Symmetry breaking in the Hartree-Fock jellium

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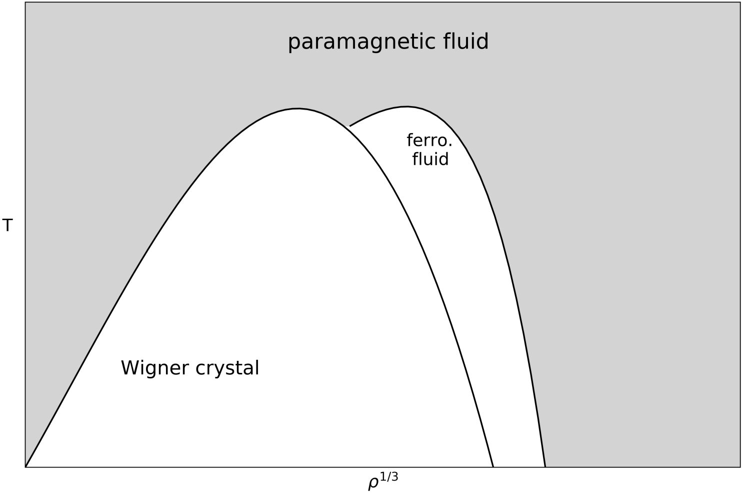
Introduction: Expected phase diagram for the 3d jellium

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



The Hartree-Fock model

Jellium (in a box Ω)

$$\mathcal{E}^{\rm Schro}(N,\Omega) = \min\left\{\langle \Psi, H_N \Psi\rangle,\ \Psi \in \mathcal{W}_N\right\},$$

Hamiltonian :

$$H_N = \sum_{i=1}^{N} -\frac{1}{2}\Delta_{\mathbf{r}_i} + \sum_{1\le i<j\le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \text{background}.$$

Set of wave-functions :

$$\mathcal{W}_N = \left\{\Psi \in L^2\left((\Omega\times\{\uparrow,\downarrow\})^N\right),\ \|\Psi\|_{L^2} = 1,\ \Psi \text{satisfies the Pauli principle}\right\}.$$

Pauli principle (since electrons are fermions)

$$\forall \sigma \in S_N,\ \Psi(\mathbf{r}_{\sigma(1)}, s_{\sigma(1)}; \cdots; \mathbf{r}_{\sigma(N)}, s_{\sigma(N)}) = \varepsilon(\sigma)\Psi(\mathbf{r}_1, s_1; \cdots; \mathbf{r}_N, s_N).$$

Hartree-Fock energy: minimise only on $\mathcal{S}_N \subset \mathcal{W}_N$, where

$$\mathcal{S}_N := \left\{\Psi = \frac{1}{\sqrt{N!}}\det\left[\phi_i(\mathbf{r}_j, s_j)\right],\quad (\phi_1,\cdots,\phi_N) \text{ orthonormal in } L^2\left(\Omega\times\{\uparrow,\downarrow\}\right)\right\}.$$

$$\mathcal{E}^{\rm HF} \ge \mathcal{E}^{\rm Schro}.$$

One-body density operator: $\gamma(\mathbf{r}, s; \mathbf{r}', s') := \sum_{i=1}^N \overline{\phi_i}(\mathbf{r}, s)\phi_i(\mathbf{r}', s')$, or

$$\gamma = \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| \quad \text{projector on } \mathrm{Vect}(\phi_1,\cdots,\phi_N).$$

Hartree-Fock jellium

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

Energy:

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

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

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

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

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)

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

HF energy for fluid states

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

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

No-spin version $\gamma \to g$, that is $g \in L^1(\mathbb{R}^3,\mathbb{R})$, $0 \leq g \leq 1$ 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

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

Proof: $\mathrm{tr}_{\mathbb{C}^2}(UD_1U^*D_2) \leq \mathrm{tr}_{\mathbb{C}^2}(D_1D_2)$ 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*

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

In particular, $g^{\uparrow}$ *and* $g^{\downarrow}$ *satisfy* $g^{\uparrow/\downarrow}(\mathbf{k}) = \left(1 + \mathrm{e}^{\beta(\frac{1}{2}k^2 - g^{\uparrow/\downarrow} * |\cdot|^{-2} - \mu)}\right)^{-1}$ *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 $g \mapsto \left(1 + \mathrm{e}^{\beta(\frac{1}{2}k^2 - g * |\cdot|^{-2} - \mu)}\right)^{-1}$ 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 $E^{\text{fluid}}_{\text{nospin}}$ has a unique minimiser, which is $g := \mathbb{1}(k^2 \le c\rho^{3/2})$. Hence

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

and

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

Proof: The minimiser is radial decreasing + the energy is concave, so $g(\mathbf{k}) \in \{0, 1\}$.

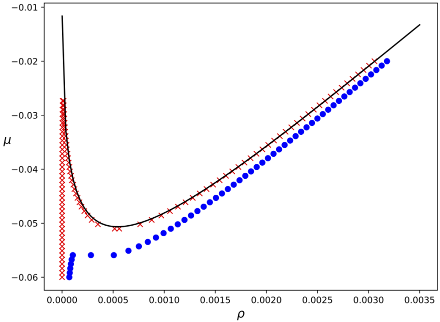


Figure: black: $T = 0$, red: $T = 0.01$ Ha, blue: $T = 0.03$ Ha.

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 $\rho = \rho_c$*.*

Fluid phase diagram

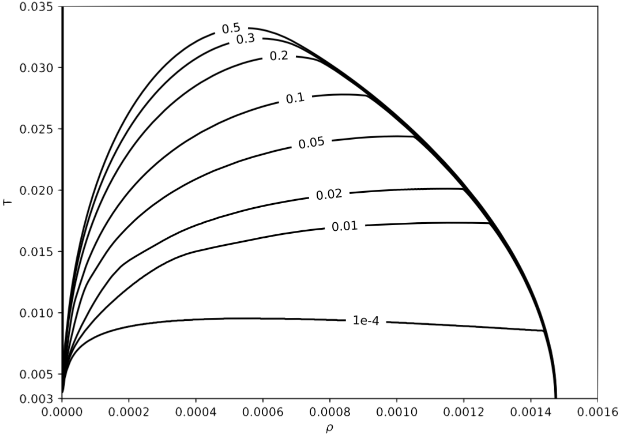


Figure: Level lines of the polarisation $t \in [0, 1/2]$.

Theorem (G-Lewin 2019)

For $T \geq C\rho^{1/3}$ or $T \geq C\mathrm{e}^{-\alpha\rho^{1/6}}$, 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

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

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

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

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,

$$\begin{aligned} V_{n+1}^- &:= \mathcal{V}[V_n^-] \quad \text{is increasing, bounded by } a \text{, hence converges to some } V_{\min}, \\ V_{n+1}^+ &:= \mathcal{V}[V_n^+] \quad \text{is decreasing, bounded by } 0 \text{, hence converges to some } V_{\max}. \end{aligned}$$

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

$$\|A(f)\|_\infty \le \|f\|_\infty \|A(1)\|_\infty.$$

For instance, for low densities,

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

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,

$$E^{\mathrm{HF}}(\rho, T=0) < E^{\mathrm{HF,fluid}}(\rho, T=0) - C\mathrm{e}^{-\alpha\rho^{1/6}}$$

Delyon, Bernu, Baguet, Holzmann, Phys. Rev. B 92.

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

$\Longrightarrow$ Much more complex phase diagram.

Phase diagram at $T = 0$ (from Baguet, Delyon, Bernu, Holzmann, Phys. Rev. B 90 (2014))

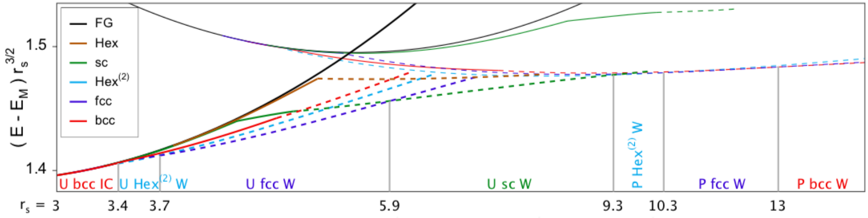


FIG. 2. Hartree-Fock phase diagram of the 3D electron gas. Energies are in Hartree per electron. $E_M = -0.89593/r_s$ is the Madelung energy of a polarized-bcc Wigner crystal. Full lines stand for incommensurate regime ($Q > Q_W$) and dashed lines for the Wigner crystal ($Q = Q_W$). Thin lines stand for the polarized gas (upper curves) and thick lines for the unpolarized gas.[14]

Theorem (G-Hainzl-Lewin 19)

- *At* $T = 0$,
$$\left| E^{\rm HF,fluid}(\rho, T=0) - E^{\rm HF}(\rho, T=0) \right| \le C \mathrm{e}^{-\alpha \rho^{1/6}}.$$
- *If* $\rho \gg 1$ *and* $T > C\mathrm{e}^{-\alpha\rho^{1/6}}$, $E^{\rm HF}(\rho, T)$ *has a unique minimiser, which is fluid and paramagnetic. In particular,* $E^{\rm HF}(\rho, T) = E^{\rm HF,fluid}(\rho, T)$.

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*

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

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

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

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

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

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

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

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

$$\begin{aligned}
\mathcal{E}_L^{\rm HF}(\gamma) - \mathcal{E}_L^{\rm HF}(\gamma_L) &\geq \frac{1}{2} \mathrm{Tr}_L \left(\left| \Delta_{\mathbf{x},L} + k_F^2 \right| Q^2 \right) - \frac{1}{2} \iint_{(\Omega_L)^2} Q^2(\mathbf{x}, \mathbf{y}) G_L(\mathbf{x} - \mathbf{y}) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{y} \\
&\geq \frac{1}{2} \int_{\Omega_L} \mathrm{d}\mathbf{y} \left(\left\langle Q(\cdot, \mathbf{y}) \middle| \, |\Delta_{\mathbf{x},L} + k_F^2| - G_L(\cdot - \mathbf{y}) \middle| Q(\cdot, \mathbf{y}) \right\rangle \right) \\
&\geq \frac{1}{2} \underbrace{\lambda_1 \left\{ |\Delta_L + k_F^2| - G_L(\mathbf{x}) \right\}}_{\leq 0} \underbrace{\iint_{(\Omega_L)^2} Q^2(\mathbf{x}, \mathbf{y}) \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{y}}_{\leq 2N} \\
&\geq N \lambda_1 \left\{ |\Delta_L + k_F^2| - G_L(\mathbf{x}) \right\}.
\end{aligned}$$

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

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

Expected Phase diagram for the HF jellium