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ABSTRACT: We have used an exact stochastic simulation of the Schroedinger equation for charged Bosons and Fermions to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

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The properties of the ground state of the electron gas, also referred to as the Fermion one component plasma and jellium, have rigorously only been established in the limit of high densities[1] where the system approaches a perfect gas and at low density[2] where the electrons crystallize. Furthermore, Hartree-Fock calculations[3], and variational calculations[4] suggest that at intermediate densities, the spin aligned state of the electrons will be more stable than the normal, unpolarized state. Precise calculations of this many-Fermion system are required to establish the regions of stability of the various phases because of the small energy differences among them. This note outlines a Monte Carlo method, that if run long enough on a computer, can give as precise a solution for the ground state of a given Fermion system as desired.

In practice, the precision of such a calculation is limited to about two orders of magnitude smaller than that of an approximate trial wave function that is introduced as an importance function in the Monte Carlo process. That the introduction of such an importance function is essential, was previously demonstrated for the many-Boson problem.[5] The extension of this Boson calculation to Fermions requires dealing with antisymmetric functions that lead to two related complications; namely the probability density of a random walk cannot be chosen everywhere positive, and unless prevented the random walk will always converge to the all positive, Boson ground state. It is demonstrated here, for the electron system, that before the effect of this inherent instability becomes serious, it is possible to extract the properties of the lowest antisymmetric state. A more general procedure which removes the effects of the instability has yet to be perfected.

The solution of the Fermion problem was carried out in two steps. In the first step the nodes, the places where the trial function vanishes, act as fixed absorbing barriers to the diffusion process. Inside a connected nodal region the wavefunction is everywhere positive and vanishes at the boundaries. With these boundary conditions, the Fermion problem is equivalent to a Boson problem. The energy calculated with this procedure, which we will refer to as the 'fixed-node' energy, is an upper bound to the exact Fermion ground state energy and generally very close to it. In principle one could next vary the nodal locations to obtain the best upper bound, by for example, varying the functions used as elements in the Slater determinant of the trial wave function. In practice the highly dimensional nodal surfaces are difficult to parameterize in a systematic fashion.

The second step, called 'nodal relaxation', begins with the population of walks from the 'fixed-node' approximation. In this second procedure, if a random walk strays across the node of the trial function it is not terminated, but the sign of its contribution to any average is reversed. At any stage of the random walk there is a population of positive walks (those that remained in the same nodal region or crossed an even number of nodes) and a population of negative walks (those that crossed an odd number of nodes). The importance function used in this process is the absolute value of the trial function. It can be easily shown that the difference population converges to the antisymmetric eigenfunction. However both the positive and negative populations grow geometrically with a rate equal to the difference between the Fermi and Bose energies. If the relaxation time from the fixed-node distribution times this energy difference is less than unity, the Fermion energy can be reliably extracted. We have found that for the electron gas this condition is satisfied if the nodes of the Hartree-Fock wavefunction are used.

Our simulation method is a simpler, though approximate, version of the Greens function Monte Carlo method of Kalos et. al.[5] A trial wavefunction $\Psi_T(R)$ of the Bijl-Jastrow-Slater type[4] and an ensemble of about 100 systems are selected from a variational Monte Carlo calculation, where R represents the 3N spatial coordinates of the systems of N electrons. Let the probability density of finding a random walk in RdR^{3N} at time t be given by $f(R,t)dR^{3N}$. Then the value of f at t=0 is given by $|\Psi_T(R)|^2$ properly normalized. The diffusion equation for f(R,t) is:

$$\frac{\partial f}{\partial t} = \frac{\hbar^2}{2m}\left[\sum_{i=1}^{N}\nabla_i^2 f - \vec{\nabla}_i(f\vec{\nabla}_i \ln|\Psi_T|^2)\right] - \left[\frac{H\Psi_T}{\Psi_T} - E_{ref}\right] f \qquad (1)$$

where H is the Hamiltonian

$$H = \frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i<j} e^2/r_{ij} \qquad (2)$$

It is easily verified that for large times, $f(r,t) = \Psi_T\phi_o \exp(-t(E_{ref}-E_o))$ where E_o and ϕ_o are the exact eigenvalue and eigenfunction. The above equation for $f(R,t)$ has a simple interpretation as a stochastic process. Each member of the ensemble of systems undergoes i) random diffusion caused by the zero point motion, ii) biasing or drift by the trial quantum force, $\nabla \ln|\Psi_T|^2$, and iii) branching with probability given by the difference between the local trial energy, $E_T = H \Psi_T/\Psi_T$ and the arbitrarily chosen refernce energy, E_{ref}. By "branching", it is meant that a particular system is either eliminated from the ensemble (if the local energy is greater than the reference energy) or duplicated in the ensemble (otherwise). A steady state population of the ensemble requires that the reference energy equal the lowest eigenvalue. This is one way of determining the eigenvalue.

The trial wavefunction employed in the present calculations are identical with those used in an earlier Monte Carlo variational calculation.[4] This trial function is a product of two-body correlation factors times a Slater determinant of single particle orbitals. The two body correlation factors are chosen such that they remove exactly the singularities in the local energy when two electrons approach each other, thus reducing tremendously the variance of the estimate of the ground state energy. For the fluid phase the single particle orbitals are plane waves, with the wave vector lying within the Fermi sea. For the polarized state, where there is only one spin for each spatial state, as opposed to two for the normal unpolarized state, the Fermi wavevector has been increased to allow for twice as many spatial orbitals. In the crystal phase, the orbitals are Gaussians centered around body centered cubic lattice sites with a width chosen variationally.

Fig. 1 shows that the relaxation from the unpolarized nodes to the ground state is rapid with a small lowering of the energy. A less accurate trial wave function with different nodes obtained from a linear combination of polarized and unpolarized Slater determinants is nevertheless shown to lead to similar energies with a somewhat larger relaxation time. This shows the insensitivity of results to the original location of the nodes. Since at all densities the relaxation from the Hartree-Fock nodes was rapid, the ground state energy of the electron gas by the method employed could be obtained with very little uncertainty.

The largest uncertainty in the results is in fact due to the number dependence. Due to the high accuracy of the results derived from employing a good trial wave function and the consequent small statistical error, the number dependence, which was empirically established for systems ranging from 38 to 246 particles is an order of magnitude larger than the statistical error. Extrapolation to infinite particle results was carried out at each density on the basis of $E(N) = E_o + E_1/N + E_2 \Delta_N$, where the coefficients E_o, E_1 and E_2 were empirically determined from the simulations. The E_1 term arises from the potential energy and is due to the correlation between a particle and its images in the periodically extended space that is used in the Ewald summation procedure[4] to eliminate the major surface effects. The E_2 term comes from the discrete nature of the Fermi sea for finite systems, and Δ_N is the size dependence of an ideal Fermi system at the same density. That term is absent for Bosons. In addition the energies have been extrapolated to zero time step by empirically establishing the validity of linear extrapolation. This correction is quite small, on the order of the statistical error for the time steps used. However this correction can be completely avoided by using an integral formulation of eq.(1).[5]

The results for the energy of the plasma in four different phases is given in Table I. These energies multiplied by r_s^2 are plotted in Fig. 2 relative to the lowest Boson state. Multiplying by r_s^2 corresponds to holding the density fixed and increasing the charge. Plotted in this manner the minute differences in energy at low density can be more clearly seen. The Boson system undergoes Wigner[6] crystallization at $r_s = 160 \pm 10$. The Fermion system has two phase transitions, crystallization at $r_s = 100 \pm 20$ and depolarization at $r_s = 75 \pm 5$. The difference in energy between a Boson crystal and a Fermion crystal is less than 1.0×10^{-6}R at $r_s = 10^{[illegible]}$. The energies of the three Fermion states are sufficiently close in the low density regime that still more accurate calculations on larger systems would be desirable to confirm these results.

In Table II the correlation energy for the unpolarized Fermi fluid, that is the ground state energy relative to the Hartree-Fock energy, is compared to that of several other theories in the metallic density range. The correlation energies are very similar for all methods. The coupled-cluster[7,8] formalism give the most accurate results. It is seen that a variational integral equation theory, the Fermi hypernetted chain,[9] gives energies below the present results, indicating that the approximations employed have compromised the variational principle.

Finally, Table III displays the differences between the pair product variational results, the fixed-node results and the final energies. Although the Bijl-Jastrow-Slater results are quite accurate, the error is different for the different phases, changing their relative stability. This demonstrates how essential it is to perform exact simulations to reliably calculate phase transitions densitites.

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Table I

r_s	E_{PMF}	E_{FMF}	E_{BF}	E_{BCC}
1.0	1.174(1)	---------	--------	---------
2.0	0.0041(4)	0.2517(6)	-0.4531(1)	---------
5.0	-0.1512(1)	-0.1214(2)	-0.21663(6)	---------
10.0	-0.10675(5)	-0.1013(1)	-0.12150(3)	---------
20.0	-0.06329(3)	-0.06251(3)	-0.06666(2)	---------
50.0	-0.02884(1)	-0.02878(2)	-0.02927(1)	-0.02876(1)
100.0	-0.015321(5)	-0.015340(5)	-0.015427(4)	-0.015339(3)
130.0	------------	-----------	-0.012072(4)	-0.012037(2)
200.0	------------	-----------	-0.008007(3)	-0.008035(1)

The ground state energy of the charged Fermi and Bose systems. The density parameter, r_s, is the Wigner sphere radius in units of Bohr radii. The energies are Rydbergs and the digits in parenthesis represent the error bar in the last decimal place. The four phases are: paramagnetic or unpolarzed Fermi fluid (PMF); the ferromagnetic or polarized Fermi fluid (FMF); the Bose fluid (BF); and the Bose crystal with a BCC lattice.

Table II

r_s	ε_{MC}	ε_{CC1}	ε_{CC2}	ε_{DE}	ε_{FHNC}
1.0	0.121(1)	0.118	0.123	0.112	0.138
2.0	0.0902(4)	0.0884	0.0917	0.089	0.098
5.0	0.0563(1)	0.0567	0.0568	0.058	0.058
10 0	0.03722(5)	0.03888	------	-----	0.037

Caption Comparison of the correlation energy with other theories. ε_{MC} is the correlation energy from this calculation with the parenthesis representing the error bar in the last decimal place. ε_{CC1}[7] and ε_{CC2}[8] are the first and second order of the coupled cluster or (e_s) theory. ε_{DE}[10] is the correlation energy in the dielectric formulation and ε_{FHNC} is the Fermi-hypernetted chain correlation energy.

Table III

r_s	δ_{PMF}	γ_{PMF}	δ_{FMF}	γ_{FMF}	δ_{BF}	δ_{BCC}
2	40	9	11.0	---	12.0	-----
5	17	2	7.2	---	6.8	-----
10	11	1	6.5	1.8	5.1	-----
20	6.7	0.7	3.0	1.0	3.3	-----
50	2.9	0.31	1.6	0.25	1.7	2.0
100	1.7	----	1.2	----	1.2	0.41
130	----	----	---	----	1.1	0.30

The error in the variational approximation in 10^{-4} Rydbergs for four different phases. $\delta = E_V - E_O$ (the difference between the Jastrow trial function and the exact ground state energy).
$\gamma = E_{FN} - E_O$ (the difference between the 'fixed-node' energy with plane wave nodes and the exact ground state energy).

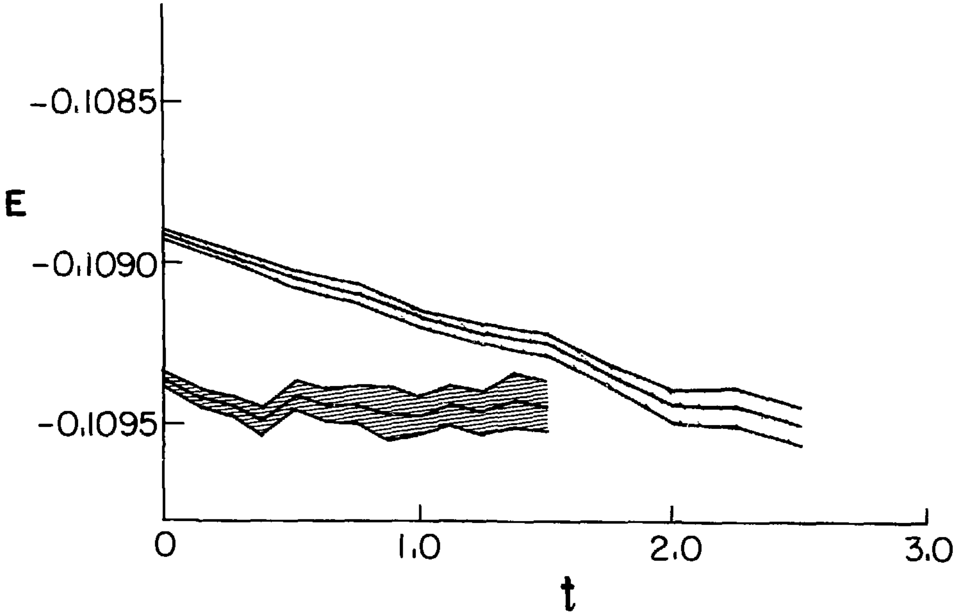

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FIG. 1. The energy in Rydbergs per particle of a 38 electron system at the density $r_s = 10$ versus diffusion time (in inverse Rydbergs) from removal of the fixed-nodes. The lower curve is the relaxation of an ensemble of 1.6×10^4 systems from the nodes of the unpolarized determinant of plane waves. The upper curve is the relaxation of 1.0×10^5 systems from the nodes of a linear combination of polarized and unpolarized determinants.

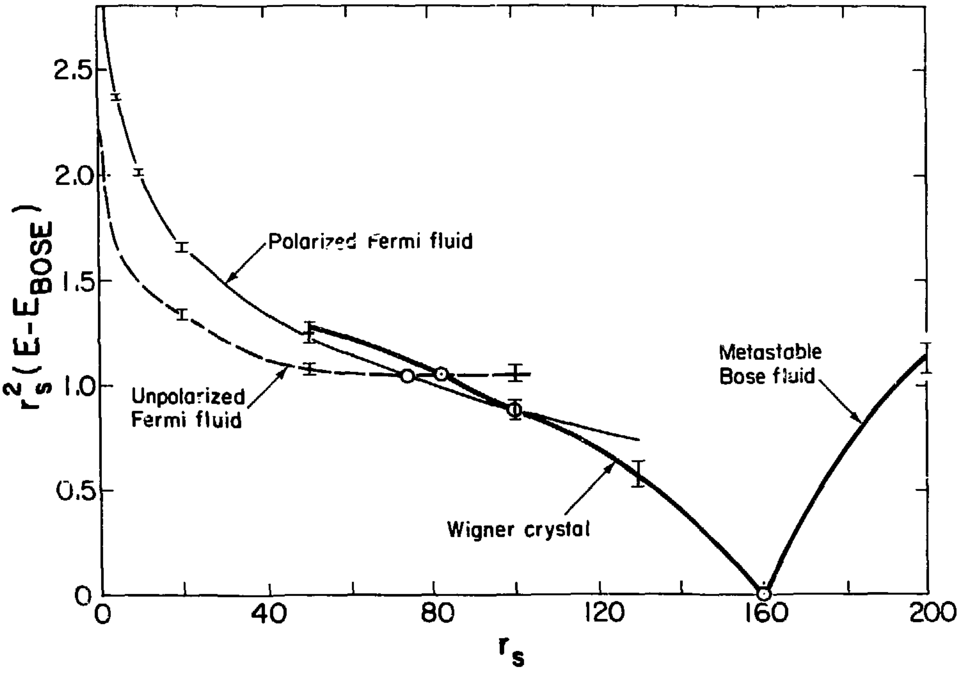

FIG. 2. The energy of the four phases studied relative to that of the lowest Boson state times r_s^2 in Rydbergs versus r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect of $r_s = 75$. The polarized (ferromagnetic) Fermi fluid will be stable between $r_s = 75$ and $r_s = 100$.