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LARGE SCALE CALCULATIONS OF THE STRUCTURE AND DYNAMICS OF DENSE MATTER

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ABSTRACT

The physics of matter at high density has been found to be strongly influenced by transient quasi-molecular phenomena, the distribution of electron charge density among several nearby atoms. Calculations performed using the self-consistent field molecular dynamics approximation, a synthesis of techniques derived from quantum chemistry and molecular dynamics, have shown that such effects can result in more than a 30% increase in the diffusion coefficient of helium at 1 g/cc. The effect of finite electron temperature is to weaken many-electron collective phenomena, but significant effects are expected to occur even in fully ionized dense plasmas.

INTRODUCTION

An understanding of the structure and dynamics of dense plasmas is important for several applications. The recent observations of the gas giant planets by the space probe Voyager II revealed anomalies in the atmospheric temperature distributions which could be affected by the energy transport rates in dense warm hydrogen-helium mixtures. At higher temperatures, models of stellar structure depend both on the equation of state of the plasma as well as the detailed radiative and collisional properties of matter under extreme conditions of temperature and density. On Earth, the inertial confinement fusion program routinely produces plasmas of many grams per cubic centimeter at temperatures of up to several kilovolts. In materials science, shock compression is being explored as a route to synthesize new materials with potential commercial applications.

Traditional methods for computing the properties of dense matter can be divided into two major categories: those based on some form of average atom approximation and statistical theories of many particles interacting via predefined potentials. Average atom approximations attempt to describe the physics of the entire plasma in terms of a single effective structure.¹ The electron distribution for the atom is constrained to occupy a fixed volume, often taken as the ion sphere volume. Boundary conditions on the wavefunction and its derivative mimic the effect of the external plasma. Finite electron temperature can be included in the calculation by distributing the electronic population over excited states according to a Fermi distribution.

In statistical theories of plasma, effective interaction potentials are employed to simulate the interaction of a large number of atoms.² Such theories include

molecular dynamics, which tracks the classical motion of a large number of atoms, and Monte Carlo approximations, which are based on generating the most probable configurations for an ensemble.

Both the average atom and the statistical theories are expected to break down at high density where the internuclear distance is comparable to an atomic diameter. When several atomic wavefunctions overlap quasi-molecular behavior can occur, leading to significant changes in interatomic interactions as well as collisional and radiative rates. It is not necessary for such structures to result in permanent or even metastable bound configurations. Random collisions resulting from thermal motion will stochastically lead to close approaches in which strong atomic orbital overlap occurs. In order to properly treat such phenomena it is essential to have a methodology which explicitly treats the self-consistent redistribution of electronic charge density during the time evolution of a many-atom ensemble.

SELF-CONSISTENT FIELD MOLECULAR DYNAMICS

Self-consistent field molecular dynamics (SCFMD) is a new computational tool for the study of dynamic processes in many-atom ensembles based on a synthesis of methods used in quantum chemistry and classical molecular dynamics. SCFMD models the time evolution of complex many-atom clusters through the repetition of three steps. First, the electronic structure of the entire ensemble is computed using a Hartree-Fock Gaussian orbital molecular structure code. Second, this charge distribution is used to calculate the electrostatic force acting on each nucleus. Third, the positions and velocities of each atom are adjusted using classical equations and the computed forces. By repeating these steps one can generate the time histories of all of the atoms in the sample.⁴

The Hartree-Fock Gaussian orbital approximation employed here is based on the HONDO code of Dupuis and King.⁵ The total wavefunction of the sample is expanded in molecular orbitals, which are in turn described by expansions over simple Gaussian functions centered on the nuclei.

Interatomic forces are computed by means of the Hellmann-Feynman approximation. This method ignores small corrections to the force due to the explicit dependence of the basis set on the nuclear coordinates. These corrections were found to be small for binary interactions involving the simple atomic structures discussed here.

Atomic motion is computed classically using the quantum forces as input. The timestep of the calculation is automatically controlled to avoid large changes in interatomic separation during a single move. Positions, velocities, accelerations, and other properties of the calculation are written to a storage file to allow later post-processing of time-averaged quantities.

The effect of finite electron temperature is included in the calculations by allocating the electronic population over the virtual orbital spectrum according to a Fermi distribution. Note that this distribution takes place within the self-

consistent field algorithm itself.

SCFMD STUDIES OF DENSE HELIUM

Helium was chosen for the initial application of SCFMD to dense matter for several reasons. It has a simple $1s^2$ ground state which can be approximately described by very small basis sets consisting of only two or three Gaussian functions. Helium has a high first excitation energy, so that the electrons will be in their ground state even at relatively high ion temperatures. High ion temperatures are desirable since it is in close atomic collisions that the simple interatomic force algorithm employed here is expected to be most accurate. A high excitation energy also implies a small polarizability so that simple basis sets are adequate to describe interactions. Finally, helium has been extensively studied using a variety of approximations in statistical mechanics and has also been observed in two-stage gas gun experiments at densities up to 0.68 g/cm^3 .⁶

Model calculation:

Plot of ratio $\frac{F_B \text{ (with CD)}}{F_B \text{ (without CD)}}$

Figure 1. Ratio of the force on a test atom B due to another atom A with the presence of neighbor atoms C and D to the force computed from atom A alone.

Before turning to the results of dynamic calculations, it is instructive to examine the effect of neighboring atoms on the interaction of two sample atoms in a static configuration. Figure 1 shows the ratio of the force on atom B due to atom A when neighbor atoms C and D are present to that where only A and B are considered. The symmetry of the sample configuration was chosen such that if interatomic forces added in a pairwise fashion, the neighbors would have no effect on the force on atom B and the ratio would be one. Departures from unity signify additional screening of the force of atom A on atom B due to the self-consistent redistribution of electronic charge density among atoms B, C, and D. The nuclear potentials of atoms B, C, and D add such that the deepest part of the potential well is at position B. Thus the largest concentration of electronic charge density will be near atom B in just the position to screen that atom from the effect of atom A.

In order to assess the effects of such screening in dynamic ensembles we

applied SCFMD to the study of dense helium at densities between 0.1-3.0 μ/cm^3 and at temperatures of 1 eV and 5 eV. We studied clusters containing 20-30 atoms contained in a three dimensional box. Approximate periodic boundary conditions were employed to mimic an infinite medium. The electronic wavefunction of the ensemble was described by two or three Gaussian basis sets located on each nucleus. Using the output from these calculations, we computed pair correlation functions, velocity autocorrelation functions, and other dynamic properties of dense helium.

Figure 2. Periodic boundary conditions and the effective range approximation.

The computational labor associated with obtaining the Hartree-Fock solution for a large ensemble of atoms increases roughly as the third power of the size of the total basis set employed. Most of this time is spent in the calculation of the two-electron matrix elements. In our application of periodic boundary conditions we employed an effective range approximation wherein each atom interacts only with the nearest image of each of the other atoms, as illustrated in Figure 2. When an atom passes through a boundary of the box it reappears at the opposite edge with the same velocity. Although such an algorithm is straightforward for pairwise additive potentials, complications arise in finite basis expansions since the spatial extent of the orbitals is fixed and the integral package employed here is not equipped to truncate the matrix element integration at the box boundary. As an approximation to true numerical periodic boundary conditions, we employed an algorithm wherein for any matrix element the orbitals are chosen so that the closest images interact at any given time. This insures that the strongest interactions are correctly modeled. Residual errors associated with the neglect of small distant interactions are expected to be small when averaged over many hundreds of cycles.

Figure 3. Pair correlation function for helium at 1 g/cm³ and 5 eV.

Figure 3 shows the pair correlation function $g(r)$

$$g(r) = n(r) / (4\pi r^2 \Delta r n_0) \quad (1)$$

computed for a 23 atom sample of helium at 1 g/cm³ and 5 eV. Here $n(r)$ is the number of atoms between r and $r+\Delta r$ from a test atom in a plasma with average number density n_0 . The pair correlation function thus gives the probability for finding another atom at a given distance from a sample atom relative to a random distribution. Peaks in $g(r)$ correspond to preferred spatial orientations such as molecular bonds or crystal lattices. The lack of structure in Figure 3 is typical of high temperature material. The position of the shoulder at small radii is indicative of the distance of closest approach and the width of the shoulder is a reflection of the convolution of the temperature distribution of the sample and the steepness of the repulsive interaction potential between atoms at short ranges. At large radii $g(r)$ approaches unity, equivalent to a random distribution of atoms in a disordered medium.

The velocity autocorrelation function

$$Z(t) = \langle v(t)v(0) \rangle / \langle v(0)v(0) \rangle \quad (2)$$

is a fundamental measure of the persistence of dynamic correlations within the

Figure 4. Velocity autocorrelation function for helium at 5 eV as a function of density. Solid curve: SCFMD; dot-dashed curve: molecular dynamics using Hartree-Fock pair potential derived from same basis set as was used in the SCFMD calculation; dotted curve: pair potential due to Aziz et al., based on an accurate Hartree-Fock calculation at short range⁷; dashed curve: pair potential due to Aziz et al. based on quantum Monte Carlo calculations at short range⁸; dot-dot-dashed curve: pair potential of Young et al. based on high density linear muffin tin orbital calculations⁹.

sample. The denominator in $Z(t)$ provides unit normalization at $t=0$. At high temperatures one expects the velocity autocorrelation function to decay with a rate related to the mean collision time. Figure 4 shows $Z(t)$ for helium at 5 eV and densities of 0.1, 0.6, and 1 g/cm³. In addition to the SCFMD curve, we show the results of classical molecular dynamics calculations using the same number of atoms and the same kinematics algorithms but with pair interaction potentials corresponding to a number of different theoretical and semi-empirical approximations for the binary interaction of helium atoms. The dotted curves in Figure 4 were derived from the pair potential of Aziz et al.⁷ based on accurate Hartree-Fock calculations for small separations. The long dashed curve corresponds to a quantum Monte Carlo short range potential in a revised potential due to Aziz et al.⁸ The dot-dot-dashed curve was calculated using a linear muffin tin orbital (LMTO) approximation for the short range potential due to Young et al.⁹ This approximation is expected to be valid at very high density and low temperature where many-atom screening is significant. It will be less accurate at low density and high temperature where atomic kinetic energy can result in the close approach of two atoms without the presence of the nearest neighbors assumed in the LMTO calculations. Finally, the dot-dashed curves in Figure 4 correspond to classical molecular dynamics calculations using a pair potential derived from the same basis set used in the full SCFMD calculations. Comparison of the solid (SCFMD) and dot-dashed curves is a direct indication of the departure of the interaction from a superposition of pair potentials.

At 0.1 g/cm³ the SCFMD results are in good agreement with the pair potential calculations except for the LMTO case. This is expected, since at low density binary collisions dominate and there is little dynamic screening. The failure of the LMTO calculation at low density and high temperature was expected, based on the arguments presented above. At 0.6 g/cm³ the SCFMD results begin to diverge from the pair potential curves, indicating a softer effective interaction. This effect is more pronounced at 1 g/cm³, where differences in the pair potentials are also apparent.

The physical mechanism for the softening of the effective atomic interaction evident from the velocity autocorrelation function is as follows. At high temperature, significant momentum transfer occurs only during close collisions. During such a collision, the addition of the potentials of the colliding nuclei results in a potential well much deeper and wider than that associated with a single atom. This well attracts not only the charge density associated with the collision partners, but also part of the electronic charge density of surrounding atoms. The concentration of negative charge in the collision region results in additional screening of the nuclear repulsion, allowing a closer approach and an associated slower decay in $Z(t)$.

Figure 5. Coefficient of self-diffusion as a function of density. The departure of the SCFMD results from the Hartree-Fock pair potential curve is an indication of dynamic screening at high densities.

The coefficient of self-diffusion D is proportional to the time integral of the velocity autocorrelation function. Figure 5 shows D as a function of density for helium at 5 eV. As the density increases to a value such that there is significant overlap among atomic orbitals D experiences a rapid rise compared to results from Hartree-Fock pair potential calculations.

A limited number of calculations have been performed using a finite electron temperature version of SCFMD. These calculations employed three-Gaussian basis sets for ten atoms. Although such basis sets cannot possibly describe diffuse excited state orbitals for isolated atoms, at high density the proximity of neighbor atoms provides additional basis flexibility which will allow for an approximate description of excitations. Continuum functions will appear as orbitals distributed over many different centers. The diagonalization of the electronic Hamiltonian will attempt to span the eigenspace within the confines of the primitive basis set given.

To describe the ionization balance of the plasma we plot in Figure 6 the number of electrons occupying negative energy states vs. temperature at densities of 0.6 and 1 g/cm³, demonstrating two competing phenomena in dense plasmas. First, one notes that there is slightly more ionization (fewer bound electrons) for the higher density case, consistent with the theory of pressure ionization. Second, as the temperature is increased at constant density there is less ionization than one would expect based on an isolated atom model of the plasma. This decrease in ionization has nothing at all to do with recombination processes (radiative,

dielectronic, three-body, etc.) which are not included in the SCFMD calculation, but is a reflection of a change in the plasma ground state. During collisions the superposition of nuclear potentials which results in dynamic screening also results in very tightly bound orbitals. This is a familiar result from elementary quantum chemistry and corresponds to the approach to the united atom limit. At high temperature the ionic collision rate is high, so that at any given time there are an appreciable number of hybrid orbitals with energies more negative than those of isolated atoms.

Figure 6. Average number of bound electrons on a helium atom vs. temperature and density, illustrating the competition between pressure ionization and the increase in ionization energy due to the formation of quasi-molecular orbitals.

DISCUSSION

The above calculations demonstrate that at high density many-electron interactions are important in determining both the structure and dynamics of dense matter. The formation of quasi-molecular structures during close collisions not only results in increased screening of the interatomic potential, but an increase in the ionization energies as well.

There are several pieces of experimental information which support these findings. First, the interpretation of the results of a two stage gas gun experiment performed on helium which achieved a density of 0.68 g/cm^3 at an estimated temperature of 2 eV required much softer effective pair interaction potentials than are deduced from binary scattering experiments or accurate theoretical calculations.^{6,9} Since the statistical calculations included the effect of many-atom

interactions, such a softening must imply a change in the potential itself rather than simply a many-body effect involving the sum of pair interactions.

A second very interesting piece of experimental data relating to energy level lowering in dense plasma is the recent observation of high energy wings on spectral lines occurring at very high density and temperature during laser fusion implosions.¹⁰ Although many phenomena can be invoked to explain low energy features in the spectrum (screening, satellite lines, etc.) an increase in transition energy requires the invocation of a more attractive potential, such as would be obtained during atomic collisions in the plasma.

Although we have concentrated on ionic transport phenomena, we expect the formation of transient quasi-molecular structures in dense matter to have a profound effect on electron transport processes as well. We are examining methods for extracting electron transport quantities from our SCFMD calculations.

Finally, we note that residual effects of orbital hybridization are expected to occur even at temperatures high enough that the plasma is completely ionized. As an illustration, consider the problem of charged particle stopping in dense matter. Traditional theory treats this process by calculating the polarization of a uniform electron gas by the particle, and then calculating the reactive force and energy loss due to this polarization. In a real plasma, however, the electron distribution is not uniform but is polarized by the plasma ions. This additional polarization mechanism reduces the ability of the test particle to polarize the plasma and hence lose energy. The result is that many-body plasma effects should decrease the net energy loss rate and hence increase the effective range of ions in dense plasmas.

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REFERENCES

1. B.F. Rozsnyai, Phys. Rev. A **5**, 1137 (1972).
2. M.P. Allen and D.J. Tildesley, **Computer Simulation of Liquids**, (Oxford University Press, Oxford, 1988).
3. S.M. Younger, A.H. Harrison, K. Fujirna, and D. Griswold, Phys. Rev. Lett. **61**, 962 (1988).
4. S.M. Younger, G. Sugiyama, and A.H. Harrison, Phys. Rev. A **40**, 5256 (1989).
5. M. Dupuis, J. Rys, and H.F. King, J. Chem. Phys. **65**, 111 (1976).
6. W.J. Nellis, N.C. Holmes, A.C. Mitchell, R.J. Trainor, G.K. Gervino, M. Ross, and D.A. Young, Phys. Rev. Lett. **53**, 1248 (1984).

7. R.A. Aziz, V.P.S. Nain, J.S. Carley, W.L. Taylor, and G.T. McConville, J. Chem. Phys. **70**, 4330 (1979).
8. R.A. Aziz, F.R.W. Mc Court, and C.C.K. Wong, Mol. Phys. **61**, 1487 (1987).
9. D.A. Young, A.K. McMahan, and M. Ross, Phys. Rev. B **24**, 5119 (1981).
10. C.F. Hooper, D.P. Kilcrease, R.C. Mancini, L.A. Woltz, D.K. Bradley, P.A. Jaanimagi, and M.C. Richardson, Phys. Rev. Lett. **63**, 267 (1989).