4Z.
\]

To interpret the result we introduce the following notation: we say that \( f_t \in L^1(\mathbb{R}_+^3 \times \mathbb{R}^3) \) with \( 0 \leq f_t \leq q \) a.e., is a fermionic bound state, if the functions \( f_t \) fulfill the following: for any \( \epsilon > 0 \) exists a radius \( R \) such that for all times \( t \geq 0 \)

\[
\int_{|x| > R} dx d\xi f_t(x, \xi) < \epsilon.
\]

Thus the theorem implies that the Vlasov equation has no bound state which has more than \( 4Z \) electrons.

We remark, that it is obvious from the proof that the right side of \( \text{(6)} \) can be improved to \( 2Z, \) if the spatial density \( \rho_t \) of the solution is radially symmetric.

Benguria’s idea suggests to multiply the Vlasov equation with a homogeneous function of degree one followed by a sharp cut-off and integrate. Instead, to deal with the partial derivatives in \( x \) and \( \xi, \) we choose the weight \( w \) given by

\[
w_R(x, \xi) := \nabla g_R(x) \cdot \xi = \frac{|x|}{1 + (x/R)^2} x \cdot \xi,
\]
i.e., \( w(x) = x|x| \cdot \xi + O(|x|^3) \) for small \( x \) and is bounded for large \( |x| \) and fixed \( R \) and \( \xi \).

To our knowledge no such result is known neither for the time-dependent Thomas-Fermi equation nor for the Vlasov equation. However, the analogue result for the Schrödinger equation was shown by Lenzmann and Lewin [12] whose proof we will follow as closely as possible.

1.3. The Time-Dependent Thomas-Fermi Equation. The time dependent Thomas-Fermi equation (Bloch [3]), see also Gombas [7], for electrons in the field of a nucleus \( Z \) reads

\[
\partial_t \varphi_t = \frac{1}{2} (\nabla \varphi_t)^2 + \int \frac{dp}{\rho_t} - \frac{Z}{|x|} + \rho_t * |\cdot|^{-1}
\]

supplemented by the continuity equation

\[
\partial_t \rho_t = \nabla (\rho_t \nabla \varphi_t).
\]

Here \( \varphi \) is the potential of the velocity field \( u \), i.e., \( u = -\nabla \varphi \), \( \rho \) is the density of electrons, and \( p \) is the pressure as a function of \( \rho \). The Thomas-Fermi choice for \( p \) is \( p(\rho) := (1/5) \gamma_{TF} \rho^{5/3} \) where \( \gamma_{TF} := (6\pi^2/q)^{2/3} \), i.e., we have

\[
\partial_t \varphi_t = \frac{1}{2} (\nabla \varphi_t)^2 + \frac{\gamma_{TF}}{2} \rho_t^{2/3} - \frac{Z}{|x|} + \rho_t * |\cdot|^{-1}.
\]

Our result is

**Theorem 2.** Assume that \( \varphi_t \) and \( \rho_t \) is a weak solution of (10) and (9) with finite energy (13), assume \( B \subset \mathbb{R}^3 \) bounded and measurable, and set

\[
N_{TF}(t, B) := \int_B d\rho_t(x)
\]

which is the number of electrons in \( B \). Then, in temporal average for large time, this does not exceed \( 4Z \), i.e.,

\[
\limsup_{T \to \infty} \frac{1}{T} \int_0^T dt N_{TF}(t, B) \leq 4Z.
\]

We can interpret the result similarly to the Vlasov case: we say that a solution \( (\varphi_t, \rho_t) \) fulfills the time dependent Thomas-Fermi equation (10) supplemented by (9) is a bound state of the Thomas-Fermi atom, if the solution \( (\varphi_t, \rho_t) \) fulfills the following: for any \( \epsilon > 0 \) exists a radius \( R \) such that for all times \( t \geq 0 \)

\[
\int_{|x| > R} d\rho_t(x) < \epsilon.
\]

Thus, the theorem implies that the time-dependent Thomas-Fermi equation has no bound state which has more than \( 4Z \) electrons. Again, in the radially symmetric the constant reduces to \( 2Z \) as is obvious from the proof.

2. Uniform Estimates on Energies

For the proof of our theorems we need some uniform estimate of the kinetic energy.

2.1. Conservation of the total energy. In this section we treat the general molecular case although not needed in this generality for our result.
2.1.1. The Vlasov Energy. Suppose that $f_t$ is a weak solution of the Vlasov equation. Then it is folklore that the energy

$$E_V(f_t) := \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{2} \xi^2 f_t(x, \xi) d\xi d\xi - \int_{\mathbb{R}^3} V(x) \rho_t(x) dx + D[\rho] + R$$

where

$$D[\rho] := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho(x) \rho(y) \frac{1}{|x-y|} dxdy$$

is conserved, i.e., it is time independent. Note that we added a constant, namely the nuclear-nuclear repulsion

$$R := \sum_{0 \leq k < l \leq K} Z_k Z_l \frac{|R_k - R_l|}{|\mathcal{R}_k - \mathcal{R}_l|}.$$

2.1.2. The Thomas-Fermi Energy. The time-dependent Thomas-Fermi energy is

$$H(\rho_t, \phi_t) := \int_{\mathbb{R}^3} \rho_t(x) \frac{1}{2} |\nabla \phi_t(x)|^2 + E_{TF}(\rho_t)$$

where

$$E_{TF}(\rho) := \int_{\mathbb{R}^3} \left( 3 \frac{\gamma_{TF}}{10} \rho(x)^{5/3} - V(x) \rho_t(x) \right) dx + D[\rho] + R.$$

The energy $H(\rho_t, \phi_t)$ is conserved along the trajectory of solutions $\phi_t, \rho_t$.

2.2. Lower Bound on the Energy. We wish to show that the energy is bounded from below uniformly in $f$. To this end we define the – slightly non-standard – spherical symmetric rearrangement in the variable $\xi$

$$f^*(x, \xi) := q\chi_{B_{\frac{6}{\pi^2} \rho_t(x)^{1/3}(0)}}(\xi)$$

where $\rho(x) := \int_{\mathbb{R}^3} dxf(x, \xi)$; note that also $\rho(x) = \int dxf^*(x, \xi)$. Thus, obviously

$$T_V(f) := \frac{1}{2} \int dxd\xi \xi^2 f(x, \xi) \geq \frac{1}{2} \int dxd\xi \xi^2 f^*(x, \xi) = \frac{3}{10} \gamma_{TF} \int dx \rho^{5/3}(x).$$

Thus, the Vlasov energy is bounded from below by the Thomas-Fermi energy $E_{TF}$

$$E_V(f_t) \geq E_{TF}(\rho_t).$$

This in turn is bounded from below by

$$E_{TF}(\rho_t) \geq \alpha \sum_{k=1}^{K} Z_k^{7/3}.$$

Note that this bound is uniform in the density $\rho$, therefore in particular uniform in the electron number, and uniform in the positions of the nuclei. (The proof uses Teller’s lemma (Teller [27], Lieb and Simon [16]), the scaling of the minimum, and the fact that the excess charge of the Thomas-Fermi functional vanishes.) Here

$$\alpha := \inf \left\{ \int_{\mathbb{R}^3} \left( 3 \frac{\gamma_{TF}}{10} \rho(x)^{5/3} - \frac{\rho(x)}{|x|} \right) dx + D[\rho] \mid \rho \geq 0, \rho \in L^{5/3}(\mathbb{R}^3), D[\rho] < \infty \right\}.$$

In other words, we have shown stability of matter for the Vlasov functional, i.e., whatever the initial conditions are, the energy is bounded from below by a quantity that decreases at most linearly in the number of involved atoms.

It is obvious that the analogous bound holds for the time-dependent Thomas-Fermi theory, since by definition

$$H(\rho, \varphi) \geq E_{TF}(\rho).$$
2.3. Upper Bounds on Norms Along the Trajectory of the Solution. We show that the kinetic energy \( T_V(f_t) \) and the Coulomb norm \( \| f_t \|_C := \sqrt{D[\rho_f]} \) is uniformly bounded along the trajectory.

By the above \( E(0) := \mathcal{E}_V(f_0) = \mathcal{E}_V(f_t) =: E(t) \), i.e.,

\[
\frac{1}{2}(T_V(f_t) + \| f_t \|_C^2) \leq E(0) + R - \frac{1}{2} \left( T_V(f_t) + \| f_t \|_C^2 - \sum_{k=1}^{K} \int_{\mathbb{R}^3} \frac{2Z_k \rho_k(x)}{|x - R_k|} + 4R \right)
\]

(17)

\[
\leq E(0) - \frac{\alpha}{2} \sum_{k=1}^{K} (2Z_k)^{7/3}
\]

where we use the uniform lower bound (15) and (16) on the total energy. In other words, both the kinetic energy \( T_f \) and Coulomb norm \( \| f_t \|_C \) are bounded along the trajectory uniformly in time.

Again, the TF-case is similar.

3. Proof of the Main Results

3.1. The Vlasov Case.

Proof of Theorem \[\text{[4]}\] First we note that – of course – \( w \not\in C_0^\infty(\mathbb{R}^6) \). Strictly speaking we need to regularize the \( w \) at the spatial origin and smoothly cutoff at infinity obtaining a weight \( w_\varepsilon \) which converges toward \( w \) as \( \varepsilon \to 0 \). We have carried such procedure through in \[\text{[4]}\]. Since this is standard and only obscures the argument, we skip it.

We do the previously announced: multiplication by \( w_\varepsilon \) defined in \[\text{[5]}\] , integration over phase space, and averaging in time. We get for the three summations \( A, B, \) and \( C \) of the Vlasov equation:

Summand A:

\[
|A| := \frac{1}{T} \int_0^T dt \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} d\xi \ w_\varepsilon(x, \xi) \partial_t f_t(x, \xi)
\]

(18) \[\leq \frac{1}{T} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} d\xi \ w_\varepsilon(x, \xi) f_T(x, \xi) - \frac{1}{T} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} d\xi \ w_\varepsilon(x, \xi) f_0(x, \xi)
\]

(19) \[\leq \frac{1}{T} \left[ \sqrt{T_f} \sqrt{\int_{\mathbb{R}^3} dx \left| \nabla g_\varepsilon(x) \right|^2 f_T(x, \xi) + \sqrt{T_f} \int_{\mathbb{R}^3} dx \left| \nabla g_\varepsilon(x) \right|^2 f_0(x, \xi) \right]
\]

(20) \[\leq c \frac{N^{1/2} R^2}{T} \to 0 \text{ as } T \to \infty
\]

where we used the Schwarz inequality to conclude line (19) from line (18).

B: First we mention that \( g \) is a convex monotone increasing function which implies convexity of \( g_\varepsilon \), i.e., \( \text{Hess}(g_\varepsilon) \) is positive. Now, we integrate by parts

\[
B := \frac{1}{T} \int_0^T dt \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} d\xi \ \nabla g_R(x) \cdot \xi \cdot \nabla f_t
\]

\[= - \frac{1}{T} \int_0^T dt \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} d\xi \ \xi \cdot \text{Hess}(g_\varepsilon)(x) \xi \cdot f_t(x, \xi) \leq 0
\]

using the positivity of the Hessian in the last step.
Eventually \( C \):

\[
\begin{align*}
(21) \quad C &:= \frac{1}{T} \int_0^T \int_{\mathbb{R}^3} dt \int_{\mathbb{R}^3} dx \, d\xi \nabla g_R(x) \cdot \xi \, \mathcal{R} \cdot \nabla \xi f_t \\
(22) \quad &\quad = \frac{1}{T} \int_0^T \int_{\mathbb{R}^3} dt \int_{\mathbb{R}^3} dx \, d\xi \nabla g_R(x) \cdot \xi \left( -\frac{x}{|x|^3} + \int_{\mathbb{R}^3} dy \frac{x-y}{|x-y|^3} \rho_t(y) \right) \cdot \nabla \xi f_t \\
(23) \quad &\quad = \frac{1}{T} \int_0^T dt \left( \int_{\mathbb{R}^3} dx Z \nabla g_R(x) \cdot \frac{x}{|x|^3} \rho_t(x) \right) \\
(24) \quad &\quad = \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{(\nabla g_R(x) - \nabla g_R(y)) \cdot (x-y)}{|x-y|^3} \rho_t(x) \rho_t(y) \\
(25) \quad &\quad \leq \frac{1}{T} \int_0^T dt \left( Z \int_{\mathbb{R}^3} dx \frac{\rho_t(x)}{(x/R)^2} \frac{1}{4} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\rho_t(x) \rho_t(y)}{(x/R)^2(y/R)^2} \right)
\end{align*}
\]

where we used Lenzmann’s and Lewin’s Lemma[1] and the notation \( \langle x \rangle := \sqrt{1+|x|^2} \) in the last step. Thus, for fixed \( R \)

\[
0 = A + B + C \leq \frac{N^{1/2} R^2}{T} + (Z \mathcal{M}_R(\rho_t)) T - \frac{1}{4} (\mathcal{M}_R(\rho_t))^2 T
\]

where we used Jensen’s inequality to estimate the last term. Thus the temporal average up to \( T \in [1, \infty] \), \( \langle \mathcal{M}_R(\rho_t) \rangle_T \), is uniformly bounded. Thus, as \( T \to \infty \),

\[
(26) \quad 0 = A + B + C \leq Z \langle \mathcal{M}_R(\rho_t) \rangle_{\infty} - \frac{1}{4} (\mathcal{M}_R(\rho_t))^2_{\infty}
\]

where we set \( \langle \mathcal{M}_R(\rho_t) \rangle_{\infty} := \limsup_{T \to \infty} T^{-1} \int_0^T dt \mathcal{M}_R(\rho_t) \). Furthermore, assume that \( B \) is contained in the ball of radius \( D \in \mathbb{R}_+ \) around the origin. Then we have

\[
(27) \quad 4Z \geq \langle \mathcal{M}_R(\rho_t) \rangle_{\infty}
\]

\[
(28) \quad = \limsup_{T \to \infty} \frac{1}{T} \int_0^T dt \int_B dx \frac{\rho_t(x)}{1 + (x/R)^2} \geq \frac{1}{T} \limsup_{T \to \infty} \int_0^T dt \int_B dx \frac{\rho_t(x)}{1 + (D/R)^2} \\
(29) \quad = \frac{1}{1 + (D/R)^2} \limsup_{T \to \infty} \frac{1}{T} \int_0^T dt \int_B dx \rho_t(x)
\]

Taking \( R \to \infty \) on both sides gives the desired result

\[
4Z \geq \limsup_{T \to \infty} \frac{1}{T} \int_0^T dt \int_B dx \rho_t(x).
\]

\( \square \)

3.2. The Thomas-Fermi Case. We now give the proof of the Thomas-Fermi case which initially requires a new idea but towards the end is similar to the above proof.

Proof of Theorem[4] We modify our strategy slightly: instead of multiplying (10) by the function \( w_R \) we multiply it from the left by the operator

\[
(30) \quad W_R := \nabla g_R \cdot \nabla,
\]
multiply by $\rho$, integrate in the space variable, and average in time. The left side of (10) becomes

\begin{equation}
L_T := \frac{1}{T} \int_0^T dt \int_{\mathbb{R}^3} dx \rho_t \nabla g_R \cdot \nabla \varphi_t \\
= \frac{1}{T} \int_0^T dt \text{div} \left( \int_{\mathbb{R}^3} dx \rho_t \nabla g_R \right) - \frac{1}{T} \int_0^T dt \int_{\mathbb{R}^3} dx \partial_t \rho_t \nabla g_R \cdot \nabla \varphi_t.
\end{equation}

Since by the Schwarz inequality

\begin{equation}
\left| \int_{\mathbb{R}^3} \rho_T(x) \nabla g_R(x) \nabla \varphi_T(x) dx \right| \leq \| \nabla g_R \| \sqrt{\int_{\mathbb{R}^3} \rho_T |\nabla \varphi_T|^2} \int_{\mathbb{R}^3} \rho_T \leq c_R,
\end{equation}

we see that it is uniformly bounded in $T$ because of the analogue of (17) for the time-dependent Thomas-Fermi equation and the fact that the particle number is conserved in time. Thus, by the continuity equation

\begin{equation}
\limsup_{T \to \infty} L_T = - \sum_{\mu, \nu = 1}^3 \limsup_{T \to \infty} \frac{1}{T} \int_0^T dt \int_{\mathbb{R}^3} dx \partial_t (\rho_t \partial_{\nu} \varphi_t) \partial_{\mu} g_R \partial_{\nu} \varphi_t = - \sum_{\mu, \nu = 1}^3 \int_{\mathbb{R}^3} dx \rho_0 \partial_{\nu} \varphi_t \partial_{\mu} g_R \partial_{\nu} \varphi_t + \sum_{\mu, \nu = 1}^3 \int_{\mathbb{R}^3} dx \rho_t \partial_{\nu} \varphi_t \partial_{\mu} g_R \partial_{\nu} \varphi_t \\
\geq \sum_{\mu, \nu = 1}^3 \int_{\mathbb{R}^3} dx \rho_t \partial_{\nu} \varphi_t \partial_{\mu} g_R \partial_{\nu} \varphi_t
\end{equation}

using integration by parts in the second but last step and the positivity of Hess$g_R$.

Next we treat the corresponding four resulting summands $R_1$ through $R_4$ of the right hand side of (10):

\begin{equation}
R_1 := \int_{\mathbb{R}^3} dx \rho_t \nabla g_R \cdot \nabla \frac{1}{2} \varphi^2 = \sum_{\mu, \nu = 1}^3 \int_{\mathbb{R}^3} dx \rho_0 \partial_{\nu} \varphi_t \partial_{\mu} g_R \partial_{\nu} \varphi_t
\end{equation}

which is identical to the last summand of the left side (35).

\begin{equation}
R_2 := \int_{\mathbb{R}^3} dx \rho_t \nabla g_R \cdot \nabla \frac{\gamma_{TF}}{2} \rho_t^{2/3} = \frac{1}{5} \gamma_{TF} \int_{\mathbb{R}^3} dx \nabla \rho_t^{5/3} \cdot \nabla g_R \leq - \frac{1}{5} \gamma_{TF} \int_{\mathbb{R}^3} dx \rho_t^{5/3} \Delta g_R \leq 0
\end{equation}

again because of the positivity of Hess$g_R$ and therefore of $\Delta g_R$.

\begin{equation}
R_3 := - \int_{\mathbb{R}^3} dx \rho_t \nabla g_R \cdot \nabla \frac{Z}{|x|} = \int_{\mathbb{R}^3} dx \rho_t \left( \frac{Z \nabla g_R(x) \cdot x}{|x|^3} \right) = \int_{\mathbb{R}^3} dx \rho_t \frac{\rho_t(x)}{|x|} = Z \left( \langle M_R(\rho_t) \rangle \right)
\end{equation}

using the notation of (25). Finally, the last summand in (10) yields

\begin{equation}
R_4 := - \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \nabla g_R(x) \rho_t(y) \frac{x - y}{|x - y|^2} \leq - \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \rho_t(x) \rho_t(y) \left( \frac{\nabla g_R(x) - \nabla g_R(y)}{|x - y|^3} \right) \cdot (x - y) \leq - \frac{1}{4} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dy \frac{\rho_t(x) \rho_t(y)}{|x/R|^2 |y/R|^2} = - \frac{1}{4} \left( \langle M_R(\rho_t) \rangle \right)^2
\end{equation}
Putting the term obtained from the left side together with all the terms obtained from the right side yields
\begin{equation}
0 \geq Z (M_R(\rho_1))_\infty - \frac{1}{4} (M_R(\rho_1))^2.
\end{equation}
The rest of the proof is now a mere copying of the Vlasov case. □

**Appendix A. A Useful Inequality**

**Lemma 1** (Lenzmann and Lewin [12]). For $g(r) = r - \arctg(r)$ we have

- For $x \neq y$ we have
\begin{equation}
\frac{g'(|x|)\omega_x - g'(|y|)\omega_y}{|x-y|^3} \cdot (x-y) \geq \frac{1}{2} \frac{g'(|x|)g'(|y|)}{|x|^2 |y|^2}.
\end{equation}

- Averaging over unit spheres yields
\begin{equation}
\int_{S^2} \frac{d\omega_x}{4\pi} \int_{S^2} \frac{d\omega_y}{4\pi} \frac{g'(|x|)\omega_x - g'(|y|)\omega_y}{|x-y|^3} \cdot (x-y) \geq \frac{g'(|x|)g'(|y|)}{|x|^2 |y|^2}.
\end{equation}

Note also the related inequality (Lenzmann and Lewin [12, Lemma 3] for $\nu = 3$) and Chen and Siedentop [4] for general $\nu$ for $x \neq y \in \mathbb{R}^\nu$:
\begin{equation}
\frac{|x|^{\nu-1}\omega_x - |y|^{\nu-1}\omega_y}{|x-y|^\nu} \cdot (x-y) \geq 2^{2-\nu}.
\end{equation}

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