The Maximal Negative Ion of the Time-Dependent Thomas-Fermi and the Vlasov Atom

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Excess Charge of Atoms

$$Q(Z) = N - Z,$$

- $Q(Z)$ Excess charge $Q(Z)$;
- N Maximal total number of electrons;
- Z the nuclear charge.

For neutral atoms, $Q(Z) = 0$.

1. Known results on different models (the idea of homogenization)

2. Vlasov equation for electrons (with point nuclei)

3. Time dependent Thomas-Fermi equation (a fluid dynamic system)

Known results on different models and the idea of homogenization

Known results on different models

Stationary models

- Thomas-Fermin, No negative ions. Gombas (1949) Lieb, Simon (1977).
- Thomas-Fermin, $Q(Z) < Z$. Benguria (unpublished).
- Thomas-Fermi-Weizsäcker. $Q(Z) \leq 0.7335$. Benguria, Lieb (1985).
- Hellmann, Hellmann-Weizsäcker, Benguria, Hoops, Siedentop (1992).
- Many body Schrödinger, $Q(Z) < Z + 1$ (proved the ionization conjecture for Hydrogen $Z = 1$), Lieb (1984)
- Many body Schrödinger, $\alpha_N(N-1) \leq Z(1 + 0.68N^{-2/3})$, Nam (2012)
- Hartree Fock, $Q(Z)$ is bounded uniformly in Z. Solovej (1993 for reduced model, 2003 for full model)
- Müller functional, Frank, Nam, Bosch (2016).
- Thomas-Fermi-Dirac-Weizsäcker, Frank, Nam, Bosch (2018).

Time dependent case

- Nonlinear Hartree, Lenzmann and Lewin (2013)
- many-body Schrödinger, Lenzmann and Lewin (2013)

Idea of homogenization (Benguria, Lieb, ...)

We take N particle Schrödinger problem as an example

$$H_N = \sum_{i=1}^{N}(-\Delta_i) - \sum_{i=1}^{N}\frac{Z}{|x_i|} + \sum_{i<j}^{N}\frac{1}{|x_i - x_j|}$$

[HVZ theorem, Winter & Zhislin, 1960]: Let $E_0(N)$ be the ground state energy of H_N. If $E_0(N) < E_0(N-1)$, then there exists a ground state eigenfunction of H_N.

Then the corresponding Schrödinger equation is

$$
\begin{aligned}
0 &= (H_N - E_0(N))\psi \\
&= \left(H_{N-1} - \Delta_N - \frac{Z}{|x_N|} + \sum_{i=1}^{N-1}\frac{1}{|x_i - x_N|} - E_0(N)\right)\psi
\end{aligned}
$$

Idea of homogenization (Benguria, Lieb, ...)

Testing this equation by $|x_N|\psi$ and noticing the fact that

$$\langle H_{N-1}\psi, |x_N|\psi\rangle - E_0(N)\langle\psi, |x_N|\psi\rangle$$
$$\geq E_0(N-1)\langle\psi, |x_N|\psi\rangle - E_0(N)\langle\psi, |x_N|\psi\rangle > 0.$$

and

one has
$$\frac{|x_i| + |x_N|}{|x_i - x_N|} \geq 1,$$

$$\left\langle \psi, \frac{|x_N|(-\Delta_N) + (-\Delta_N)|x_N|}{2}\psi \right\rangle - Z + \frac{N-1}{2} < 0.$$

Thus, Lieb's inequality 1984 $|\mathfrak{q}||\mathfrak{p}|^2 + |\mathfrak{p}|^2|\mathfrak{q}| > 0$ implies

$$N < 2Z + 1.$$

CI & Siedentop, 2013 $a + b \leq n$ and $\min\{a, b\} \in [0, 2]$,

$$0 < \mathcal{J}_{a,b,n} := \frac{1}{2}(|\mathfrak{p}|^a|\mathfrak{q}|^b + |\mathfrak{q}|^b|\mathfrak{p}|^a).$$

Generalization of Lieb's inequality

CI & Siedentop, 2013, Exact error term in the inequality.

$a + b \leq n$, $\min\{a, b\} \in (0, 2)$, then

$$(\psi, (\mathcal{J}_{a,b,n} - L_{a,b,n}|\mathfrak{q}|^{b-a})\psi) = (\psi, |\mathfrak{q}|^{\frac{b}{2}} \mathcal{H}_{a,n}|\mathfrak{q}|^{\frac{b}{2}}\psi)$$
$$+ \alpha_{a,n} \int_{\mathbb{R}^n} \mathrm{d}x \int_{\mathbb{R}^n} \mathrm{d}y \frac{(|x|^{\frac{b}{2}} - |y|^{\frac{b}{2}})^2 |\psi(x)|x|^{\gamma} - \psi(y)|y|^{\gamma}|^2}{2|x|^{\gamma}|x - y|^{n+a}|y|^{\gamma}}$$

where

$$\gamma = (n + b - a)/2, \qquad L_{a,b,n} = 2^a \frac{\Gamma(\frac{n-b+a}{4})\Gamma(\frac{n+b+a}{4})}{\Gamma(\frac{n+b-a}{4})\Gamma(\frac{n-b-a}{4})}.$$

and

$$\mathcal{H}_{a,n} := |\mathfrak{p}|^a - 2^a \left[\Gamma(\frac{n+a}{4})/\Gamma(\frac{n-a}{4})\right]^2 |\mathfrak{q}|^{-a} > 0, \ a \in (0, n).$$ Herbst 1977

- Monotonicity of the constant $L_{a,b,n} \downarrow 0$, as $b \to (n - a)_-$.
- Sharpness of the inequality

$$\mathcal{J}_{a,b,n} > L_{a,b,n}|\mathfrak{q}|^{b-a} + |\mathfrak{q}|^{b/2}\mathcal{H}_{a,n}|\mathfrak{q}|^{b/2}, \qquad \text{also true for } a = 2.$$

Vlasov equation for electrons (with point nuclei)

The Vlasov equation in the field of a point charge

$f_t(x, \xi)$ the spin summed phase space density of fermions.

$\rho_t(x) := \int_{\mathbb{R}^3} d\xi f_t(x, \xi)$ the density at position x and time t.

$$\partial_t f_t + \xi \cdot \nabla_x f_t + \mathfrak{K} \cdot \nabla_\xi f_t = 0,$$

where the force $\mathfrak{K}$ is

$$\mathfrak{K}(x) := \nabla V_{\text{tot}}(x) = -\sum_{k=1}^{K} Z_k \frac{x - \mathfrak{R}_k}{|x - \mathfrak{R}_k|^3} + \int_{\mathbb{R}^3} dy \rho_t(y) \frac{x - y}{|x - y|^3}.$$

with potential

$$V_{\text{tot}} := V - V_{\text{MF}} := \sum_{k=1}^{K} Z_k \delta_{\mathfrak{R}_k} * |\cdot|^{-1} - \rho * |\cdot|^{-1}.$$

For simplicity, we consider the atomic case, $K = 1$, $Z = Z_1$, $\mathfrak{R}_1 = 0$.

- Rigorous derivation from many body Schrödinger (without point charge), Porta, Rademacher, Saffirio, Schlein, 2017.
- No wellposedness result for the point charge case!

Result for Vlasov equation

Let f_t be a weak solution of the Vlasov equation of finite energy $\mathcal{E}_V(f_t)$, $B \subset \mathbb{R}^3$ bounded and measurable, and set

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

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

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

- The energy is conserved in time.

$$\mathcal{E}_V(f_t) := \iint \frac{1}{2} \xi^2 f_t(x, \xi) dx đ\xi - \int \frac{Z}{|x|} \rho_t(x) dx + D[\rho] = \mathcal{E}_V(f_0)$$

where

$$D[\rho] := \frac{1}{2} \iint \frac{\rho_t(x) \rho_t(y)}{|x - y|} dx dy.$$

Stability of matter (Vlasov functional)

By spherical symmetric rearrangement in the variable ξ, ($\|f\|_\infty = q$)

we have $f^*(x,\xi) := q\chi_{B_{(\frac{6\pi^2}{q}\rho(x))^{1/3}}(0)}(\xi), \quad \gamma_{\mathrm{TF}} := (6\pi^2/q)^{2/3}$

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

Therefore, the total energy is bounded from blow by the TF energy

$$\begin{aligned}
\mathcal{E}_V(f_t) &:= \iint \frac{1}{2}\xi^2 f_t(x,\xi) - \int \frac{Z}{|x|}\rho_t(x) + D[\rho_t] \\
&\geq \int\left(\frac{3}{10}\gamma_{\mathrm{TF}}\rho_t(x)^{5/3} - \frac{\rho_t(x)Z}{|x|}\right) + D[\rho_t] =: \mathcal{E}_{TF}(\rho_t) \geq \alpha Z^{\frac{7}{3}}
\end{aligned}$$

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

Estimates for the kinetic energy and Coulomb norm

Conservation of the total energy

$$\mathcal{E}_V(f_0) = \mathcal{E}_V(f_t) = \iint \frac{1}{2}\xi^2 f_t(x,\xi) - \int \frac{Z}{|x|}\rho_t(x) + D[\rho_t]$$

$$= T_V(f_t) - \int \frac{Z}{|x|}\rho_t(x) + \|f_t\|_C^2,$$

where we have use the Coulomb norm $\|f_t\|_C := \sqrt{D[\rho_t]}$, shows that

$$\frac{1}{2}\left(T_V(f_t) + \|f_t\|_C^2\right)$$

$$= \mathcal{E}_V(f_0) - \frac{1}{2}\left(T_V(f_t) + \|f_t\|_C^2 - \int \frac{2Z\rho_t(x)}{|x|}\right)$$

$$\leq \mathcal{E}_V(f_0) - \frac{\alpha}{2}(2Z)^{7/3} \leq T_V(f_0) + \|f_0\|_C^2$$

Both the kinetic energy $T_V(f_t)$ and Coulomb norm $\|f_t\|_C$ are bounded along the trajectory uniformly in time.

Main idea of the proof (homogenization)

Vlasov equation in the field of a point charge

$$\partial_t f_t + \xi \cdot \nabla_x f_t + \Big(- Z \frac{x}{|x|^3} + \int \frac{x-y}{|x-y|^3} \rho_t(y) dy \Big) \cdot \nabla_\xi f_t = 0$$

Intuitively we should use $x \cdot \xi |x|$ as a test function, in order to homogenize the singularity from $-Zx/|x|^3$.

Technically we choose the test function as

$$w_R(x,\xi) := \nabla g_R(x) \cdot \xi = \frac{|x|}{1+(x/R)^2} x \cdot \xi,$$

where

$$g_R(x) := R^3 g(|x|/R), \ g(r) = r - \operatorname{arctg}(r), \quad \textbf{\textcolor{red}{Lenzmann, Lewin (2013)}}$$

Properties of g_R

$$|\nabla g_R| \le R^2, \quad D^2 g_R \ge 0,$$

$$\frac{(\nabla g_R(x) - \nabla g_R(y)) \cdot (x-y)}{|x-y|^3} \ge \frac{1}{\langle x/R \rangle^2 \langle y/R \rangle^2}, \quad \langle x \rangle = \sqrt{1+x^2}.$$

Estimates

$$
\begin{aligned}
|A| &:= \left| \frac{1}{T} \int_0^T \iint w_R(x,\xi) \partial_t f_t(x,\xi) \right| \\
&\leq \frac{1}{T} \left[\sqrt{T_V(f_T)} \sqrt{\int |\nabla g_R(x)|^2 f_T(x,\xi)} + \sqrt{T_V(f_0)} \sqrt{\int |\nabla g_R(x)|^2 f_0(x,\xi)} \right] \leq c \frac{N^{1/2} R^2}{T} \to 0
\end{aligned}
$$

$$
B := \frac{1}{T} \int_0^T \iint \nabla g_R(x) \cdot \xi \xi \cdot \nabla_x f_t = -\frac{1}{T} \int_0^T \iint \xi \cdot \mathrm{Hess}(g_R)(x) \xi \; f_t(x,\xi) \leq 0
$$

$$
\begin{aligned}
C &:= \frac{1}{T} \int_0^T \iint \nabla g_R \cdot \xi \left(-Z \frac{x}{|x|^3} + \int \frac{x-y}{|x-y|^3} \rho_t(y) \right) \cdot \nabla_\xi f_t \\
&= \frac{1}{T} \int_0^T \left[\int Z \frac{\nabla g_R \cdot x}{|x|^3} \rho_t - \frac{1}{2} \iint \frac{(\nabla g_R(x) - \nabla g_R(y)) \cdot (x-y)}{|x-y|^3} \rho_t(x) \rho_t(y) \right] \\
&\leq \frac{1}{T} \int_0^T \left(Z \underbrace{\int \frac{\rho_t(x)}{\langle x/R \rangle^2}}_{=:M_R(\rho_t)} - \frac{1}{4} \int \int \frac{\rho_t(x) \rho_t(y)}{\langle x/R \rangle^2 \langle y/R \rangle^2} \right)
\end{aligned}
$$

As $T \to \infty$, $\langle M_R(\rho_t) \rangle_\infty := \limsup_{T \to \infty} T^{-1} \int_0^T \mathrm{d}t \; M_R(\rho_t)$ satisfies

$$
0 = A + B + C \leq Z \langle M_R(\rho_t) \rangle_\infty - \frac{1}{4} \langle M_R(\rho_t) \rangle_\infty^2
$$

Time dependent Thomas-Fermi equation

Time dependent Thomas-Fermi (a fluid dynamic system)

The time dependent Thomas-Fermi equation (Bloch 1933, Gombas 1949), for electrons in the field of a nucleus Z reads

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

together with the continuity equation (ρ the density of electrons)

$$\partial_t \rho_t = \nabla \cdot (\rho_t \nabla \varphi_t).$$

Here φ is the potential of the velocity field $\mathfrak{u}$, i.e., $\mathfrak{u} = -\nabla \varphi$.
If we write it with velocity field, it is the Euler Poisson system

$$\partial_t \rho + \text{div}(\rho \mathfrak{u}) = 0$$

$$\partial_t \mathfrak{u} + \mathfrak{u} \cdot \nabla \mathfrak{u} + \nabla p(\rho) = \nabla V, \qquad p(\rho) = \frac{3}{10} \gamma_{\text{TF}} \rho^{\frac{5}{3}}$$

$$-\Delta V = \rho - \delta Z.$$

Time dependent Thomas-Fermi (a fluid dynamic system)

- The corresponding hydrodynamic system can be formally obtained from the Vlasov equation by using the Ansatz $f_t(x, \xi) = \rho_t(x)\delta_{\mathfrak{u}_t}(\xi)$. Rigorous derivation ???
- No any wellposedness result so far.

$$\partial_t \rho + \mathrm{div}(\rho\mathfrak{u}) = 0$$

$$\partial_t \mathfrak{u} + \mathfrak{u} \cdot \nabla\mathfrak{u} + \nabla p(\rho) = \nabla V, \qquad p(\rho) = \frac{3}{10}\gamma_{\mathrm{TF}}\rho^{\frac{5}{3}}$$

$$-\Delta V = \rho - \delta Z.$$

Possible future projects:

- Asymptotic stability of the TF ground state.
- Existence of nontrivial stationary solutions (subsonic, supersonic, transonic?), i.e. $\mathfrak{u} \neq 0$ and its asymptotic stability.
- Global energy weak solution...
- If $(\rho_t, \mathfrak{u}_t)$ as a solution of HD exists, Is this solution stable in the Vlasov equation

Let φ_t and ρ_t be a weak solution of TTF with finite energy $\mathcal{H}(\rho_t, \varphi_t)$, assume $B \subset \mathbb{R}^3$ bounded and measurable, and set

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

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

$$\limsup_{T \to \infty} \frac{1}{T} \int_0^T N_{\mathrm{TF}}(t, B)\mathrm{d}t \leq 4Z.$$

The time-dependent Thomas-Fermi energy

$$\mathcal{H}(\rho_t, \varphi_t) := \int \frac{\rho_t(x)}{2} |\nabla \varphi_t(x)|^2 \mathrm{d}x + \mathcal{E}_{\mathrm{TF}}(\rho_t)$$

is conserved along the trajectory of solutions φ_t, ρ_t.

Main idea of the proof (homogenization)

Time dependent Thomas-Fermi
(Fluid dynamic system of electrons in the field of a point charge)

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

Intuitively we should use $\rho(x)|x|x \cdot \nabla$ as a test function in order to homogenize the singularity from $Z/|x|$.
(simply us $|x|\rho_t$ as in the stationary case will not work).
Technically (Lenzmann and Lewin's function), we choose the test function as

$$\rho_t(x)W_R(x) := \rho_t(x)\nabla g_R(x) \cdot \nabla.$$

The continuity equation plays an role in the time derivative term,

$$
\begin{aligned}
L_T \quad &:= \quad \frac{1}{T}\int_0^T \int \rho_t \nabla g_R \cdot \nabla \partial_t \varphi_t \\
&= \quad \frac{1}{T}\int_0^T \partial_t \int \rho_t \nabla g_R \cdot \nabla \varphi_t - \frac{1}{T}\int_0^T \int \partial_t \rho_t \nabla g_R \cdot \nabla \varphi_t.
\end{aligned}
$$

where the first term ist bounded by the kinetic energy $\int \rho |\nabla \varphi|^2$, which

vanishes as $T \to \infty$.

Estimates

$$
\begin{aligned}
\limsup_{T \to \infty} L_T &= -\limsup_{T \to \infty} \frac{1}{T} \int_0^T \int \left(\nabla \cdot (\rho_t \nabla \varphi_t) \right) \left(\nabla g_R \cdot \nabla \varphi_t \right) \\
&= \left\langle \int \rho_t (\nabla \varphi_t)^T D^2 g_R \nabla \varphi_t + \int \rho_t (\nabla \varphi_t)^T D^2 \varphi_t \nabla g_R \right\rangle_\infty \\
&\geq \left\langle \int \rho_t (\nabla \varphi_t)^T D^2 \varphi_t \nabla g_R \right\rangle_\infty
\end{aligned}
$$

where the last term canceled with the convection term

$$
R_1 := \left\langle \int \rho_t \nabla g_R \cdot \nabla \frac{1}{2} (\nabla \varphi_t)^2 \right\rangle_\infty = \left\langle \int \rho_t (\nabla \varphi_t)^T D^2 \varphi_t \nabla g_R \right\rangle_\infty
$$

The pressure term is negative since g_R is convex:

$$
\begin{aligned}
R_2 &:= \left\langle \int \rho_t \nabla g_R \cdot \nabla \frac{\gamma_{\mathrm{TF}}}{2} \rho_t^{2/3} \right\rangle_\infty \\
&= \frac{1}{5} \gamma_{\mathrm{TF}} \left\langle \int \nabla \rho_t^{5/3} \cdot \nabla g_R \right\rangle_\infty = -\frac{1}{5} \gamma_{\mathrm{TF}} \left\langle \int \rho_t^{5/3} \Delta g_R \right\rangle_\infty \leq 0
\end{aligned}
$$

Estimates

Furthermore the remaining terms contribute in getting the final estimates

$$
\begin{aligned}
R_3 &:= -\left\langle \int \rho_t \nabla g_R \cdot \nabla \frac{Z}{|x|} \right\rangle_\infty = \left\langle \int \rho_t(x) \frac{Z \nabla g_R(x) \cdot x}{|x|^3} \right\rangle_\infty \\
&= Z \left\langle \int \frac{\rho_t(x)}{\langle x/R \rangle^2} \right\rangle_\infty = Z \langle M_R(\rho_t) \rangle_\infty
\end{aligned}
$$

$$
\begin{aligned}
R_4 &:= -\left\langle \iint \nabla g_R(x) \rho_t(x) \rho_t(y) \frac{x-y}{|x-y|^3} \right\rangle_\infty \\
&= -\frac{1}{2} \left\langle \iint \rho_t(x) \rho_t(y) \frac{(\nabla g_R(x) - \nabla g_R(y)) \cdot (x-y)}{|x-y|^3} \right\rangle_\infty \\
&\leq -\frac{1}{4} \iint \frac{\rho_t(x) \rho_t(y)}{\langle x/R \rangle^2 \langle y/R \rangle^2)} = -\frac{1}{4} \langle M_R(\rho_t) \rangle_\infty^2
\end{aligned}
$$

Therefore, $\langle M_R(\rho_t) \rangle_\infty$ satisfies

$$
0 \leq Z \langle M_R(\rho_t) \rangle_\infty - \frac{1}{4} \langle M_R(\rho_t) \rangle_\infty^2
$$

Thank you !