

Computer Simulation of Phase Transitions in Classical and Quantum Systems*

B. J. ALDER, D. M. CEPERLEY, and E. L. POLLOCK
*University of California, Lawrence Livermore National Laboratory,
Livermore, California 94550*

Abstract

The melting transition of classical hard disks is reviewed, emphasizing evidence from computer simulation for the order of the transition, mechanism of melting, and convergence of the virial expansion. Next, the graph theoretical treatment of a dilute mixture of electrolytes consisting of stripped iron ions in a hydrogen plasma is examined for fluid phase separation at the center of the sun. For quantum many-body systems a stochastic numerical scheme is outlined and applied to the Fermi electron gas at 0 K to locate the melting transition and the region of stability of the ferromagnetic fluid phase. Finite temperature results for the electron gas are used to estimate the region of convergence of the expansion away from the classical limit. Results for the superfluid transition of helium are compared to those of the ideal gas. Preliminary results leading to a prediction for the molecular to metal transition in hydrogen are also presented.

1. Phase Transition in Classical Systems

Phase transitions are both the most spectacular and the most difficult aspect of the equilibrium behavior of materials because they indicate radical changes in properties across sharp boundaries of the state variables describing the system. Any statistical mechanician worth his salt must have a try to work on these phenomena and Professor Mayer is no exception. He must also expect to be on the wrong track because of the inherent mathematical complexity of having to look for singularities in the equations, and Professor Mayer is no exception to that either. However, he is in good company since there is as yet no theory of melting, there are just good empirical rules.

One of Professor Mayer's good ideas which turned sour is his introduction of the "Derby Hat," a transition region between the gas and liquid phase around the critical point. The idea of spreading any transition over some finite region has many forms, for example premelting, and is a very attractive one. What Professor Mayer proposed was that just before the liquid completely condenses as the temperature is lowered, small liquid droplets (clusters) would form in the gas phase. They no doubt do, however, the process is a continuous one as the temperature decreases and no definitive region where this occurs can be identified. The beautiful experiments to determine the exponents with which various

* Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

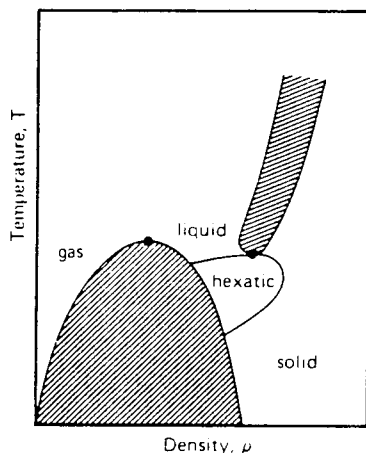


Figure 1. Symbolic phase diagram of a two-dimensional system showing the location of the various phases including the hexatic phase. Hatched areas represent two-phase coexistence.

properties diverge at the critical point have clearly demonstrated that this transition is sharp. It is, however, also true that the region over which these asymptotic laws hold have as yet not been clearly established. Further work needs to be done to define, in this sense, the range of the critical transition.

Amusingly enough, the recent activity in the theory of melting [1] has recreated, in a subtle and sophisticated form, a Mayer "Derby Hat" as shown in Figure 1, around the melting point of some two dimensional systems at low pressures. I like to call this the cocked Mayer Derby hat. It, too, is an effort to spread out the first-order melting transition into two successive second-order transitions. The solid would, in the first of these transitions, lose translational order and its resistance to shear by the thermally driven mechanism of unbinding of dislocation pairs. This leads to an intermediate hexatic phase which still retains angular order and resistance to torsional shear, which in the subsequent second-order phase transition disappears through the mechanism of unbinding of disclination pairs. As attractive as these ideas might be in finding a universal mechanism of melting, the possibility that a first-order transition intervenes before these unbinding events take place must be reckoned with. This would not be the first time that an instability criterion for a metastable solid had been postulated. One example of those sets a limit to the stability of a solid as the bottom of the van der Waals loop (infinite compressibility).

The unbinding of dislocation pairs leads to a universal melting criterion, based on certain combinations of elastic constants, that is remarkably close to the actual conditions [2]. Although all present two-dimensional melting studies on computers appear to say that a first-order melting transition intervenes, they should be distrusted. For the relatively small systems (of the order of a 1000

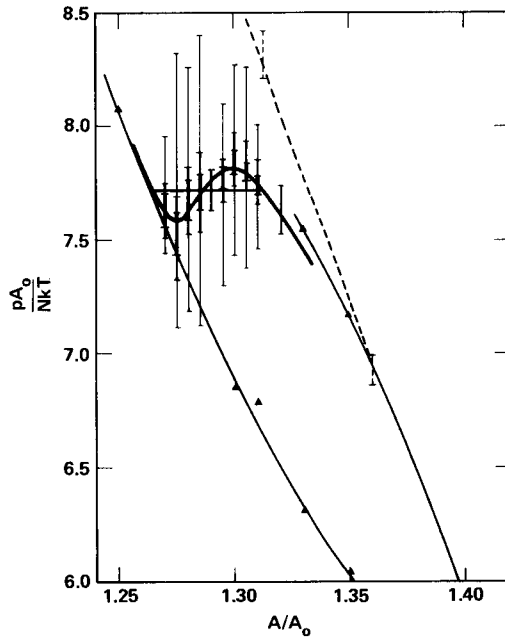


Figure 2. Equation of state of hard disks in the melting region. Reduced pressure versus the area relative to the area of close packing. Result for small systems is indicated by triangles. Result for larger systems is indicated by the vertical error bars where successively heavier bars indicate smaller uncertainties for longer runs. Dashed line results from extrapolation of the virial series by various Padé approximates and the error bars, the resulting uncertainty.

particles) that can be investigated there cannot be a significant number of dislocation pairs generated at equilibrium, since their concentrations is estimated to be of the order of 1 part in 1000. Besides, the dynamics of such defects might be very slow, leading to equilibration difficulties.

In our earlier study [3] of hard disk melting, we went to considerable trouble to establish the equilibrium melting behavior for a system of about 1000 particles. This is reproduced in Figure 2 which shows a van der Waals-like loop. The apparent existence of a negative region of compressibility was sufficiently puzzling that it attracted Professor Mayer's attention [4]. He explained it on the basis that in finite systems the effect of surface tension could cause such an effect. By estimating the magnitude of the surface tension he could explain the size of the loop. The idea is that on the solid-rich side of the coexistence region, the solid, being dominant, preferentially orders the interfacial region in its image, hence the undershoot. Very recent studies on the Lennard-Jones system have reaffirmed Professor Mayer's explanation [5] and have added a small additional twist; namely that the van der Waals loop is not quite symmetric, which is also apparent from a close look at Figure 2. The solid branch is found to undershoot

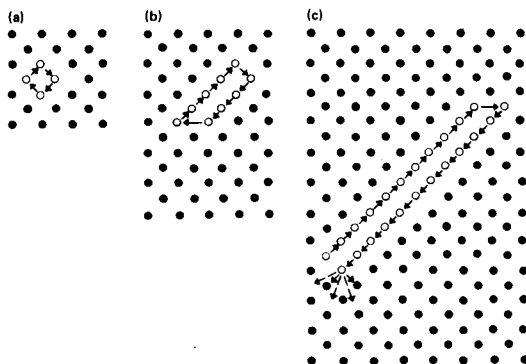


Figure 3. Schematic diagram of the particle motion (indicated by arrows) in a two-dimensional solid at three successively closer densities to the melting density.

a bit more and the rise to the maximum is a bit more vertical. This happens because the solid cannot be disordered enough in these small systems, as a study of a purposely generated defective solid shows.

Even though the hexatic phase may not be realizable, the study of melting mechanisms on computers closely conforms to the idea of unbinding of dislocation pairs. The details, as found from computer studies, of these mechanisms are schematically presented in Figure 3. Starting out with a solid about 1% higher in density than where the tie line in Figure 2 predicts the pure solid to be first stable leads to the observation that the only particle motion taking place in the solid was an extremely rare exchange of three or four particles [Fig. 3(a)]. As the density was lowered slightly to the coexisting solid density, still extremely rarely larger rings of particles could move in a circular fashion as shown in Figure 3(b). These closed-loop motions tended to consist primarily of particles in neighboring rows with the end particles jumping across the rows. As the density was changed to a value close to the coexisting solid, the loop became very long and the dislocations at the two ends of the elongated loop were no longer correlated in their jump across the rows (they became unbound) and the solid melted.

There is one more idea of Professor Mayer's on phase transitions that does not appear to be valid and that is that the virial series diverges at condensation. That very attractive idea seems difficult to prove or disprove because of mathematical complexities. In spite of much effort nothing is certainly known about the maximum radius of convergence of this series. The empirical evidence presented in Figure 2 for hard disks is that the virial series appears to still converge beyond the solidification density. The first seven virial coefficients which are known, complemented by various means of predicting the higher ones, such as Padé approximates lead to an equation of state [6] as shown by the dashed curve in Figure 2. The indicated error bars estimate the uncertainty involved in the various means of extrapolation. To be sure the extrapolation of the equation of

state is not very large beyond the region where it agrees with computer results but under the assumption that there is no radical change in the functional behavior of this virial series beyond the ones that are known, the series extends the fluid phase to densities higher than solidification smoothly by a metastable branch.

We thought we could use another virial-like series which Professor Mayer developed to predict an interesting phase transition for a mixture of ions. For ionic systems, because of the long-range forces; the virial expansion has to be resummed to get convergent results and, in particular, Professor Mayer showed how the lowest-order result leads to the Debye-Hückel theory or mean field theory and how corrections to that theory could be evaluated [7]. The phase transition we considered is that of highly ionized iron in very low concentration (one part in 10^5) dissolved in a hydrogen plasma at the center of the sun [8]. Such a phase separation could help explain the low solar neutrino count and indeed the Debye-Hückel theory predicted phase separation for even much lower iron concentrations in hydrogen than the assumed abundance. The result, however, is not credible because even though the dilute iron phase can be treated by the Debye-Hückel theory, the iron-rich phase that separates out cannot. So we thought we might be able to show with this cluster expansion that at least the conditions at the center of the sun lie within the two-phase region, that is below the critical point of the iron-hydrogen phase separation. This would tell us whether phase separation is possible and allow us to do deal with much lower iron concentrations, namely, those at the critical point. Unfortunately, the iron concentration is still too high at the critical point (about 1% iron) for the two or three corrections to the Debye-Hückel theory which we could evaluate, to converge.

2. Stochastic Quantum Many-Body Method

The variational approach to the quantum many-body problem, which typically involves expanding the wave function in a basis set, severely restricted in dimensionality and functional form, was originally developed for the few-body problem and its application to very many particles has many difficulties. The stochastic methods advocated here are an outgrowth of the successful computational techniques developed in classical statistical mechanics for the many-body problem. Of prime importance in the classical situation was the *a priori* introduction in the stochastic process of the known probability density with which the system covers phase space, which is known once the potential of interaction is specified. A completely random process of covering phase space would have a vanishingly small probability of finding the region of lowest potential energy. Knowing the probability density permitted the development of a Markov process by which configurations were generated with that probability density [9] and consequently each configuration developed in the stochastic process has equal weight. This is an optimal situation from the view point of computational efficiency.

In the quantum case this cannot be achieved because the probability density, namely the wave function squared or the density matrix, is in fact to be determined by the stochastic process. What is hence essential for computational efficiency is to introduce an approximate probability density which incorporates as much of what is known about this probability density function as possible and let the stochastic process correct this approximate function. This introduction of such a trial function is called importance sampling [10]. Furthermore, as the stochastic process adds additional knowledge about the probability density, that information could be used to improve the importance function, leading to still greater computational efficiency through an adaptive process. This process would further reduce the computer time requirements to obtain the answer to the desired statistical error.

In the quantum case the functional integration method, as originally proposed, did not make use of importance sampling. Subsequently, a number of ways to introduce importance sampling for the calculation of the density matrix ρ have been proposed, and we shall outline some of them. The density matrix, from which the equilibrium thermodynamic properties of the system can be calculated, satisfies the Bloch equation

$$\partial\rho/\partial\beta = -H\rho, \quad (1)$$

where β is the reciprocal of the temperature and H is the system Hamiltonian. From the formal solution to this equation, it can be easily verified that

$$\rho(R, R'; \beta_1 + \beta_2) = \int \rho(R, R''; \beta_1) \rho(R'', R'; \beta_2) dR'', \quad (2)$$

so that repeated application of this identity gives:

$$\rho(R, R'; \beta) = \int \rho(R, R_1; \beta/M) \rho(R_1, R_2; \beta/M) \cdots \rho(R_{M-1}, R'; \beta/M) dR_1 \cdots dR_{M-1}. \quad (3)$$

When β/M , the "time step," is sufficiently small the semiclassical limit for the density matrix, $\rho(R_i, R_j; \beta/M)$, can be used. Taking the limit $M \rightarrow \infty$ gives the Feynman-Kac path integral formula [11]

$$\rho(R, R'; \beta) = \langle \exp(-\int_0^\beta V(t') dt') \rangle, \quad (4)$$

where the angular brackets denote an average over all Brownian diffusion paths from R to R' in a time β and V is the potential energy.

The above approach has not been very useful computationally, because a small time step is generally required in order to accurately integrate the potential energy function along the path, that is for large β or low temperatures too many steps are required. More significantly, for a potential with short-range repulsion, for example, paths where particles approach each other closely have a negligible weight, that is they contribute negligibly to the density matrix. To sample efficiently the small set of paths that do contribute, importance sampling must be

introduced. This can be achieved by realizing that evaluating the path integral is formally equivalent to calculating the partition function for a polymer [12,13] allowing the use of the same stochastic method employed previously in classical statistical mechanics. In this analogy a single polymer consists of a series of M links, where each link represents a step in the diffusive process along the path. These links are a chain of Gaussians, which in the analogy are viewed as harmonic oscillator potentials with force constants $mM/\hbar^2\beta = 2\pi M/\lambda^2$, where λ is the deBroglie wavelength. This single polymer is connected to N other such polymers, where N is the number of particles in the system, through the intermolecular potential. For these strongly interacting large polymer systems even the classical method is prohibitive for most problems of interest. This can be partially overcome by successively moving small subsections of the polymer rather than individual links, because that would sample the important regions of phase space more efficiently.

The situation would be considerably improved if one could reduce the number M of links, that is the size of the polymer, since the number of Monte Carlo moves necessary to sample phase space increases as the cube of the number of such polymer links. This could be achieved if an accurate representation of the density matrix at some lower temperature than the semiclassical limit were available. In that case, the method is again analogous to calculations for a classical polymer but one of shorter length and with different interactions than before; namely, one where the actual intermolecular potential is replaced by a pseudopotential derived from the representation of the density matrix, for example, in the pair product approximation,

$$\rho(R,R') = \prod_i \rho_1(r_i, r'_i) \prod_{i < k} \frac{\rho_2(r_i, r_k, r'_i, r'_k)}{\rho_1(r_i, r'_i) \rho_1(r_k, r'_k)}, \quad (5)$$

where ρ_1 is the ideal gas one-body density matrix and ρ_2 is the two-body density matrix. The pseudopotential is derived from the logarithm of the above density matrix and reduces to the actual potential in the high-temperature limit.

The application of the method requires discussion of how Bose or Fermi statistics are introduced in the above process. To account for statistics the process must be allowed to sample with proper weight from all possible permutations P so that the density matrix is given by

$$\sum_P (-1)^P \rho(R, PR'; \beta) \quad (6)$$

for Fermi statistics. For Bose statistics all permutations have the same sign. The probability of such exchanges becomes significant only at or below the Bose-Einstein condensation temperature, or the temperature at which the deBroglie wavelength becomes comparable to the interparticle spacing. For small values of M such exchanges can be sampled with reasonable probability near the Bose-Einstein condensation temperature. For example for $M = 1$, equivalent

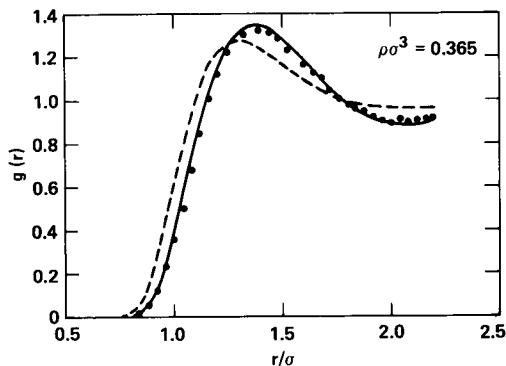


Figure 4. Radial distribution function of helium, $g(r)$, at 2.5 K and normal density, $\rho\sigma^3 = 0.365$, calculated with 20 diffusive steps ignoring statistics (—) compared to the variational result (---), and the ground-state result obtained by the Monte Carlo method (●).

to a variational calculation, the calculated specific heat for 32 particles interacting with a Lennard-Jones potential at a density corresponding to $\rho\sigma^3 = 0.365$ with a mass of He^4 , was found to have a peak about $1/3$ of a degree below the ideal Bose-Einstein transition temperature. This shift in temperature comes about because the short-range repulsion in ρ_2 modifies the result contained in the ideal gas, ρ_1 . This short-range repulsion increases the average near-neighbor distance over an ideal gas and hence a larger deBroglie wavelength, or lower temperature, is required before appreciable particle exchange occurs.

However, a more accurate calculation of the Bose-Einstein transition for interacting particles requires larger M values, for which the computational equilibration time for exchanges becomes very large. This is because the calculation for the Bose-Einstein condensation is then carried out at an effective high temperature, β/M , where the deBroglie wavelength is much shorter than the interparticle spacing, and consequently exchange is extremely rare. Hence the results for the diagonal part of the density matrix, that is the radial distribution function for He^4 at $kT/\epsilon = 0.25$ or about 2.5 K at normal density ($\rho\sigma^3 = 0.365$) given in Figure 4 are for Boltzmanons, that is symmetry requirements were ignored. The variational calculation ($M = 1$) utilizes a density matrix of the form given by Eq. (5) but with ρ_2 the diagonal part of the exact two-particle density matrix. Increasing values of diffusive steps (M) showed at this temperature that the radial distribution function no longer significantly changed for values of M beyond 20. This radial distribution function is very similar to the ground-state one and the small differences would be significant except for the fact that Bose statistics has not been taken into account in the finite temperature calculations.

In order to reduce this large value of M , so that exchange can be sampled, it is necessary within this scheme to introduce better pseudopotentials. This is easier to do in systems that do not have such steep repulsive potentials as the

Lennard-Jones interaction. For the electron gas the softer repulsive Coulomb potential leads to a trial pair density matrix as given by the random-phase approximation that is quite accurate to low temperature, so that convergence occurs for small values of M and the Bose-Einstein condensation could be calculated by this method for this system.

Alternatively, a method that makes even more use of importance sampling can be tried. This is a scheme analogous to the one with which the ground-state problem was previously successfully solved. The importance function is introduced by multiplying the Bloch equation by the trial density matrix ρ_T . The transformed Bloch equation is written in terms of

$$f(R, \tau \| R_i, R_f; \beta) = \rho_T(R, R_f; \beta - \tau) \rho(R, R_i; \tau), \quad (7)$$

where the trial density matrix must satisfy $\rho_T(R, R_f; 0) = \delta(R - R_f)$. This delta function condition is automatically satisfied if ρ_T approaches the semiclassical form at high temperatures. As a consequence of the definition of f at $\tau = 0$ and $\tau = \beta$

$$\rho(R_f, R_i; \beta) = \rho_T(R_i, R_f; \beta) [f(R_f, \beta \| R_i, R_f; \beta) / f(R_i, 0 \| R_i, R_f; \beta)]. \quad (8)$$

The Bloch equation rewritten in terms of f becomes

$$\frac{\partial f}{\partial \tau} = \frac{\hbar^2}{2m} \nabla^2 f - \nabla \cdot (f \mathbf{S}) + Bf, \quad (9)$$

where

$$\mathbf{S} = (\hbar^2/m)(\nabla \rho_T / \rho_T)$$

and

$$B = (1/\rho_T)(\partial/\partial \tau - H)\rho_T. \quad (10)$$

The multidimensional diffusion process representing the above equation for the probability density f corresponds to a diffusion process with a diffusion coefficient of $\hbar^2/2m$ in a space and time-dependent drift velocity field \mathbf{S} with a branching process determined by the birth and death rate, B . Thus at time $\tau = 0$, the system is localized at $R = R_i$ with a probability determined from ρ_T and after a time β the flow field \mathbf{S} forces relocalization at $R = R_f$ by the above delta function condition on ρ_T . Along this diffusion path, the branching process corrects the total weight of the initial and final configuration to the correct one as given by Eq. (8). Only when a series of configurations starting from the initial point neither increases or decreases in number when reaching the final point, that is branching is zero, is the trial function the correct density matrix.

What has introducing the trial density matrix done to make this diffusion method more efficient? First of all the drift term forces the diffusion process

to reach the correct destination. Secondly, in the path integral solution of the modified Bloch equation

$$\rho(R_f, R_i; \beta) = \rho_T(R_i, R_f; \beta) \langle \exp [\int_0^\beta B(t') dt] \rangle, \quad (11)$$

where the angular brackets now denote an average over all diffusion paths from R_i to R_f in the flow field S in time β , the potential which generally contains singularities is replaced by B , proportional to the difference between the real potential and the potential for which trial density matrix would be a solution to Bloch's equation. Thus, B should be much smoother than the intermolecular potential. This basic method has been used for ground-state calculations [14] in which $\rho_T(R, R_f; \beta)$ is replaced by $\psi_T(R) \psi_T(R_f)$. At zero temperature ($\beta = \infty$) the method simplifies since the infinite diffusion paths do not have to close as they must at finite temperature. Instead one searches for a value of the ground-state energy E that leads to a steady-state population, that is a value of E that leads on the average to no branching. The integral reformulation of this process is the basis of the "Green's function Monte Carlo method."

3. Results for Quantum Systems

The electron gas is easier to deal with than helium because the potential varies less abruptly with distance and accurate pair product importance functions can be readily obtained. The random phase approximation leads to an importance function [15] which exactly satisfies the cusp conditions when two particles approach each other and which also has the correct behavior at large particle separations. The importance function is made antisymmetric by multiplying this pair approximation by a Slater determinant of single-particle orbitals. For the various phases investigated [16] in the ground state the Slater determinant contains the translational symmetry of that phase. Thus, for the crystal phase, the orbitals are Gaussians centered around body-centered cubic lattice sites with a width chosen variationally. For the fluid phases, of various degrees of polarization, the single particle orbitals are plane waves with the wave vector lying within the Fermi sphere corresponding to the state of polarization. The resulting phase diagram is shown in Figure 5. The crystal phase is stable at low density corresponding to values of r_s , the ion sphere radius in Bohr radii, greater than 100. At that Wigner crystallization density the fluid in equilibrium with the solid is partially polarized. Since we have so far studied only spin aligned (100% polarization), spin-paired or unpolarized, and 50% polarized systems, we can only say that the coexisting fluid phase of lowest energy is ferromagnetic with a polarization somewhere between 50 and 100%. At high density, for values of r_s less than 20, the completely unpolarized electron fluid is stable. Between the densities corresponding to r_s equals 100 and 20, the ground state is found to continuously decrease its state of polarization from above 50 to 0%.

Work on extending this phase diagram to finite temperature is in its infancy. So far some high-temperature results, where statistical effects are small, have

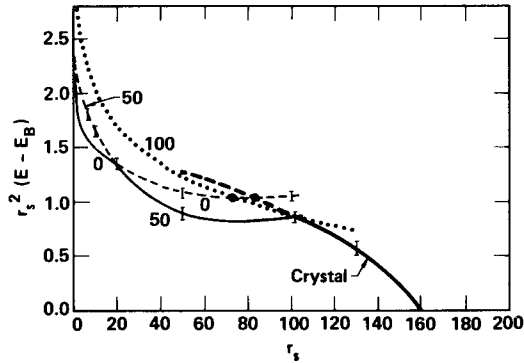


Figure 5. Difference in the ground-state energy of the various phases of the electron gas to that of the boson state, $E - E_B$, in rydbergs, times r_s^2 vs. r_s , the Wigner-Seitz radius, given in bohr radii. Stability of the crystalline, 50 and 0% polarized fluids, are shown at increasing density regions (decreasing value of r_s). The 100% polarized state (---) is never stable.

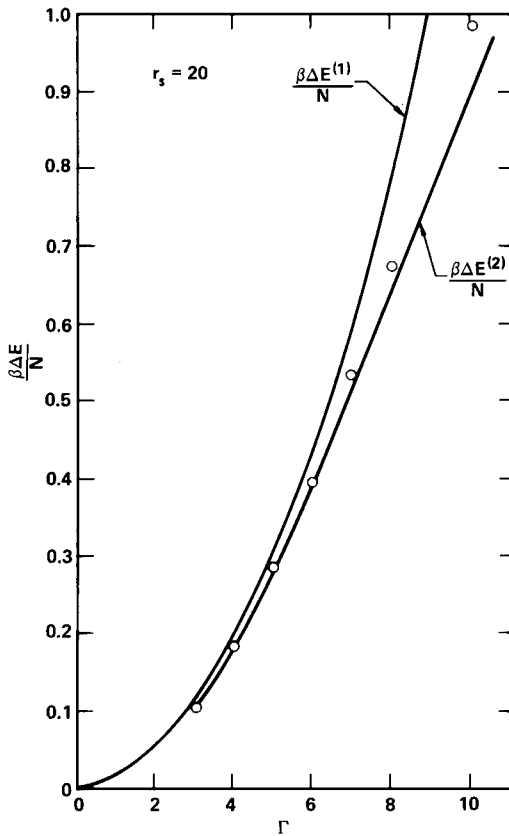


Figure 6. Energy per electron, $\beta \Delta E/N$, vs. $\Gamma = e^2/kTr_s$ at a density corresponding to a Wigner-Seitz radius of 20. Curves labeled (1) and (2) correspond to the Wigner-Kirkwood theory including one and two expansion terms, respectively, (O) Monte Carlo results.

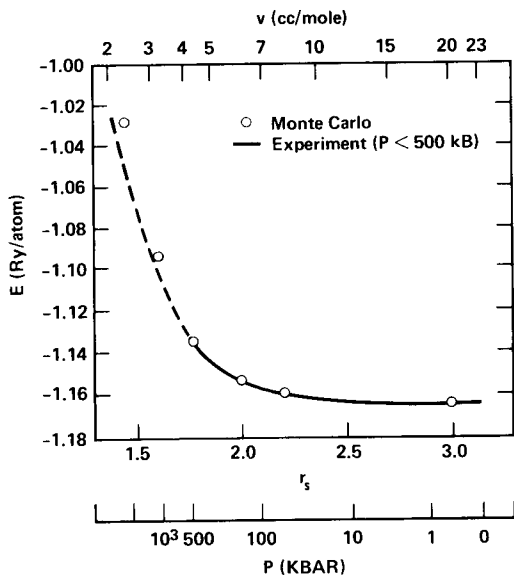


Figure 7. Ground-state energy of molecular hydrogen in the α nitrogen phase in rydbergs as a function of volume, V , in cm^3/mol (upper scale) by the stochastic method (points) compared to experiments (solid curve, with dashed curve extrapolation). Volume scale is also given in units of the Wigner-Seitz sphere (r_s) and the corresponding pressure in kbar.

been obtained. Including only diffraction effects, that is ignoring statistics and utilizing the random phase importance sampling function, the results for 54 particles could readily be extrapolated to infinitely small diffusive steps, since rapid and smooth convergence could be established from results for values of M less than 10. The results for the energy per particle are compared in Figure 6 with those obtained from the Wigner-Kirkwood expansion which corrects the classical result for quantum effects. At sufficiently high temperatures, or low values of $\Gamma = \beta e^2/r$, the results as expected merge. The increasing difference between the first, the sum of the first, and second term in the Wigner-Kirkwood expansion and the stochastic result at lower temperature allow one to judge the rate of convergence of the power series.

Removing the uniform background approximation of the electron gas model and replacing it by protons, that is studying hydrogen, has also been started for the ground state [17]. For this system we plan to investigate the phase transition in the molecular phase associated with the freezing of the molecular rotation with pressure, as well as the transition to the metallic state. The metallic ground-state results compare well with existing theories. The stochastic calculation gives in addition a reliable estimate for the zero point energy of the protons since they are allowed to diffuse as well as the electrons and hence the calculation is not subject to the Born-Oppenheimer approximation. The preliminary results

for the molecular phase are compared to experiment [18] in Figure 7. Up to the highest pressure investigated (500 kbars) the agreement is within the statistical error bars. At that pressure the hydrogen is nearly freely rotating. At higher pressures the extrapolation of the experimental data disagrees with the stochastic results. Further investigations by the stochastic method are in progress to determine whether the differences are real and in particular whether the crystal structure stable at these higher pressures is the same as at the lower pressures.

Bibliography

- [1] J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1973); D. R. Nelson and B. I. Halperin, *Phys. Rev. B* **19**, 2457 (1979).
- [2] F. F. Abraham, *Phys. Rep.*, to be published.
- [3] B. J. Alder and T. W. Wainwright, *Phys. Rev.* **127**, 359 (1962).
- [4] J. E. Mayer and W. W. Wood, *J. Chem. Phys.* **42**, 4268 (1965).
- [5] J. Q. Broughton, G. H. Gilmer, and J. D. Weeks, *J. Chem. Phys.*, to be published.
- [6] K. W. Kratky, *J. Chem. Phys.* **69**, 2251 (1978).
- [7] J. E. Mayer, *J. Chem. Phys.* **18**, 1426 (1950).
- [8] B. J. Alder, E. L. Pollock, and J. P. Hansen, *Proc. Natl. Acad. Sci.* **77**, 6272 (1980).
- [9] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. M. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1089 (1953).
- [10] P. Whitlock and M. H. Kalos, *J. Comput. Phys.* **30**, 361 (1979).
- [11] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- [12] J. A. Barker, *J. Chem. Phys.* **70**, 2914 (1979).
- [13] D. Chandler and P. G. Wolynes, *J. Chem. Phys.* **74**, 4078 (1981).
- [14] D. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, K. Binder, Ed. (Springer-Verlag, Berlin, 1979).
- [15] D. Ceperley, *Phys. Rev. B* **18**, 3126 (1978).
- [16] D. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [17] D. Ceperley and B. J. Alder, *Physica B* **108**, 875 (1981).
- [18] J. van Straaten, R. J. Wijngaarden, and I. F. Silvera, *Phys. Rev. Lett.* **48**, 97 (1982).

Received March 30, 1982