Symmetry breaking in the Hartree-Fock jellium

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joint work with Mathieu Lewin and Christian Hainzl

Introduction: Expected phase diagram for the 3d jellium

From Jones, Ceperley, PRL 76 (1996) and Zing, Lin, Ceperley, Phys. Rev. E 66 (2002).
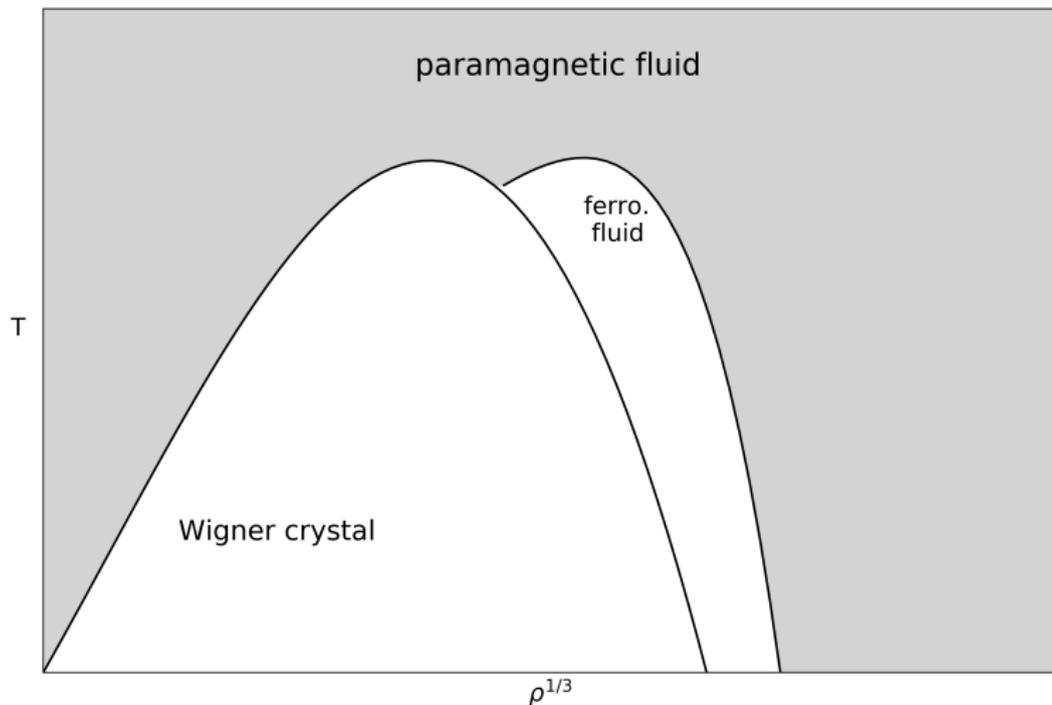
Hartree-Fock jellium

= Electrons in uniform positive background, described with Hartree-Fock.

States = one-body density matrices: $\gamma \in \mathcal{S}(L^2(\Omega, \mathbb{C}^2))$, $0 \le \gamma \le 1$. We write $\gamma = \begin{pmatrix} \gamma^{\uparrow\uparrow} & \gamma^{\uparrow\downarrow} \\ \gamma^{\downarrow\uparrow} & \gamma^{\downarrow\downarrow} \end{pmatrix}$.

Energy:

$$\mathcal{E}^{HF}(\gamma, \rho, T) = \frac{1}{2} \text{Tr}\left(-\Delta\gamma\right) + \frac{1}{2} \iint_{\Omega^2} \frac{(\rho_\gamma(\mathbf{r}) - \rho)(\rho_\gamma(\mathbf{r}') - \rho)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}'$$

$$- \frac{1}{2} \iint_{\Omega^2} \frac{\text{tr}_{\mathbb{C}^2}|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\, d\mathbf{r}' - T\, \text{Tr}\left(S(\gamma)\right)$$

where $S(t) := -t\log(t) - (1-t)\log(1-t)$ is the entropy.

Constraint: $\text{Tr}(\gamma) = \rho|\Omega|$.

Thermodynamic limit: $\Omega \to \mathbb{R}^3$, and ρ constant $\to E^{HF}(\rho, T)$.

> **Goal:** Study the phase diagram: features of the minimisers in the (ρ, T) plane.

Spatial symmetry breaking
If $\gamma(\mathbf{r}, \mathbf{r}') = \gamma(\mathbf{r} - \mathbf{r}', \mathbf{0})$, then γ is invariant by translation (fluid phase).
Otherwise, γ breaks spatial symmetry (e.g. Wigner crystallisation).

Spin symmetry breaking
If $\gamma^{\uparrow\uparrow} = \gamma^{\downarrow\downarrow}$ and $\gamma^{\uparrow\downarrow} = \gamma^{\downarrow\uparrow} = 0$, then γ is paramagnetic.
Otherwise, it is (partially) ferromagnetic.

The fluid phase

Perform the minimisation only on translational-invariant states: $\gamma(\mathbf{r}, \mathbf{r}') = \gamma(\mathbf{r} - \mathbf{r}')$.
$\implies \rho_\gamma = \rho = \gamma(\mathbf{0})$ is constant $\implies$ the direct term vanishes.

Fourier operator, γ is multiplication operator in Fourier by (still denoted by γ)

$$\gamma(\mathbf{k}) = \begin{pmatrix} \gamma^{\uparrow\uparrow}(\mathbf{k}) & \gamma^{\uparrow\downarrow}(\mathbf{k}) \\ \gamma^{\downarrow\uparrow}(\mathbf{k}) & \gamma^{\downarrow\downarrow}(\mathbf{k}) \end{pmatrix}, \quad \gamma(\mathbf{k}) = \gamma(\mathbf{k})^*, \quad 0 \le \gamma(\mathbf{k}) \le \mathbb{I}_2.$$

HF energy for fluid states

$$\frac{1}{2(2\pi)^3} \int_{\mathbb{R}^3} k^2 \mathrm{tr}_{\mathbb{C}^2} \gamma(\mathbf{k}) \mathrm{d}\mathbf{k} - \frac{1}{(2\pi)^5} \iint_{(\mathbb{R}^3)^2} \frac{\mathrm{tr}_{\mathbb{C}^2} [\gamma(\mathbf{k})\gamma(\mathbf{k}')]}{|\mathbf{k} - \mathbf{k}'|^2} \mathrm{d}\mathbf{k} \, \mathrm{d}\mathbf{k}' - \frac{T}{(2\pi)^3} \int_{\mathbb{R}^3} S(\gamma(\mathbf{k})) \mathrm{d}\mathbf{k}.$$

Constraints $\quad \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \mathrm{tr}_{\mathbb{C}^2} \gamma(\mathbf{k}) \mathrm{d}\mathbf{k} = \rho.$

No-spin version $\gamma \to g$, that is $g \in L^1(\mathbb{R}^3, \mathbb{R}), 0 \le g \le 1$ and $(2\pi)^{-3} \int_{\mathbb{R}^3} g = \rho.$

$$\frac{1}{2(2\pi)^3} \int_{\mathbb{R}^3} k^2 g(\mathbf{k}) \mathrm{d}\mathbf{k} - \frac{1}{(2\pi)^5} \iint_{(\mathbb{R}^3)^2} \frac{g(\mathbf{k})g(\mathbf{k}')}{|\mathbf{k} - \mathbf{k}'|^2} \mathrm{d}\mathbf{k} \, \mathrm{d}\mathbf{k}' - \frac{T}{(2\pi)^3} \int_{\mathbb{R}^3} S(g(\mathbf{k})) \mathrm{d}\mathbf{k}.$$

Lemma

Any minimiser among fluid states is of the form

$$\gamma(\mathbf{k}) = U \begin{pmatrix} g^{\uparrow}(\mathbf{k}) & 0 \\ 0 & g^{\downarrow}(\mathbf{k}) \end{pmatrix} U^* \quad \text{with} \quad U \in \mathrm{SU}(2).$$

Proof: $\mathrm{tr}_{\mathbb{C}^2}(U D_1 U^* D_2) \leq \mathrm{tr}_{\mathbb{C}^2}(D_1 D_2)$ with D_1, D_2 diagonal with ordered entries.

Corollary

$$E^{\mathrm{HF,fluid}}(\rho, T) = \inf_{t \in [0, 1/2]} \left\{ E^{\mathrm{HF,fluid}}_{\mathrm{nospin}}(t\rho, T) + E^{\mathrm{HF,fluid}}_{\mathrm{nospin}}((1-t)\rho, T) \right\}.$$

The best $t \in [0, \frac{1}{2}]$ is called the polarisation.

Lemma (Euler-Lagrange)

Any such minimiser γ must satisfy the Euler-Lagrange equation

$$\gamma = \left(1 + e^{\beta(\frac{1}{2}k^2 - \gamma * |\cdot|^{-2} - \mu)}\right)^{-1} \quad \text{for some Lagrange multiplier} \quad \mu \in \mathbb{R}.$$

In particular, $g^{\uparrow}$ and $g^{\downarrow}$ satisfy $g^{\uparrow/\downarrow}(\mathbf{k}) = \left(1 + e^{\beta(\frac{1}{2}k^2 - g^{\uparrow/\downarrow} * |\cdot|^{-2} - \mu)}\right)^{-1}$ for the same μ.

Remark: Spin symmetry breaking ($g^{\uparrow} \neq g^{\downarrow}$) can only happen if
- the map $\rho \mapsto \mu(\rho, T)$ is not one-to-one;
- the equation $g \mapsto \left(1 + e^{\beta(\frac{1}{2}k^2 - g * |\cdot|^{-2} - \mu)}\right)^{-1}$ has at least two fixed points.

An important example: the $T = 0$ case.

Lemma

At $T = 0$, for all $\rho > 0$, the no-spin energy $E_{\text{nospin}}^{\text{fluid}}$ has a unique minimiser, which is $g := \mathbb{1}(k^2 \leq c\rho^{3/2})$. Hence

$$E_{\text{nospin}}^{\text{fluid}}(\rho, T = 0) = C_{\text{TF}}\rho^{5/3} - C_D\rho^{4/3},$$

and

$$\mu(\rho, T = 0) = \frac{\partial}{\partial \rho} E_{\text{nospin}}^{\text{fluid}} = \frac{5}{3}C_{\text{TF}}\rho^{2/3} - \frac{4}{3}C_D\rho^{1/3} \quad \text{(not one-to-one)}.$$

Proof: The minimiser is radial decreasing + the energy is concave, so $g(\mathbf{k}) \in \{0, 1\}$.
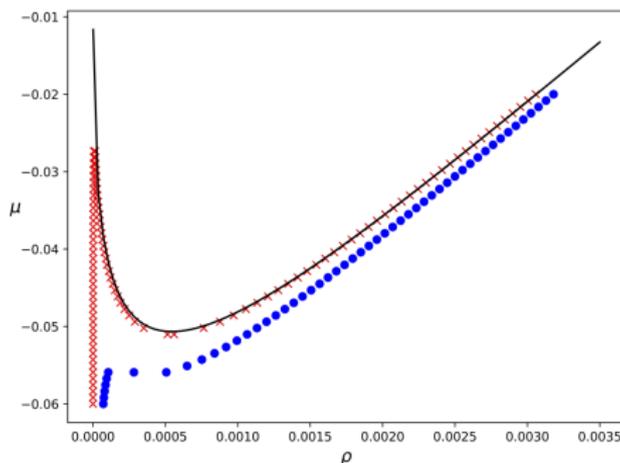
Figure: black: $T = 0$, red: $T = 0.01$ Ha, blue: $T = 0.03$ Ha.

Symmetry breaking at $T = 0$ case.

Including the spin, we just need to study the map

$$t \mapsto C_{\mathrm{TF}} \rho^{5/3}(t^{5/3} + (1-t)^{5/3}) - C_D \rho^{4/3}(t^{4/3} + (1-t)^{4/3}).$$

Theorem (G-Lewin 2019, but well-known result)

There is a first order phase transition at $\rho_c = \dfrac{125}{24\pi^5} \left(\dfrac{1}{1 + 2^{1/3}} \right)^3$ ($r_s \approx 5.45$):

- *For $\rho < \rho_c$, the minimiser is unique up to global spin rotation, and it is pure ferromagnetic ($g^{\downarrow} = 0$);*
- *For $\rho > \rho_c$, the minimiser is unique, and is paramagnetic.*

The energy is continuous, and has a kink at $\rho = \rho_c$.
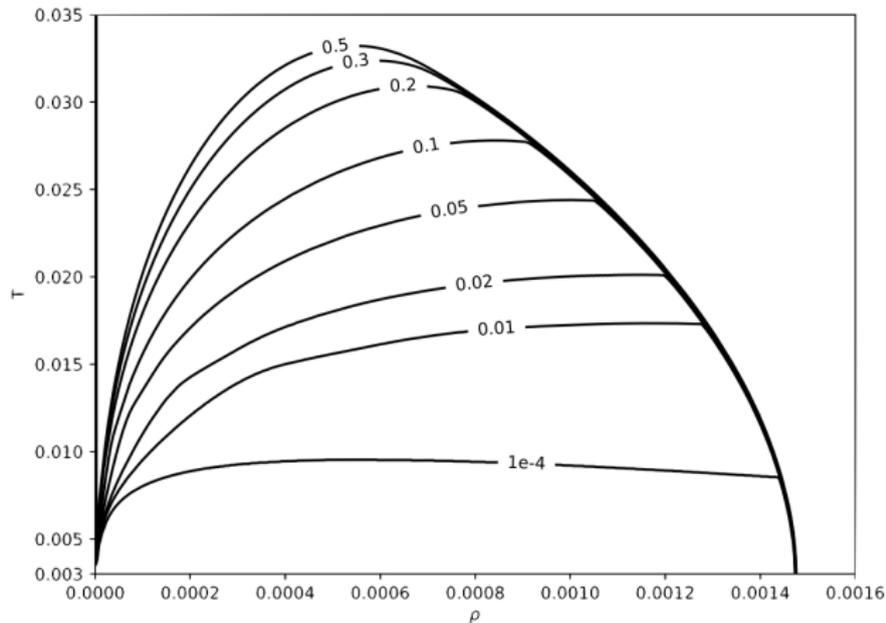
Figure: Level lines of the polarisation $t \in [0, 1/2]$.

Theorem (G-Lewin 2019)

For $T \geq C\rho^{1/3}$ or $T \geq Ce^{-\alpha\rho^{1/6}}$, the minimiser for the spin-fluid energy is unique and paramagnetic.

Idea of the proof (D. Gontier, M. Lewin, arXiv 1812.07679.)

We prove that, «in some regime», there is a unique solution to the fixed-point equation

$$g = \mathcal{G}_{T,\mu}[g] \quad \text{where} \quad \mathcal{G}_{T,\mu}[g](\mathbf{k}) := \frac{1}{1 + e^{\frac{1}{T}\left(\frac{1}{2}k^2 - g*w(\mathbf{k}) - \mu\right)}} \qquad \text{(Hammerstein integral equation)}$$

Setting $V := g * w \in L^\infty(\mathbb{R}^3)$, this is also

$$V = \mathcal{V}_{T,\mu}[V] \quad \text{where} \quad \boxed{\mathcal{V}_{T,\mu}[V](\mathbf{k}) := \frac{1}{1 + e^{\frac{1}{T}\left(\frac{1}{2}k^2 - V - \mu\right)}} * w.}$$

Step 1: $V \mapsto \mathcal{V}[V]$ is increasing: $V_1 \leq V_2 \implies \mathcal{V}[V_1] \leq \mathcal{V}[V_2]$.
Define $V_0^- = 0$ and $V_0^+ = a$ with $a \in \mathbb{R}$ large enough. Then,

$$V_{n+1}^- := \mathcal{V}[V_n^-] \quad \text{is increasing, bounded by } a, \text{ hence converges to some } V_{\min},$$

$$V_{n+1}^+ := \mathcal{V}[V_n^+] \quad \text{is decreasing, bounded by } 0, \text{ hence converges to some } V_{\max}.$$

The functions $V_{\min}(T, \mu)$ (resp. $V_{\max}(T, \mu)$) are minimal (resp. maximal) fixed point of $\mathcal{V}_{T,\mu}$.

Remark: This gives *a priori* bounds $\mu \leftrightarrow \rho$.

Step 2: For μ small enough ($\mu \to \infty$), we must have $V_{\min}(T, \mu) = V_{\max}(T, \mu)$.
The map $\mathcal{V}_{T,\mu}$ becomes a contraction among its fixed points.

Step 3: At a fixed point V (or g), study the linearised operator

$$\mathcal{L} := \mathrm{d}_V \left(V - \mathcal{V}_{T,\mu}[V] \right) : v \mapsto v - \underbrace{\frac{1}{T} w * (g(1-g)v)}_{:=A_g v}.$$

If $\|A\|_{\infty,\infty} < 1$, the operator $\mathcal{L} = 1 - A$ is invertible with bounded inverse.

The operator A has positive kernel, so

$$\|A(f)\|_{\infty} \leq \|f\|_{\infty} \|A(1)\|_{\infty}.$$

For instance, for low densities,

$$\|A(1)\|_{\infty} = \frac{1}{T} \|w * g(1-g)\|_{\infty} \leq \frac{1}{T} \|w * g\|_{\infty} \leq C \frac{\rho^{1/3}}{T}.$$

For high densities, use that $g(1-g)$ is small away from the Fermi surface.

Conclusion: With the implicit function theorem, $(T,\mu) \mapsto V_{\min}(T,\mu)$ and $(T,\mu) \mapsto V_{\max}(T,\mu)$ have unique continuations, hence are equal.

Spatial symmetry breaking

Theorem (Overhauser, Phys. Rev. Lett. 4, 462 (1960))

At $T = 0$, the fluid minimiser is *never* a HF minimiser. Actually,

$$E^{\mathrm{HF}}(\rho, T = 0) < E^{\mathrm{HF,fluid}}(\rho, T = 0) - Ce^{-\alpha\rho^{1/6}} \qquad \text{Delyon, Bernu, Baguet, Holzmann, Phys. Rev. B 92.}$$

Fluid states are **unstable** with respect to the formation of Spin Density Waves (SDW).

$\implies$ Much more complex phase diagram.

Phase diagram at $T = 0$ (from Baguet, Delyon, Bernu, Holzmann, Phys. Rev. B 90 (2014))
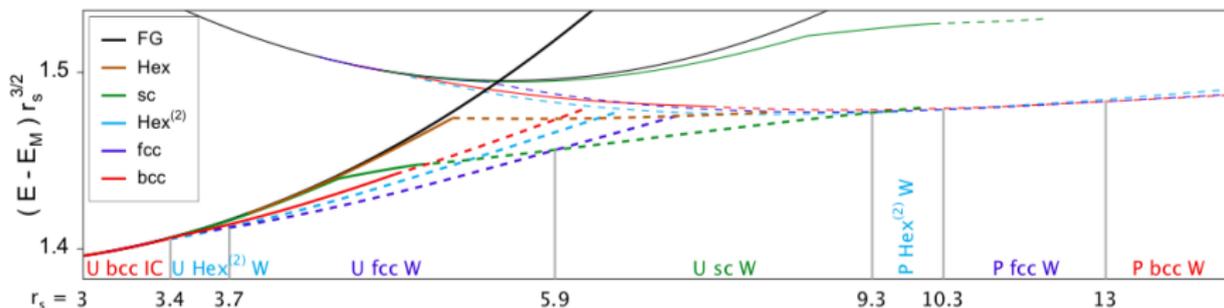
FIG. 2. Hartree-Fock phase diagram of the 3D electron gas. Energies are in Hartree per electron. $E_M = -0.89593/r_s$ is the Madelung energy of a polarized-bcc Wigner crystal. Full lines stand for incommensurate regime ($Q > Q_W$) and dashed lines for the Wigner crystal ($Q = Q_W$). Thin lines stand for the polarized gas (upper curves) and thick lines for the unpolarized gas.[14]

Theorem (G-Hainzl-Lewin 19)

- At $T = 0$,
$$\left| E^{\mathrm{HF,fluid}}(\rho, T = 0) - E^{\mathrm{HF}}(\rho, T = 0) \right| \leq C\mathrm{e}^{-\alpha \rho^{1/6}}.$$

- If $\rho \gg 1$ and $T > C\mathrm{e}^{-\alpha \rho^{1/6}}$, $E^{\mathrm{HF}}(\rho, T)$ has a unique minimiser, which is fluid and paramagnetic. In particular, $E^{\mathrm{HF}}(\rho, T) = E^{\mathrm{HF,fluid}}(\rho, T)$.

Idea of the proof: Control the difference with the first eigenvalue of the Schrödinger-like operator

$$H(\varepsilon) := |\Delta + 1| - \frac{\varepsilon}{|\mathbf{r}|}.$$

Lemma (G-Hainzl-Lewin 19)

The first eigenvalue $\lambda_1(\varepsilon)$ of $H(\varepsilon)$ satisfies

$$-C\mathrm{e}^{-\alpha/\sqrt{\varepsilon}} \leq \lambda_1(\varepsilon) \leq -C'\mathrm{e}^{-\alpha'/\sqrt{\varepsilon}}.$$

Based on similar results: *Hainzl, Seiringer 2008*: For $1 < s < 2$,

$$-C\mathrm{e}^{-\alpha/\varepsilon} \leq \lambda_1 \left(|\Delta + 1| - \frac{\varepsilon}{|\mathbf{r}|^s} \right) \leq -C'\mathrm{e}^{-\alpha'/\varepsilon}$$

In our case, use that, for $a > 0$,

$$\frac{\mathrm{e}^{-a|\mathbf{x}|}}{|\mathbf{x}|} \leq \frac{1}{|\mathbf{x}|} \leq \frac{\mathrm{e}^{-a|\mathbf{x}|}}{|\mathbf{x}|} + a,$$

and optimise $a := a(\varepsilon)$.

Idea of the proof for $T = 0$: Fix k_F the Fermi level. In a finite box Ω_L of size L with PBC, let γ_L be the (periodised) free Fermi state

$$\hat{\gamma}_L(\mathbf{k}, \mathbf{k}') = \delta_{\mathbf{k}, \mathbf{k}'} \mathbb{1}(k \leq k_F) = \delta_{\mathbf{k}, \mathbf{k}'} \left(\mathbb{1}\left[H_L(\mathbf{k}) \leq H_L(k_F) \right] \right),$$

with

$$H_L(\mathbf{k}) := \frac{1}{2}k^2 - \frac{4\pi}{L^3} \sum_{\mathbf{k}' \neq \mathbf{k}} \frac{\mathbb{1}(k' \leq k_F)}{|\mathbf{k} - \mathbf{k}'|^2} \quad \text{(mean-field fluid Hamiltonian)}.$$

Since H_L is the sum of two increasing functions, we have

$$|H_L(\mathbf{k}) - H_L(k_F)| \geq \frac{1}{2}|k^2 - k_F^2|, \quad \text{or, as operators,} \quad \left| H_L - \varepsilon_F^L \right| \geq \frac{1}{2}\left| -\Delta_L - k_F^2 \right|.$$

After some computations, we get, for all projectors γ with the same density, and with $Q := \gamma - \gamma_L$,

$$\mathcal{E}_L^{\mathrm{HF}}(\gamma) - \mathcal{E}_L^{\mathrm{HF}}(\gamma_L) \geq \frac{1}{2}\mathrm{Tr}_L\left(\left| \Delta_{\mathbf{x}, L} + k_F^2 \right| Q^2 \right) - \frac{1}{2}\iint_{(\Omega_L)^2} Q^2(\mathbf{x}, \mathbf{y})G_L(\mathbf{x} - \mathbf{y})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}$$

$$\geq \frac{1}{2}\int_{\Omega_L} \mathrm{d}\mathbf{y} \left(\left\langle Q(\cdot, \mathbf{y}) \right| \left| \Delta_{\mathbf{x}, L} + k_F^2 \right| - G_L(\cdot - \mathbf{y}) \left| Q(\cdot, \mathbf{y}) \right\rangle \right)$$

$$\geq \frac{1}{2} \underbrace{\lambda_1 \left\{ \left| \Delta_L + k_F^2 \right| - G_L(\mathbf{x}) \right\}}_{\leq 0} \underbrace{\iint_{(\Omega_L)^2} Q^2(\mathbf{x}, \mathbf{y})\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}}_{\leq 2N}$$

$$\geq N\lambda_1 \left\{ \left| \Delta_L + k_F^2 \right| - G_L(\mathbf{x}) \right\}.$$

After normalisation, and limit $L \to \infty$,

$$\boxed{E^{\mathrm{HF}} - E^{\mathrm{HF, fluid}} \geq \lambda_1 \left\{ |\Delta + k_F^2| - \frac{1}{|\mathbf{x}|} \right\} = k_F^2 \lambda_1 \left\{ |\Delta + 1| - \frac{1}{k_F|\mathbf{x}|} \right\}.}$$

Expected Phase diagram for the HF jellium