Computer Modeling of Quantum Liquids and Crystals

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There are a number of many-body systems which exhibit quantum effects on a macroscopic scale. These include liquid and crystal states of both He-3 and He-4, the electron gas, and neutron matter which probably constitutes the interior of pulsars. In addition, "nuclear matter" - a hypothetical extensive system of nucleons has been studied for the insight one may gain into the nature of finite nuclei. The theoretical studies of these systems have by now a long history, but are by no means concluded. In the last few years, significant advances have been made. This has come in part from the maturity of and gradual unification of many-body theory, in part from the development and application of powerful new expansion procedures, especially varieties of hypernetted-chain equations (1) and finally to the growing power of computer simulation methods for quantum systems. This article is intended as a review of some recent development in computational methods for extensive quantum systems, and of the relation between results so obtained to the evolution of other theoretical work.

Computational modelling of quantum many-body systems is not especially novel. The early history of Monte Carlo methods included many proposals for the solution of Schrodinger's equation with intended application to the many-body problem. Unfortunately, the computational power available was not adequate to do more than simple exercises. The first work in which a significant contribution to theory was made was that of W. L. McMillan (2) who noted that the general sampling algorithm of Metropolis et al. (3) developed to treat equilibrium chemical systems could be used equally well to obtain variational estimates of the energy of a many-body system when the trial function has a product form. Since then, a large number of similar
calculations have been carried out treating extensive systems of atoms from hydrogen to neon. For a thorough review of these calculations see reference (4). It is likely that calculations of this kind will be even more used in the future since they are well suited for modern minicomputers.

We would like to emphasize here some additional methodological developments and their results. The first is the variational treatment of fully antisymmetrized trial functions (5). The second is the Green's function Monte Carlo algorithm (4, 5) which has, in effect, made possible the numerical integration of the Schrodinger equation.

**Fermion Monte Carlo**

Consider a Hamiltonian

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i<j} V(r_{ij}).$$  \hspace{1cm} (1)

Let $r^A$ stand for the coordinates of all particles and $\Psi_T(R^A)$ be a trial function that depends upon a set of parameters $A$. Then the variational principle states that

$$E_T \equiv \int \Psi_T(R)H\Psi_T(R) dR/\int |\Psi_T(R)|^2 dR \geq E_0,$$  \hspace{1cm} (2)

where $E_0$ being the energy of the ground state of the system. McMillan noted that if Eq. (2) were rewritten as

$$E_T = \int |\Psi_T(R)|^2 \Psi_T(R)^{-1}H\Psi_T(R) dR/\int |\Psi_T(R)|^2 dR$$  \hspace{1cm} (3)

and if a population of points $\{R_m\}$ were drawn at random from a probability density function

$$p_T(R) = |\Psi_T(R)|^2/\int |\Psi_T(R)|^2 dR$$  \hspace{1cm} (4)

Then the average over the population of the quantity

$$E_M = \frac{1}{M} \sum_{m=1}^M [H\Psi_T(R_m)]/\Psi_T(R_m)$$  \hspace{1cm} (5)

is $E_T$. Furthermore if we take $\Psi_T(R)$ to have the product form:

$$\Psi_T(R^A) = \prod_{i<j} f(r_{ij}; A) \equiv \exp(-\frac{1}{2} \sum_{i<j} u(r_{ij}; A))$$  \hspace{1cm} (6)

then sampling $p_T$ is exactly analogous to sampling the Boltzmann distribution since $u(r_{ij}; A)$ is a repulsive function which serves to keep the particles apart similar to the role of the potential, $v(r_{ij})$, for classical systems. The sampling may be accomplished by the Monte Carlo method of Metropolis et al. (3). This method is a useful simulation method for Bose liquids like He-4. Crystals can also be studied with a trial function of the form

$$\Psi_T(R) = \exp(-\frac{1}{2} \sum_{i<j} u(r_{ij})) \prod_k \phi(r_k - s_k)$$  \hspace{1cm} (7)

where $\phi(r)$ is a single particle orbital which localizes particle $k$ close to lattice site $s_k$. Usually $\phi$ is set as

$$\phi(r) = \exp(-\frac{1}{2} Cr^2)$$  \hspace{1cm} (8)

As with other variational calculations, $E_T$ is minimized with respect to parameters $A$ and $C$.

The calculation of properties of fermion systems was accomplished by simulating the corresponding Bose system and estimating the effect of antisymmetry by an expansion procedure due to Wu and Feenberg (7) and extended by Schiff and Verlet (8). In the latter, it is assumed that a fermion wave function is

$$\Psi_F(R) = \prod_{i<j} \exp(-\frac{1}{2} \sum_{i<j} u(r_{ij}) \det \phi^A(r_k, \sigma_k)$$  \hspace{1cm} (9)

where $\phi^A$ are plane wave orbitals times spin eigenfunctions. Then one expands the energy expectation in successive permutations deriving from the determinant. The first order of correction comes from pair permutations. Schiff and Verlet minimized the corrected fermion energy of liquid states of He-3 with respect to parameters in $u$, finding apparently good convergence of the Wu-Feenberg expansion. These calculations used a Lennard-Jones potential:

$$v(r) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]; \varepsilon = 10.22^{-6} K, \sigma = 2.556 A$$  \hspace{1cm} (10)

Ceperley, Chester, and Kalos (5) showed that with a trial function of the form given by Eq. (9), the Metropolis algorithm could be carried out directly to sample $|\Psi_F|^2$ in a way that was computationally economical in spite of the necessity of evaluating several determinants at each step of the random walk. They found that the convergence of the permutation expansion appears satisfactory at only one density - that for which the pressure is zero. At other densities,
or for the kinetic or potential energies separately, the convergence is poor. For example at $\rho o^3 = 0.414$, the fermion Monte Carlo gives an energy of 2.840K per atom while the first order permutation expansion gives 1.770K. In fact the first order gives only half the full antisymmetrization correction. It should be stressed that these calculations still do not give correctly the observed energy of liquid He-3 (-1.30K instead of -2.50K; of course there is considerable cancellation; the potential energy is about -110K per atom). This can be ascribed to an incorrect potential but there is even more serious doubt about the accuracy of the product trial function. We will discuss in the next section some consequences of the neglect of three body correlations in the trial function.

Reference (5) also treated fermion systems which model neutron and nuclear matter interacting by simplified pair potentials having the form of a linear combination of Yukawa functions:

$$v(r) = \frac{1}{r} \sum_i e_i \exp(-\xi_i r) \quad (11)$$

The Wu-Feenber expansion always underestimated the energy calculated by the fermion Monte Carlo method. In treating crystal phases of fermion systems it is known that the effect of antisymmetry (the exchange energy) is very small. Eqs. (7) and (8) may then be used for the trial functions. The equation of state of fermions interacting with a single repulsive Yukawa was determined for both liquid and crystal phases and a critical strength determined for the existence of a phase transition.

It is also worth mentioning that recently developed integral equations (9, 10) that extend the HNC method to include antisymmetrization (the FHNC equations) give a good account of the neutron fluid energies at low densities. At high densities, different expressions for the kinetic energy that would be equal in a correct variational calculation give rather different answers indicating that the expansions are not well behaved. Interestingly, one of the expressions for the kinetic energy, that due to Pandharipande and Bethe (1), gives good agreement with the fermion Monte Carlo results in all cases. This fact is not yet explained.

Ceperley (11) has applied the methods discussed here to the treatment of an electron gas in both two and three dimensions with a uniform neutralizing background. He considered three possible states: fluid with half the spins up; fluid with all spins aligned; and crystal phases. He found that at low density the crystal phase is favored. At intermediate densities the totally polarized fluid is most stable and at high densities the equilibrium state is that of the unpolarized fluid. In three dimensions the transition densities occur at $(5.4 \pm 0.4) \times 10^{13}$ cm$^{-3}$ and at $(9.2 \pm 1.8) \times 10^{13}$ cm$^{-3}$. He finds good agreement for the unpolarized fluid with other theoretical work (12, 13) at low densities but not at high density where the Monte Carlo is at its most accurate. The equation of state for the crystal is in agreement with an anharmonic expansion method (14).

We believe that fermion Monte Carlo will find significant future applications, possibly in Quantum Chemistry.

Green's Function Monte Carlo

This is a class of algorithms which makes feasible on contemporary computers an exact Monte Carlo solution of the Schrodinger equation. It is exact in the sense that as the number of steps of the random walk becomes large the computed energy tends toward the ground state energy of a finite system of bosons. It shares with all Monte Carlo calculations the problem of statistical errors and (sometimes) bias. In the simulations of extensive systems, in addition, there is the approximation of a uniform fluid by a finite portion with (say) periodic boundary conditions. The latter approximation appears to be less serious in quantum calculations than in corresponding classical ones.

We can give here only a sketch of the basis of the method; for more details consult reference (4) and (6).

In dimensionless form and in the space $\mathbb{R}^{3N}$ for an N body system, Schrodinger's equation may be written as:

$$-\left[\nabla^2 + V(R)\right]\psi(R) = E\psi(R) \quad (12)$$

where $V(R)$ is the total potential energy.

Suppose the potential energy is bounded from below

$$V(R) \geq - V_0 \quad (13)$$

Then Eq. (12) may be rewritten as

$$(-\nabla^2 + V(R) + V_0)\psi(R) = (E + V_0)\psi(R) \quad (14)$$
Consider Green's function for the operator on the left, which satisfies
\[ (-\nabla^2 + V(R) + V_0) G(R, R_0) = \delta(R-R_0) \]  
(15)
and all appropriate boundary conditions for \( \psi(R) \). For example, in simulating an extensive system using a finite number of particles and periodic boundary conditions, \( G \) must be periodic with respect to every coordinate. Equation 13 implies that \( G(R, R_0) \) is always nonnegative and can be interpreted as a density function.

With the help of such a Green's function, Eq. (14) may be formally integrated to give
\[ \psi(R) = (E + V_0) \int G(R, R') \psi(R') dR' . \]  
(16)
This equation may be solved by iteration giving a function \( \psi(n) \) at the \( n \)th iterate. Asymptotically \( \psi(n) \) is proportional to \( \psi_0 \), the ground state wave function. The coefficient is asymptotically constant if \( E \) in Eq. (16) is set equal to the ground state energy \( E_0 \). It is not difficult to see that if at any stage \( n \) one has a population of points \( \{R(n)\} \) drawn at random from \( \psi(n) \), and if one samples \( \{R(n+1)\} \) at random using the density function \( (E + V_0) G(R(n+1), R) \), then the expected density of the new population near \( R \) is
\[ \int (E + V_0) \psi(n)(R') dR' \equiv \psi(n+1)(R) \]  
(17)
This defines one step of a random walk whose asymptotic density is \( \psi_0(R) \).

\( G(R, R_0) \) is not known explicitly (or by quadrature) for any but the most simple (and uninteresting) problems. But it is clearly related to the solution of a diffusion problem for a particle starting at \( R_0 \) in a 3N dimension space and subject to absorption probability \( V(R) + V_0 \) per unit time. We therefore expect to be able to sample points \( R \) from \( G(R, R_0) \) conditional on \( R_0 \). It turns out to be possible by means of a recursive random walk in which each step is drawn from a known Green's function for a simple subdomain of the full space for the wavefunction. References (4) and (6) contain a thorough discussion of this essential technical point, and also of the methods which permit the accurate computation of the energy and other quantum expectations such as the structure function, momentum density, Bose-Einstein condensate fraction, and crystal structure. One technical point is well worth reiterating here: if one modifies Eq. (16) by multiplying through by \( \psi_T(R) \), a trial function of the kind used in variational methods, then the Monte Carlo variance of all quantities may be considerably reduced. When this transformation of Eq. (16) is carried out, it is possible to establish an estimator for the energy whose variance vanishes in the limit \( \psi_T \to \psi_0 \). In practice we find that optimum variational wavefunctions always reduce the variance of the energy by large ratios. Limited exploration has also shown that significant departures from such trial functions may change the variance (usually, but not always, for the worse) but that within statistics the answers agree.

Results Obtained with GFMC

A number of systems have been studied with algorithms of the class described here. All those to be discussed here used the acceleration technique outlined at the end of the previous section by employing a \( \psi_T \) which had the form of Eq. (6) for fluids and Eqs. (7, 8) for crystals.

Ceperley, Chester, and Kalos carried out two studies (15, 16) of boson systems in which pair Yukawa forces (one term with \( \epsilon > 0 \) in Eq. (11)) were used. For the most part, the energy values agreed rather well with variational results, usually lying only 1% lower. In certain cases disagreements of up to 4% were noted. On the other hand, the radial distribution function was found to be significantly sharper in the GFMC calculations; the first peak of the radial distribution was usually 10% more peaked than in the corresponding variational calculation.

The generally good agreement with the variational energies indicates that the equations of state of fluids and crystals with Yukawa and similar forces are given adequately for most purposes by the ordinary variational method. For the strongly coupled electron fermion fluid (i.e. at low densities) one can estimate that the change in energy from the corresponding Bose fluid is small. This suggests that the error in using a product trial function as in Eq. (9) is correspondingly small. But there is one point about the comparison of GFMC to variational results that seems generally applicable and important: variational results for the crystal energies are closer to the exact numerical results than are corresponding results for the fluid. That means that the estimation of melting and freezing
densities from variational results will have a systematic bias favoring crystal states.

Kalos, Levesque, and Verlet (6) reported a study on the hard-sphere fluid and crystal. They found the energy about 3-5% deeper than had been obtained variationally (17) and a structure function some 10-20% sharper. The authors also developed a perturbation theory connecting hard-sphere and other strongly repulsive potentials. Using this relation they estimated a minimum energy for fluid He-4 with Lennard-Jones potentials (Eq. (10)) as $-6.8\pm0.2$ K/atom occurring at $1.0\pm1$ of the experimentally observed density, $\rho_0$.

Currently, Whitlock et al. (18) have been treating the Lennard-Jones fluid and FCC crystal by means of the GFMC method. The analysis and calculation of certain corrections is not entirely complete but preliminary results support the perturbation theory results. The equilibrium fluid is found at $\rho/\rho_0 = 1.03$ with an energy of $-6.85\pm0.5$ K/atom. This is in striking contrast with the variational treatment based on a product wavefunction, Eq. (6) for which no calculation has given a result deeper than $-6.6$ K. The experimental result is $-7.14\pm0.5$ K. Thus the Lennard-Jones parameters of Eq. (10) give substantially better equation of state than had been supposed on the basis of variational calculations. Variational calculations with the product trial function give rather crude upper bounds to the equation of state and hence rather limited information about the He-He potential.

Two theoretical studies have shed light on the discrepancy between the variational and GFMC energies for liquid He-4. Chang and Campbell (19) estimated by a perturbational theory that about half the discrepancy between the two results could be ascribed to the neglect of three-body correlations in the trial function. More recently, Pandharipande (20) used a trial function with a three-body correlation corresponding to a linearized "back-flow" (21). Within the framework of integral equations of the HNC type, he calculated a minimum energy of $(-6.72\pm0.2)$ K at a $\rho/\rho_0$ of 1.05. These three-body correlation effects are undoubtedly important in He-3 as well.

A significant part of the discrepancy between the structure function deduced from variational calculations and from experiment can also be ascribed to the neglect of three-body correlations in the trial functions. Figure 1 shows a comparison of experimental, variational, and GFMC estimates of $S(k)$. It is clear that the latter agrees better with experiment than the
variational result.

It is also clear, in spite of the improvement of the equation of state and of $S(k)$ that results from the use of GFMC, that the Lennard-Jones potential cannot be the correct one. Three body potential effects are small in He-4; we estimate that at $\rho = \rho_0$ the triple-dipole force contributes about 0.16 K/atom, fairly close to the result given by Murphy and Barker (22). There is good reason to believe in general that the effect of three body forces on the equation of state will be small as suggested by this particular result. This is a consequence of the high energy of the first excited state of helium. It is not unreasonable to hope that two body forces determined from scattering, virial and transport data should also be consistent with the properties of helium liquids and crystals.

Conclusions

In this brief review we have chosen to concentrate upon the character of some new methods for the Monte Carlo modelling of quantum systems. In so doing we have emphasized certain deficiencies of the older method which rests upon the product trial function in a variational expression. It is necessary to remark that this latter technique remains useful: it is a reasonable guide to the phenomena in quantum systems and for soft-core systems gives results for the equation of state of liquids and crystals which are adequate for most purposes. The extension of the Monte Carlo variational method to include three-body correlations is straightforward but computationally slow; it should be done to provide reliable checks on the theoretical work on such effects in He-4. The study of inhomogeneous systems and mixtures remains largely unexplored.

The fermion and Green's Function Monte Carlo are important in themselves and interesting as hints to the richness of methodology that can be brought to the bear on the computation of quantum systems. In the short term we expect to broaden the specific trial functions used in fermion Monte Carlo to permit the treatment of more realistic models of nuclear and neutron matter. We expect also to try a variant in Quantum Chemistry problems.

The most immediate research we plan with the Green's Function Monte Carlo is the exploration of the equation of state of He-4 liquids and crystals with two body potentials which fit more data than the Lennard-Jones-de Boer-Michels form we have used. The exploration of inhomogeneous systems is a logical next step. At the moment only GFMC offers an unambiguous approach to the calculation of the density profile at an interface, for example.

For the future we anticipate the development of practical methods for the treatment of systems at finite temperatures (some of the technical problems of extending GFMC to temperatures greater than zero have recently been solved for the two-body hard sphere problem (23)). An extension to permit the exact or very reliable treatment of fermion systems seems possible and useful.

Acknowledgment

This work was supported in part by the Department of Energy, Contract No. EY-76-C-02-3077*000 and in part by the National Science Foundation under Grant DMR-74-23494 through the Material Science Center, Cornell University.

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From Microphysics to Macrochemistry via Discrete Simulations

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Historically there are two distinct classes of problems in chemistry to which discrete microscopic simulations have been applied widely and with considerable success: At one extreme the bulk physical properties of atomic and molecular fluids are studied as the "exact" dynamical evolution of a collection of representative particles is followed in "computer experiments" using the well-established method of molecular dynamics (1-10). At the other extreme similar techniques (11-16) are used to explore the chemical transformations which may occur in an isolated collision between potentially reactive species (e.g., in a very dilute gas). Between these mutually exclusive limits lies an increasingly important area of chemistry in which macroscopic properties are a direct consequence of cooperative interplay between molecular motion and chemical dynamics. Of immediate interest in this area are chemical systems which may undergo nonequilibrium instabilities and transitions between different regimes of macroscopic physicochemical behavior (See Ref. 17 for a recent survey of the field). Fully analogous to equilibrium phase transitions and critical phenomena, these "nonequilibrium phase transitions" present even more formidable difficulties in both microscopic theory and laboratory experiment. Hence an obvious need exists for detailed computer simulations to provide "experimental" data for theorists and "theoretical" guidance for experimentalists. Since the development of appropriate simulation methods in this area is in its infancy, the purpose of this paper will be to provide motivation for such investigations in the more familiar context of molecular dynamics in classical fluids, to review feasible methods at two levels of description which have emerged in the last few years (18, 19, 20, 21, 22), and to illustrate their application using two simple models which exhibit chemical instabilities and transitions.

In all three classes of problems the systems of interest are characterized by the interaction of large numbers of individual degrees of freedom. It is this feature which leads to great theoretical difficulties in both classical and quantum systems,