Quantum Monte Carlo Study of the Two-Dimensional Homogeneous Electron Gas

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Two-Dimensional Homogeneous Electron Gas (I)

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

- Hamiltonian (for finite system):
  \[
  \hat{H} = \sum_i -\frac{1}{2} \nabla_i^2 + \sum_{j>i} v_E(r_{ij}) + \frac{Nv_M}{2}.
  \]

  Infinite-system ground-state 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.**
  - **Inversion layers in MOS devices.** Can easily tune density. Electrons far from dopants; fewer complications due to disorder; technologically important.
  - Electrons in **2D semiconductors** (gallium chalcogenides, etc.).
Two-Dimensional Homogeneous Electron Gas (II)

- **Quantum Monte Carlo** is the most accurate first-principles method available for studying the ground-state properties of the HEG.

- We have carried out QMC studies of the 2D HEG to determine:
  1. The zero-temperature phase diagram.\(^1\)
  2. The pair-correlation function, structure factor and momentum distribution.\(^2\)
  3. The energy band and hence quasiparticle effective mass.\(^3\)

- Our data are of interest to
  - Experimentalists looking for ferromagnetism, Wigner crystallisation and changes to the effective mass in low-density 2D HEGs.
  - Theorists interested in constructing 2D XC functionals for DFT calculations.

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**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\(^4\) and in inversion layers in MOSFET devices\(^5\).

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

- Can we be more precise?

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Wigner Crystallisation in 2D (II)

- Triangular lattice has lowest Madelung constant. Wins at low density.

- Hartree–Fock theory\textsuperscript{7}: antiferromagnetic square lattice $\rightarrow$ ferromagnetic triangular lattice at $r_s = 2.6$ a.u.

- We consider only triangular lattices.

**Magnetic Behaviour of the Fermi Fluid (I)**

- **Bloch transition**: paramagnetic fluid favoured at high density (doubly occupy low-momentum states to minimise KE); ferromagnetic fluid favoured at low density (keep electrons apart to minimise XC energy).
Magnetic Behaviour of the Fermi Fluid (II)

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

- **VMC**\textsuperscript{8}: Bloch transition at $r_s = 13(2)$ a.u.; crystallisation at $r_s = 33(2)$ a.u.

- **DMC**\textsuperscript{9}: Bloch and crystallisation transitions at $r_s = 37(5)$ a.u.

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

- **Experiment**\textsuperscript{11}: “Possible evidence” of spontaneous spin polarisation at $r_s = 7.6$ a.u.

- **Open question**: is there a range of densities at which the 2D HEG forms a ferromagnetic fluid?

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Magnetic Behaviour of the Wigner Crystal

- **Hartree-Fock theory**\(^{12}\): ferromagnetic for \( r_s > 2.6 \) a.u.

- **Multispin exchange model**\(^{13}\): frustrated antiferromagnetism (spin liquid) \( \rightarrow \) ferromagnetism at \( r_s \leq 175(10) \) a.u.

- We have studied both ferromagnetic and antiferromagnetic triangular crystals.

- We have used striped antiferromagnetic crystals. Energy should be close to that of the spin liquid.

### References


Fermi Fluid: Boundary Conditions (I)

- **Orbitals for Fermi fluid:**
  \[ \phi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}). \]

- **Periodic boundary conditions** on a finite cell: \( \{ \mathbf{k} \} \) 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 get occupied.
Fermi Fluid: Boundary Conditions (II)

- **Twisted boundary conditions:** $\mathbf{k}$ are simulation-cell $\mathbf{G}$ vectors offset by $\mathbf{k}_s \in 1$st Brillouin zone of simulation cell.

- **Twist averaging in canonical ensemble:** average over all $\mathbf{k}_s$, keeping $N$ fixed.
  - Replaces grid of $\mathbf{k}$ by a Fermi area (equal to area of Fermi circle), greatly reducing single-particle finite-size effects.
  - Shape isn’t quite right: leaves small positive bias in KE.

- Previous QMC studies of 2D HEG have not used twist averaging.
Long-Range Finite-Size Errors

- Compression of XC hole and neglect of long-range two-body correlations in finite cell give error in 2D energy per electron going as $\mathcal{O}(N^{-5/4})$.\textsuperscript{14} Extrapolate using:

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

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

\textbf{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.\(^\text{15}\)

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

- BF is more significant in fluids than crystals, where electrons are already kept apart by localisation on lattice sites.

- Parallel spins are already kept away from each other by wave-function antisymmetry. BF is much less important in ferromagnetic systems.

<table>
<thead>
<tr>
<th>System (r_s = 30) a.u.</th>
<th>Lowering of DMC energy due to BF ((\mu\text{Ha / elec.}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paramagnetic fluid</td>
<td>36(3)</td>
</tr>
<tr>
<td>Ferromagnetic fluid</td>
<td>6(4)</td>
</tr>
<tr>
<td>Antiferromagnetic crystal</td>
<td>2.4(6)</td>
</tr>
<tr>
<td>Ferromagnetic crystal</td>
<td>2.3(3)</td>
</tr>
</tbody>
</table>

Optimisation of Crystal Orbitals (I)

- **Crystal orbitals**: $\phi_R(r) = \exp(-C|r - R|^2)$.

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

**DMC energy against $C$ at $r_s = 30$ a.u. (left) and $r_s = 40$ a.u. (right) (ferro.).**
Optimisation of Crystal Orbitals (II)

- **Ferromagnetic crystals**: optimal exponent is $C^F_{\text{DMC}} = 0.071 r_s^{-3/2}$.
  - CF, VMC exponent is $C^F_{\text{VMC}} = 0.15 r_s^{-3/2}$;
  - HF exponent is $C^F_{\text{HF}} = 0.46 r_s^{-3/2}$.

- **Antiferromagnetic crystals**: optimal exponent is $C^A_{\text{DMC}} = 0.082 r_s^{-3/2}$. 
2D HEG Energy Diagram (I)

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

- R&S ferro. crystal
- R&S ferro. fluid
- R&S para. fluid
2D HEG Energy Diagram (I)

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

- D&N ferro. crystal
- D&N antiferro. crystal
- D&N ferro. fluid
- D&N para. fluid

$r_s$ (a.u.)

20 30 40 50
Fully polarised fluid is never stable.

Wigner crystallisation occurs at $r_s = 31(1)$ a.u. Transition is from a paramagnetic fluid to an antiferromagnetic Wigner crystal.

Further transition: antiferromagnetic $\rightarrow$ ferromagnetic crystal at $r_s = 38(5)$ 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.\(^\text{16}\)

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

– New phases could “round off corners” in energy diagram.

Contact PCF of Paramagnetic Fluid (I)

- $g(0)$ is an important parameter in construction of GGA XC functionals for use in DFT.

- Most theoretical calculations of $g(0)$ have used ladder theory to solve approximately the Bethe–Goldstone equation for the effective interaction between two electrons. Exact in high-density limit, but not at low densities.

- Disagreement between old approximation\(^{17}\) in ladder theory and a better approximation,\(^{18}\) and between the better approximation in ladder theory and QMC.\(^{19}\) Which is right?

- We evaluate $g(r)$ [including $g(0)$] by binning interparticle distances. Easier in 2D than 3D. Easier at high density than low density.

- Earlier study used Slater–Jastrow wave function and no twist averaging; ours used Slater–Jastrow–backflow wave functions and twist averaging.


Contact PCF of Paramagnetic Fluid (II)

Present work
Gori-Giorgi et al.
Nagano et al.
Polini et al.
Qian
Fermi Liquid Theory

- **Fermi liquid theory**\(^{20}\): *low-energy excitations in a fluid of interacting electrons can be treated as excitations of quasiparticles occupying plane-wave states.*

- **Justification:** Pauli exclusion principle. Scattering rate of quasiparticles between plane waves is low (vanishes at Fermi surface). Single-particle momenta are approximately good quantum numbers.

\(^{20}\) L. D. Landau, JETP 3, 920 (1957); L. D. Landau, JETP 5, 101 (1957); L. D. Landau, JETP 8, 70 (1959).
Landau Energy Functional

- **Total energy** $E$:

\[
E = E_0 + \sum_{k, \sigma} \mathcal{E}_\sigma(k) \delta N_{k, \sigma} + \frac{1}{2} \sum_{k, \sigma} \sum_{k', \sigma'} f_{\sigma \sigma'}(k, k') \delta N_{k, \sigma} \delta N_{k', \sigma'},
\]

where $E_0$ is the ground-state energy and $\delta N_{k, \sigma}$ is the change in quasiparticle occupancy relative to the ground state.

- **Quasiparticle energy band**: $\mathcal{E}_\sigma(k)$ is the energy of an isolated quasiparticle.
  - **Linear approximation**: near the Fermi surface, $\mathcal{E}_\sigma(k) = E_F + (k_F/m^*)(k - k_F)$, where $E_F$ is the Fermi energy and $m^*$ is the quasiparticle effective mass.

- **Landau interaction function**: $f_{\sigma \sigma'}(k, k')$ describes quasiparticle interactions.
  - Near the Fermi surface, $f_{\sigma \sigma'}$ only depends on the angle $\theta_{kk'}$ between $k$ and $k'$. 
The effective mass ($m^*$) of a paramagnetic 2D HEG has been the subject of great controversy in recent years:

- Some experiments\textsuperscript{21} found a large enhancement of $m^*$ at low density; other experiments\textsuperscript{22} have contradicted this.
- $GW$ calculations give a range of possible results depending on the choice of effective interaction.\textsuperscript{23}
- Previous QMC studies have predicted (i) much less\textsuperscript{24} and (ii) much more\textsuperscript{25} enhancement of $m^*$ than found in recent experiments.

Experiment\textsuperscript{22} and theory\textsuperscript{26} suggest that $m^*$ in paramagnetic and ferromagnetic HEGs behaves quite differently as a function of density.

Calculating the Effective Mass and Landau Interaction Functions

- **To calculate the quasiparticle effective mass:**
  - The DMC energy band $\mathcal{E}(k)$ was determined at a range of $k$ by taking the energy difference when an electron is added to or removed from a closed-shell ground-state.
  - A quartic $\mathcal{E}(k) = \alpha_0 + \alpha_2 k^2 + \alpha_4 k^4$ was fitted to the energy band values.
  - The effective mass was then calculated as $m^* = k_F / (d\mathcal{E}/dk)_{k_F}$.

- **To calculate the Landau interaction functions and hence Fermi liquid parameters:**
  - Electrons were promoted from $(\sigma, k)$ just below the Fermi edge to $(\sigma', k')$ just above it, to obtain the energy difference $\Delta E_{\sigma\sigma'}(k, k')$ relative to the ground state.
  - The single-particle contribution was subtracted from the excitation energy, to give $-f_{\sigma\sigma'}(\theta_{kk'}) = \Delta E_{\sigma\sigma'}(k, k') - [\mathcal{E}(k') - \mathcal{E}(k)]$.
  - The first few Fourier components of $f_{\sigma\sigma'}(\theta)$ were found by numerical integration in order to obtain the *Fermi liquid parameters*.
Fermi Liquid Parameters

- Fermi liquid parameters:

\[ F_{l}^{s,a} = \frac{Am^*}{4\pi^2} \int \left[ f_{\uparrow\downarrow}(\theta_{kk'}) \pm f_{\uparrow\uparrow}(\theta_{kk'}) \right] \cos(l\theta) \, d\theta, \]

where \( A = \pi r_s^2 N \) is the area of the simulation cell.

- For a ferromagnetic HEG, the Fermi liquid parameters \( \{F_l\} \) are given by the expression above with \( f_{\uparrow\downarrow} = 0 \).

- We need to obtain a description of the interaction parameters according to a well-defined prescription for energy differences in a finite cell, then extrapolate the Fermi liquid parameters to the thermodynamic limit.

- Armed with the effective mass and the Fermi liquid parameters, nearly all thermodynamic and transport properties of the fully interacting electron gas can be calculated.
Finite-Size Errors

- The calculations were performed in finite cells subject to periodic boundary conditions.

- Major source of error and uncertainty in the QMC results: finite size effects.

- Momentum quantisation:
  - In our finite simulation cell subject to (twisted) periodic boundary conditions, the available momentum states fall on the (offset) grid of reciprocal lattice points.
  - This restricts the $k$ values we can consider.

- There are also finite size errors in the excitation energies due to the neglect of long-range interactions and correlations in a finite cell.
  - These errors have been shown to fall off slowly, as $N^{-1/4}$, near the Fermi surface.\(^\text{27}\)

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Pathological Behaviour at the Fermi Surface (I)

- Fermi liquid theory is only valid near the Fermi surface.

- Energy band is defined by Landau energy functional at all \( k \), but does not correspond to quasiparticle band except near Fermi surface.

- In the infinite-system limit, the exact energy band is smooth and well-behaved everywhere, including the Fermi surface.

- The Hartree–Fock band is pathological.
  - In the infinite-system limit it has a logarithmic divergence at the Fermi surface.
  - In finite systems it behaves very badly.
Pathological Behaviour at the Fermi Surface (II)

- DMC may take you 99% of the way from HF to reality, but this does not get rid of the pathological behaviour from HF theory.

- Hence we need to consider excitations away from the Fermi surface in order to obtain the gradient of the energy band at $k_F$.

- Finite-size effects in the Fermi liquid parameters are a killer.
Assessing the Accuracy of our DMC Calculations (I)

- Occupied bandwidth: \[ \Delta \mathcal{E} = \mathcal{E}(k_F) - \mathcal{E}(0) = E_-(0) - E_-(k_F). \]

- DMC BW is expected to be an upper bound: assuming DMC retrieves the same fraction of the correlation energy in the ground and excited states, the BW will lie between the Hartree-Fock value \( E_{\text{HF}}^-(0) - E_{\text{HF}}^-(k_F) \), which is too large, and the exact result \( E_{\text{exact}}^-(0) - E_{\text{exact}}^-(k_F) \).

- Likewise, Slater-Jastrow DMC BWs are expected to be greater than Slater-Jastrow-backflow DMC BWs.

- To obtain an accurate BW, it is essential to retrieve a very large fraction of the correlation energy in the DMC calculations, which explains why the inclusion of backflow is so important.

- The extent to which the BW is overestimated in HF theory grows with \( r_s \) so that, assuming DMC retrieves a constant fraction of the correlation energy, the DMC bands become less accurate at low density.
Assessing the Accuracy of our DMC Calculations (II)

- Extrapolating the VMC energy with different trial wave functions to zero variance suggests that our DMC calculations retrieve more than 99% of the correlation energy, and that the fraction retrieved is similar in both the ground and excited states.

- The free-electron BW is greater than or approximately equal to the exact BW. Hence the error in the HF BW is less than or approximately equal to $\Delta \mathcal{E}^{\text{HF}} - \Delta \mathcal{E}^{\text{free}} = k_F(1 - 2/\pi)$.

- So the error in the DMC BW is less than $0.01 k_F(1 - 2/\pi) \approx 0.007/r_s$ for a ferromagnetic HEG and less than about $0.01 k_F(1 - 2/\pi) \approx 0.005/r_s$ for a paramagnetic HEG.

  - Since the BW falls off as $r_s^{-2}$, the error is more significant at large $r_s$.
  - In the worst case (the paramagnetic HEG at $r_s = 10$) this argument suggests that DMC overestimates the BW by $\sim 9\%$. In the next-worse case (paramagnetic, $r_s = 5$), the BW is overestimated by $\sim 4\%$.
  - It is reasonable to assume that DMC underestimates $m^*$ by a similar amount.
To Reoptimise or Not To Reoptimise

- We optimise the trial wave function in the ground state and then continue to use the same Jastrow factor and backflow function in our excited-state calculations.

- The excitation of a single electron has no effect on the optimal Jastrow factor or backflow function in the thermodynamic limit.
  - Hence the fact that the Jastrow factor and backflow function can be re-optimised in an excited state in a finite cell\(^{28}\) is simply a finite-size effect.
  - More finite-size bias is introduced into the energy band by re-optimising the Jastrow factor and backflow function in each excited state considered.

- It is essential not to re-optimise the wave function when an electron is promoted, to maximise the cancellation of errors that occurs when the single-particle contribution is subtracted out from a difference in total energy.

- Promoting an electron results in smaller finite-size errors than adding two electrons, since the latter modifies the density of the finite system.

\(^{28}\) For example, re-optimising the wave function when an electron is subtracted from \(k = 0\) in a 74-electron HEG at \(r_s = 1\) lowers the DMC energy by 0.000241(4) a.u.
Paramagnetic Single-Particle Energy Band: $r_s = 1$

(a) $r_s = 1$

![Graph showing the paramagnetic single-particle energy band with various symbols and labels indicating different electron counts and optimized electron counts.](image)
Paramagnetic Single-Particle Energy Band: \( r_s = 5 \)

(b) \( r_s = 5 \)

- Free electron
- Hartree-Fock

\( \epsilon(k) \) (a.u.)

- \( N = 26 \)
- \( N = 50 \)
- \( N = 74 \)
- \( N = 114 \)
Paramagnetic Single-Particle Energy Band: $r_s = 10$

\[
\varepsilon(k) \text{ (a.u.)}
\]

- Free electron
- Hartree-Fock

- $N = 26$
- $N = 50$
- $N = 74$
- $N = 114$

(c) $r_s = 10$
Ferromagnetic Single-Particle Energy Band: $r_s = 1$

\begin{align*}
\varepsilon(k) \text{ (a.u.)} \\
(k / k_F) \\
\end{align*}

(a) $r_s = 1 \text{ a.u.}$

- Orange solid line: Free-electron band
- Purple dashed line: Hartree-Fock band
- Black circles: $N = 29$
- Red squares: $N = 57$
- Green diamonds: $N = 101$
Ferromagnetic Single-Particle Energy Band: $r_s = 5$

(b) $r_s = 5$ a.u.

Graph showing the energy band structure with markers for different $N$ values: $N = 29$, $N = 57$, $N = 101$. The graph compares the free-electron band and Hartree-Fock band for $r_s = 5$.
Ferromagnetic Single-Particle Energy Band: $r_s = 10$

(c) $r_s = 10$ a.u.

- Free-electron band
- Hartree-Fock band

- $N = 29$
- $N = 57$
- $N = 101$
Extrapolation of the Effective Mass to the Thermodynamic Limit

- Effective mass against system size:

![Graph showing effective mass against system size with different parameters for different $r_s$ values.]

- Scaling is not the $N^{-1/4}$ predicted by Holzmann et al. near the Fermi surface, because we have fitted to the entire band.
  
  - Assume an $N^{-1}$ scaling of the finite-size error.
Quasiparticle Effective Masses (I)

![Graph showing the relationship between $r_s$ (a.u.) and $m^*$ (a.u.) for Para; DMC and Ferro; DMC.](image)

- Para; DMC
- Ferro; DMC
Quasiparticle Effective Masses (II)

- **Paramagnetic HEG**: effective mass remains close to 1.

- **Ferromagnetic HEG**: $m^*$ *decreases* when the density is lowered.

- Our results therefore support the qualitative conclusions of Padmanabhan *et al.*

- Our results suggest that $m^*$ in paramagnetic 2D HEGs does not grow rapidly as the density is reduced.
Conclusions

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

- Wigner crystallisation occurs at $r_s = 31(1)$ a.u. in 2D. Crystallisation transition is from a paramagnetic fluid to a (frustrated) antiferromagnetic triangular crystal.

- Transition from an antiferromagnetic to a ferromagnetic crystal at $r_s = 38(5)$ a.u.

- QMC results for contact PCF change little when wave function is improved. Suggests they are accurate. Disagreement with recent ladder theory calculation; agreement with old ladder theory calculation.

- Our data show that the quasiparticle effective mass of the ferromagnetic HEG decreases at low density, unlike the paramagnetic HEG.