Warm Dense Matter

**Principle Supervisor:** Matthew Foulkes (Physics, Imperial College London)

**2nd supervisor:** Derek Lee (Physics, Imperial College London)

**Collaborators:** James Shepherd (Chemistry, Cambridge, MA, USA)
Michael Bonitz (Physics, University of Kiel, Germany)

**Abstract**

Density matrix quantum Monte Carlo (DMQMC) [1] is a new finite-temperature analogue of full configuration interaction QMC [2,3]. It can be used to sample the exact $N$-electron density matrix for systems of at least 50, and perhaps $>100$, electrons.

We are applying DMQMC to “warm dense matter” (WDM), which is in fact extremely hot — $kT \approx E_F$ — and no denser than ordinary matter (blame the astro/plasma physics communities for the name). WDM can be found in laser fusion and shock-wave experiments, radiation damage cascades, solids illuminated by powerful lasers, and planetary cores. Hot electrons created by the decay of plasmons in metallic nanospheres at room temperature catalyse chemical reactions that normally require much higher temperatures [4].

Our understanding of hot materials is very limited. DFT works in principle, but the high-temperature exchange-correlation functional was not known accurately until very recently, when we and our collaborators in Germany used DMQMC and other methods [5,6,7] to calculate the data required. We also helped to resolve a serious disagreement in previous work [8,9].

This project will apply DMQMC to real warm dense materials. What happens to chemical bonds when electrons are suddenly heated? It is thought that they weaken and the nuclear repulsion pushes the atoms apart. If this cannot easily happen, as in a radiation damage cascade, a “Coulomb explosion” takes place. DMQMC will allow phenomena such as this to be studied accurately and quantitatively for the first time.

What is the multi-scale nature of the project?
There are many models of warm dense matter, including simple equations of state, temperature-dependent (or temperature-independent) force fields, and DFT-based approaches, but nobody knows how well they work. Most of the available experimental data is rough and ready and no accurate computational approaches exist. Our DMQMC work will provide accurate data that we will use to fit models designed to work at longer length scales.

Our recent work on the high-temperature exchange-correlation free-energy functional is provided the electron-scale data required to allow finite-temperature DFT simulations at longer length scales. The results will enable us to construct an accurate high-temperature equivalent of the LDA, but will not address the question of whether Mermin’s finite-temperature generalisation of DFT works well or not. Part of the new student’s work will be to benchmark finite-temperature DFT simulations against DMQMC simulations, to judge the extent to which finite-temperature DFT within the LDA is likely to provide an accurate and reliable description of warm dense matter on longer length scales of hundreds or thousands of atoms. Another multi-scale aim is to use DMQMC to calculate equations of state in the warm dense regime and compare these with empirical equations of state. Finally, and perhaps most importantly, we want to investigate how the classical potentials used to describe inter-atomic forces must be modified when the electron temperature is high.

How do the expertises of the supervisors complement each other?
Lee and Foulkes co-supervised Fionn Malone’s successful PhD project on the warm dense electron gas. Lee brings a broad knowledge of many-body physics and mathematical and analytic skills to the project; Foulkes is an expert in QMC for solids and invented the DMQMC method in collaboration with James Spencer and two Imperial College MSci project students. The project is highly computational, so Eamonn Murray’s computational expertise and broad knowledge of electronic structure theory will be invaluable. Our two collaborators, James Shepherd and Micheal Bonitz, link us to other communities: James to quantum chemistry and experimental work in the field; Michael to plasma physics.

Literature Review
Warm dense matter from first principles

8. Tobias Dornheim, Simon Groth, Travis Sjostrom, Fionn D. Malone, W. M. C. Foulkes, and Michael Bonitz, Ab initio quantum Monte Carlo simulation of the warm dense electron gas in the

**MSc Project**

In the MSc project, the student will learn how to reproduce some of the DMQMC simulations of the warm dense electron gas carried out by Fionn Malone. Once the student is at ease with the computational tools, he or she will adapt our DMQMC code to allow the calculation of additional physical quantities such as momentum densities and static structure factors. One effect of introducing repulsive Coulomb interactions between electrons in a box is to reduce the effective volume available to each electron, suggesting that the total kinetic energy ought to increase. This is indeed the case at T=0, but there is good reason to believe [Burkhard Militzer and E.L. Pollock, Phys. Rev. Lett. 89, 280401 (2002)] that electron-electron interactions can sometimes lower the total kinetic energy at high temperature. By studying the momentum density, we will be able to investigate this strange result. The static structure factor is closely related to the dielectric function and is required to correct the finite-size errors that occur when infinite systems are approximated by small simulation cells subject to periodic boundary conditions.