Phase Diagram of the Two-Dimensional Homogeneous Electron Gas

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ESDG Meeting
Wednesday 13th February, 2008
Two-Dimensional Homogeneous Electron Gas (I)

- **2D HEG**: set of electrons moving in 2D in a uniform, inert, neutralising background.

- Hamiltonian (for finite system):

\[
\hat{H} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_{j>i} v_E(r_{ij}) + \frac{N v_M}{2}.
\]

Infinite-system GS energy per particle depends only on the **density** (specified by radius \(r_s\) of circle containing one electron on average) and **spin polarisation** \(\zeta = (N_\uparrow - N_\downarrow)/N\).

- Physical realisations:
  - *Electrons on metal surfaces.* E.g. Cu [111].
  - *Electrons on droplets of liquid He.* Held in place by image charges
  - *Inversion layers in MOS devices.* Can easily tune density. Electrons far from dopants; fewer complications due to disorder; technologically important.
Two-Dimensional Homogeneous Electron Gas (II)

- HEG is simplest fully interacting quantum many-body system.
- QMC is the only accurate method available for studying its ground-state properties.
- We have carried out QMC studies of the 2D HEG:
  1. We have calculated the zero-temperature phase diagram.\(^1\)
  2. We have calculated the PCF, structure factor and momentum distribution.\(^2\)
- Our data will be of interest to
  - Experimentalists looking for ferromagnetism and Wigner crystallisation in low-density 2D HEGs.
  - Theorists interested in constructing 2D XC functionals for DFT calculations.
- Our calculations are more accurate than previous ones because of (i) a better treatment of finite-size errors; (ii) a more accurate nodal surface; (iii) Darwin.

Wigner Crystallisation in 2D (I)

- Kinetic energy dominates at high density: *form Fermi fluid to minimise it.*

- Potential energy dominates at low density: *form Wigner crystal to minimise it.*

- Wigner crystals have been observed on the surface of liquid helium\(^3\) and in inversion layers in MOSFET devices\(^4\).

- 2D Wigner crystals could be of use in quantum computing devices.\(^5\)

- Previous QMC studies\(^6\) indicate that fluid–crystal transition occurs somewhere between \(r_s = 25\) and 40 a.u.

- Can we be more precise?

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Hartree–Fock Theory of 2D Wigner Crystals (I)

• Full Hartree–Fock calculations using a PW basis have been performed. Here we derive an approximate analytic theory.

• At low densities Wigner crystal orbitals are of form

\[ \phi_R(r) = \exp(-C|r - R|^2) \]

where \( R \) is a lattice site and \( C \) is an optimisable parameter.

• (This is like the Einstein approximation to the ZPE of a crystal.)

• Exchange effects are negligible in low-density limit. Approximate Slater determinant by a Hartree product.

\[ ^7 \text{J. R. Trail et al., Phys. Rev. B 68, 045107 (2003).} \]
Hartree–Fock Theory of 2D Wigner Crystals (II)

- Total energy per electron is sum of kinetic energy and Hartree energy (electrostatic energy of a periodic array of Gaussian charge distributions) minus the self energy of each Gaussian charge distribution:

\[
E = C - \frac{\sqrt{\pi C}}{2} + \frac{1}{r_s^2} \sum_{G \neq 0} \frac{1}{G} \exp\left(\frac{-G^2}{4C}\right).
\]

- Demand that energy is minimised with respect to \(C\):

\[
0 = \left(\frac{\partial E}{\partial C}\right)_{r_s} = 1 - \frac{1}{4} \sqrt{\frac{\pi}{C}} + \frac{\pi}{4AC^2} \sum_{G \neq 0} G \exp\left(\frac{-G^2}{4C}\right).
\]

\[
\approx 1 - \frac{1}{4} \sqrt{\frac{\pi}{C}} + \frac{1}{8C^2} \int_0^{\infty} G^2 \exp\left(\frac{-G^2}{4C}\right) dG
\]

\[
\approx 1 - \frac{1}{3C^2 r_s^3} + O(r_s^{-1/4}).
\]
Hartree–Fock Theory of 2D Wigner Crystals (III)

• Hence the optimal $C$ is $C = r_s^{-3/2}/\sqrt{3}$.

• Integrate $(\partial E/\partial C)_r$ w.r.t. $C$. At low densities $E$ must tend to Madelung energy $M/r_s$, so integration constant is $M/r_s$. Insert optimal value of $C$:

$$E \approx \frac{2}{\sqrt{3}r_s^{3/2}} + \frac{M}{r_s}. $$

<table>
<thead>
<tr>
<th>$r_s$ (a.u.)</th>
<th>Kinetic energy ($10^{-4}$ a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Analytic Approx.</td>
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<tr>
<td>10</td>
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<tr>
<td>100</td>
<td>5.773502692</td>
</tr>
</tbody>
</table>
Triangular lattice has lowest energy in HF theory.
Magnetic Behaviour of the Fermi Fluid

- Bloch transition: para. fluid favoured at high density (want to minimise KE); ferro. fluid favoured at low density (keep electrons apart to minimise XC energy).

- Hartree–Fock theory: Bloch transition at $r_s = 2.01$ a.u. No region of stability for ferromagnetic fluid.

- VMC$^8$: Bloch transition at $r_s = 13(2)$ a.u.; crystallisation at $r_s = 33(2)$ a.u.

- DMC$^9$: Bloch and crystallisation transitions at $r_s = 37(5)$ a.u.

- DMC$^{10}$: Bloch transition at $r_s = 20(2)$ a.u. and crystallisation at $r_s = 34(4)$ a.u.

- Experiment$^{11}$: “Possible evidence” of ferromagnetism at $r_s = 7.6$ a.u.

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Fermi Fluid: PBC, TBC and TABC

- Orbitals for Fermi fluid:
  \[ \phi_k(r) = \exp(ik \cdot r). \]

- Periodic boundary conditions: \( \{k\} \) are simulation-cell \( \mathbf{G} \)-vectors.

- Single-particle finite-size effects: Increase \( N \) at fixed density; grid of \( \mathbf{G} \)-vectors gets finer; energy per electron jumps as shells of \( \mathbf{G} \) vectors pass through Fermi line.

- Twisted boundary conditions: \( k \) are simulation-cell \( \mathbf{G} \) vectors offset by \( k_s \in 1\text{st BZ} \) of simulation cell.

- Twist averaging: average over all \( k_s \). Replaces grid of \( k \) by a Fermi area (equal to area of Fermi circle), greatly reducing single-particle finite-size effects. Shape of Fermi line isn’t quite right: gives negligibly small positive bias to KE.

- Previous QMC studies of 2D HEG have not used twist averaging.
Static Structure Factors

Static structure factor:

$$S(r, r') = \frac{A}{N} \langle [\hat{\rho}(r) - \rho(r)][\hat{\rho}(r') - \rho(r')] \rangle$$

where $\hat{\rho}(r) = \sum_i \delta(r - r_i)$ is the density operator, $\rho(r) = \langle \hat{\rho}(r) \rangle$ is the density and $A$ is the area of the simulation cell.

Translationally averaged structure factor:

$$S(r) = \frac{1}{A} \int_A S(r' + r, r') \, dr'.$$

Fourier transform of the translationally averaged structure factor:

$$S(G) = \frac{1}{N} \left( \langle \hat{\rho}(G)\hat{\rho}^*(G) \rangle - \rho(G)\rho^*(G) \right),$$

where $\hat{\rho}(G) = \sum_i \exp(-iG \cdot r_i)$ is the Fourier transform of the density operator.
Hartree and XC Energies

\[
\langle \hat{V}_{Ew} \rangle = \frac{Nu_M}{2} + \frac{\int |\Psi(R)|^2}{\int |\Psi|^2} \sum_{i \neq j}^N \int v_E(r_i - r_j) dR \\
= \frac{1}{2} \int \int [\rho(r, r') - \rho(r)\rho(r')] [v_E(r - r') - v_M] \, dr \, dr' \\
+ \frac{1}{2} \int \int v_E(r - r')\rho(r)\rho(r') \, dr \, dr' \\
= \frac{N}{2} \left( \sum_{G \neq 0} \frac{2\pi}{A|G|} [S(G) - 1] + v_M \right) + \sum_{G \neq 0} \frac{\pi A}{|G|} \rho(G)\rho^*(G),
\]

where \(\rho(r, r') = \langle \sum_{i \neq j} \delta(r - r_i)\delta(r' - r_j) \rangle\) is the pair density.

First term: exchange-correlation energy (interaction of electrons with their XC holes).
Second term: Hartree energy (interaction of charge densities). Zero for HEG.
Finite-Size Effects in 2D (I)

**Old assumption**: finite-size errors are due to slow convergence of $v_E(r)$ to $1/r$ in XC energy. (This is main cause of finite-size effects at typical densities in 3D.)

Can cure this “problem” by using *model periodic Coulomb* interaction. But it was found that MPC doesn’t change energies much in 2D.$^{12}$

Alternative approach for curing the “problem": finite-size error is due to summation rather than integration over $G$ in reciprocal-space expression for interaction energy.$^{13}$

**Poisson summation formula**: $[1/(2\pi)^3] \int f(k) \, dk = (1/A) \sum_G f(G) - \sum_{R \neq 0} f(R)$.

So, if XC hole [and hence $S(k)$] has converged, finite-size correction is zero in 2D because $\lim_{k \to 0} v_E(k)S(k) = 0$ (unlike 3D).$^{14}$

**New understanding**$^{14}$: 2D finite-size errors are caused by (i) slow convergence of the XC hole (screening is reduced in 2D) and (ii) neglect of long-ranged correlations in the KE.

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Finite-Size Effects in 2D (II)

• Long-ranged nonoscillatory behaviour of the XC hole is known analytically\textsuperscript{15}: \( \rho_{xc}(r) = -\tilde{\Lambda} r^{-7/2} \).

• Hence the XC charge outside radius \( r \) is \( \tilde{Q} = -4\pi\tilde{\Lambda}/(3r^{3/2}) \).

• Infinite-system XC charge outside finite simulation cell is ignored.

• So the error in the total Ewald energy due to the missing tail of the XC hole is

\[
\Delta V_{Ew} \approx -\frac{N}{2} \int_{R_A}^{\infty} \frac{1}{A} \frac{4\pi\tilde{\Lambda}}{3r^{5/2}} 2\pi r \, dr = \mathcal{O}(N^{-1/4}),
\]

where \( R_A \) is the radius of a circle of area \( A \).

• Error resulting from distortion of XC hole inside the simulation cell is of the same order (can estimate by adding “missing” charge \( \tilde{Q} \) in sensible fashion).

Finite-Size Effects in 2D (III)

• **RPA**: exact long-ranged correlation described by \( \exp[\sum_{i>j} u(r_{ij})] \) in Jastrow factor.

• Write “TI” estimator of KE \( \langle (−1/4) \nabla^2 \log(\Psi) \rangle \) in reciprocal space.

• Finite-size error in the TI estimate can be regarded as a difference between a sum and an integral, à la the Ewald energy.\(^{16}\)

• Leading-order KE correction is due to omission of \( G = 0 \) term in sum.

• Use analytic RPA expression for \( u(k) \) at small \( k \) and integrate over area of \( (2\pi)/A \) to obtain missing contribution to KE.

• Error in total KE goes as \( O(N^{-1/4}) \).\(^{17}\)

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Finite-Size Effects in 2D (IV)

- Both sources of finite-size error in the 2D energy per electron go as $O(N^{-5/4})$. So we should extrapolate energies to infinite system size using

$$E_N = E_\infty - bN^{-5/4}.$$ 

- Previous QMC studies have incorrectly used $N^{-3/2}$ for crystals and $N^{-1}$ for fluid.

Left: crystal extrapolation at $r_s = 35$ a.u.; right: fluid extrapolation at $r_s = 30$ a.u.
Backflow Transformation

- Evaluate Slater wave function at quasiparticle coordinates related to actual electron coordinates by electron–electron backflow functions.\textsuperscript{18}

- Moves nodal surface of wave function; can therefore improve the fixed-node DMC energy.

- At $r_s = 30$ a.u., BF lowers fluid DMC energy by $36(3) \, \mu$Ha per electron and lowers crystal DMC energy by $1.0(4) \, \mu$Ha per electron. (DMC energies extrapolated to zero time step and infinite system size.)

- Backflow is significant for the fluid, but not for the crystal, where electrons are already kept apart by localisation on lattice sites.

- Antiparallel-spin BF functions are much longer ranged than parallel-spin functions. Parallel spins are already kept away from each other by wave function antisymmetry.

Optimisation of Crystal Orbitals

Only parameter affecting crystal nodal surface: Gaussian exponent $C$. Minimise DMC energy w.r.t. $C$ to minimise fixed-node error.

\[ \text{Optimal exponent is } C_{\text{DMC}} = 0.071 r_s^{-3/2}. \]

CF, VMC exponent is $C_{\text{VMC}} = 0.15 r_s^{-3/2}$ and HF exponent is $C_{\text{HF}} = 0.46 r_s^{-3/2}$. 
Time-Step and Population-Control Biases

Population-control bias is bad at low density.$^{19}$

Use about 1600 configurations to make population-control bias negligible.

Time-step bias is linear; extrapolate DMC energies to zero time step.

$\text{DMC energy against time step for a crystal at } r_s = 20 \text{ a.u. (left) and fluid at } r_s = 30 \text{ a.u. (right).}$

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2D HEG Energy Diagram (I)

\[(E + \frac{1.106103}{r_s}) r_s^{3/2}\] (a.u.)

- R&S crys.
- R&S crys. (fit)
- R&S para. fl.
- R&S para. fl. (fit)
- R&S ferro. fl.
- R&S ferro. fl. (fit)
$E + \frac{1.106103}{r_s^{3/2}}$ (a.u.)
2D HEG Energy Diagram (II)

- Fully polarised fluid is never stable.

- Wigner crystallisation occurs at $r_s = 33 \pm 1$ a.u.

- At $r_s = 35$ a.u., the energy of a fluid with $\zeta = 2/5$ agrees with the paramagnetic and ferromagnetic fluid energies. Very unlikely that a region of stability for a partially polarised fluid exists.

- Phase transitions in 2D HEG cannot be first order.\(^\text{20}\)

- It’s energetically favourable to form boundaries between macroscopically separated phases, so a “microemulsion” is formed at crystallisation density.

- Doesn’t affect basic features of phase diagram; just blurs boundaries.

Hybrid Phases

• It’s been alleged that there exist hybrid phases that are neither fluid nor crystal\(^{21}\).

• Orbitals are long-ranged Wannier functions.

• Have tried using orbitals of the form

\[
\phi_{\mathbf{R}}(\mathbf{r}) = \exp\left(-C|\mathbf{r} - \mathbf{R}|^2\right) + \sum_{S} c_S \sum_{\mathbf{G} \in S} \cos[\mathbf{G}.(\mathbf{r} - \mathbf{R})],
\]

where \(C\) and the \(c_S\) are optimisable. \(S\) runs over stars of \(\mathbf{G}\) vectors. This form of orbital can describe the proposed hybrid phase (and the crystal phase).

• Have looked, but haven’t found the hybrid phase. Does it exist?

• Fact that fluid–crystal transition is from a paramagnetic fluid rather than a ferromagnetic one makes hybrid phase more unlikely.

Conclusions

• **There is no region of stability for a ferromagnetic Fermi fluid in 2D.**

• **Wigner crystallisation occurs at** $r_s = 33 \pm 1$ a.u. **in 2D.**

• **Have looked for a recently proposed “hybrid” phase. Didn’t find it.**

• **Have calculated structure factors, pair-correlation functions and momentum distributions.** Didn’t talk about them today, but I’ll tell you all about them next time someone pulls out of their ESDG slot at short notice. . . **So don’t do this.**
Acknowledgements

Financial support was received from Jesus College, Cambridge and the Engineering and Physical Sciences Research Council.

Computing resources were provided by the Cambridge High Performance Computing Service.