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Simulation studies of a model of high-density metallic hydrogen

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Upper bounds for the ground-state energies of liquid and solid phases of metallic hydrogen and metallic deuterium have been calculated with variational methods and Monte Carlo techniques. At four densities ($r_s = 0.8$, 1.2, 1.36, and 1.488) crystalline phases are clearly preferred in the sense that the energy difference, when compared to the liquid, is in excess of the errors inherent in the numerical procedures. At a fifth density $r_s = 1.6$, the energy differences between solid and liquid phases are smaller than these errors.

The purpose of this Comment is to present the results of simulation studies of the ground state of a model of metallic hydrogen. Let r_s be the standard measure of density $\{a_0 r_s = [3/(4\pi n)^{1/3}]$, where n is the electron or proton density$\}$. We seek to answer the question: Is metallic hydrogen in the range $0.8 \leq r_s \leq 1.6$ a liquid or a crystal in its ground state? There have been a number of calculations made on the equation of state of metallic hydrogen[1] and also of various properties of postulated crystal phases[2], usually monatomic Bravais lattices. Generally metallic hydrogen has been a subject of interest both because of its astrophysical importance[3] and because of its theoretical novelty. As far as we are aware the simulation studies to be reported below are the first such calculations of the structure-dependent part of the total energy and pressure of a possible simple liquid phase. At four selected densities ($r_s = 0.8$, 1.2, 1.36, and 1.488) a crystalline phase has the lower energy whether we are dealing with metallic hydrogen *or* metallic deuterium. At a fifth density ($r_s = 1.6$) liquid and crystalline phases have energy differences that are *less* than the estimated errors in the numerical procedures of our method. In this method, accurate ground-state *variational* calculations for both phases are carried out, and by comparing the energies at fixed r_s, we may determine which is preferred. Although we cannot claim complete accuracy for these results, based as they are on the variational principle, there are some arguments which strongly support our conclusions. These are presented below.

Within the adiabatic approximation we write our starting Hamiltonian for protons or deuterons as

$$H = H_s + E_0(r_s) , \qquad H_s = \sum_i \frac{P_i^2}{2m} + V , \tag{1}$$

where m is the mass of the proton (mass 1) or deuteron (mass 2) and E_0 is the sum of all terms independent of structure after the electron degrees of freedom have been integrated out. In the structure-dependent part H_s, the term V is represented by a sum of density-dependent pair potentials

$$V = \sum_{i<j}^{N} \Phi(r_{ij}, r_s) , \tag{2}$$

where Φ is a screened proton-proton interaction. At the level of linear response we take Φ to be the potential used by Straus and Ashcroft[4] in the self-consistent harmonic approximation to dynamic crystalline metallic hydrogen. For a Lindhard-type dielectric function[5] (corrected for exchange and correlation[6]), the pair potential has the character shown in Fig. 1. Note in particular the location of a typical nearest-neighbor separation (e.g., fcc) reflecting the influence of $E_0(r_s)$. Because the screening is density dependent, Φ depends in a fairly complex fashion[7] on r_s.

The Hamiltonian we use is not exact, either for

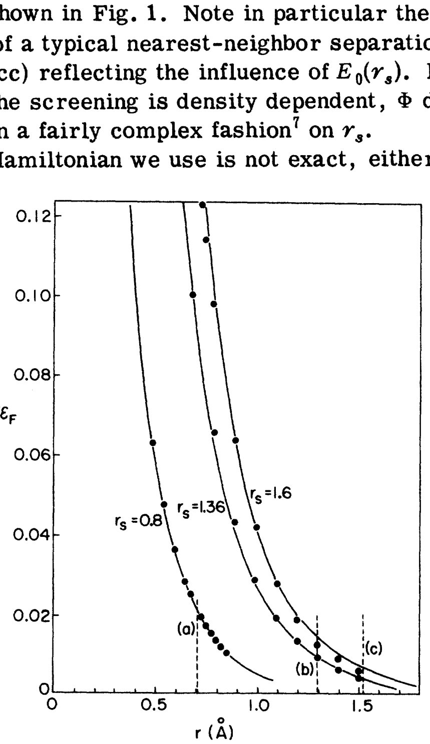

FIG. 1. Effective pair potentials and their fit to the Yukawa form for (a) $r_s = 0.8$, (b) $r_s = 1.36$, (c) $r_s = 1.6$. Vertical dashed line shows nearest-neighbor separation for face-centered-cubic structures, and solid lines are the fit to the Yukawa form.

the proton fluid or the proton crystal. There are terms more complex (than those retained in Φ) that arise when the electronic degrees of freedom are eliminated via perturbation theory. The effects of some of these have been estimated in a recent paper by Chakravarty and Ashcroft,[8] who show that by incorporating the first nonlinear response correction to H_s, the possibility arises that near $r_s = 1.64$ metallic hydrogen is a ground-state liquid metal. If response to all orders is included,[9] pairing of the protons may still occur for $r_s \gtrsim 1.2$. These effects are not included in the present model for H_s.

We have carried out variational calculations for a system of protons described by H_s, but first regarded as an assembly of "bosons." The results of these calculations permit us to construct an argument that determines the relative stability of the liquid and solid phases of the protons when subsequently treated by Fermi-Dirac statistics. This method, though indirect, is simple to carry out in practice because of the ease in treating boson systems by variational means. Thus, in the liquid (L) phase we use a trial Jastrow wave function:

$$\psi^L = \exp\left(-\sum_{i<j} U(r_{ij})\right) , \tag{3}$$

where the "pseudopotential" U is chosen to have the form

$$U(r_{ij}) = (A/r_{ij})^\alpha \exp(-a r_{ij}^\beta) h(r_{ij}) .$$

The choice of U was made for reasons of flexibility since it was necessary for us (i) to explore a relatively wide range of function shapes for the variational wave function and, (ii) to investigate effects of the density dependence of the pair potential Φ. Note that the parameters of ψ^L (i.e., A, a, α, and β) can depend on r_s. At each choice of r_s (or density) the minimization procedure is carried out within the parameter space of A, a, α, and β. To ensure that the resulting upper bounds on energy are rigorous, the quantity $h = \exp(-b r_{ij}^\xi)$ is so chosen that U approaches zero smoothly at the edge of the simulation cube.

For the crystal (C) phase (taken here as an fcc lattice), we adopt the standard form (the "Boltzmann wave function")

$$\psi^C = \prod_{i=1}^{N} \{\exp[-c(\vec{r}_i - \vec{R}_i)^2]\} \psi^L , \tag{4}$$

which is neither symmetrical nor antisymmetrical with respect to permutation of the particles on the lattice sites $\{\vec{R}_i\}$. (We shall see shortly that the matter of symmetry has only a small effect on the energy of crystalline phases.) The parameter c in (4) is a localization parameter and at each r_s is added to the parameters of ψ^L in a complete variational search.

Given trial states of the form (3) and (4), the ground-state energies of the two phases take on the forms

$$NE = \sum_{i<j} \int d\tau |\psi^L|^2 \left(\frac{\hbar^2}{2m} \nabla_i^2 U(r_{ij}) + \Phi(r_{ij})\right) \Big/ \int d\tau |\psi^L|^2 \qquad \text{(liquid)} \tag{5}$$

and

$$NE = \frac{3\hbar^2 N}{2m} c + \sum_{i<j} \int d\tau |\psi^C|^2 \left(\frac{\hbar^2}{2m} \nabla_i^2 U(r_{ij}) + \Phi(r_{ij})\right) \Big/ \int d\tau |\psi^C|^2 \qquad \text{(crystal)}, \tag{6}$$

where $d\tau = \prod d\vec{r}_i$. The integrals in these expressions have been evaluated by standard Monte Carlo techniques[10], and the pressures p resulting from those energies specifically related to structure are determined by an application of the virial theorem. For the crystalline phase, the Lindemann ratio (defined here to be the ratio of the root-mean-square deviation of a particle from a lattice site and the *nearest-neighbor separation*) can also be determined directly. At $r_s = 1.36$ we find values of 0.169 and 0.154 for mass 1 and 2, respectively (Table I gives values computed at other densities). These ratios are large when viewed in the context of normal solids but are smaller by about a factor of 2 than those found in He^3 and He^4. Metallic hydrogen is quite anomalous in this respect; there is no other known system with this intermediate value of Lindemann ratio.

Tables I, II, and III summarize the results for systems of 108 and 256 particles. At four densities ($r_s = 0.8$, 1.2, 1.36, and 1.488) the crystalline phase has the lower energy. Although the difference in energy between liquid and crystal is small (it varies between one and three percent of the total structurally dependent energy), it is a relatively large fraction (10% at $r_s = 1.36$) of the dynamic energy of the protons. At $r_s = 1.6$ the energies are so close that we cannot draw any definitive conclusion. We note at this point that at $r_s = 1.36$ (where a crystal *is* preferred) the solid-phase variational energy and Lindemann ratio are in good agreement with the self-consistent harmonic-approximation results of Straus and Ashcroft.[4,11]

So far as numerical accuracy is concerned, we have carefully assessed the possible errors and conclude that the uncertainties are about $\frac{1}{4}$% of the structural energies or about 1.5% of the dynamic energies. Typically, a few hundred thousand con-

TABLE I. Results of the variational calculations of the structural energy E and pressure P for mass 1. The variational parameters are defined in Eqs. (3) and (4); α, β, and ξ are dimensionless. The last two rows refer to results for 256 particles; the rest are for 108 particles.

r_s	A (Å)	α	a (Å$^{-\beta}$)	β	b (Å$^{-\xi}$)	ξ	c (Å^{-2})	E (eV)	P (eV/Å^3)	P (Mbar)
1.6	2.3	2.5	0.7	2.5	0.000079	12.0	0.0	0.8086 ± 0.003	0.5546 ± 0.001	0.8885 ± 0.0016
	1.8	2.5	0.7	2.5	0.000079	12.0	5.0	0.8060 ± 0.003	0.4544 ± 0.002	0.7280 ± 0.003
1.488	2.4	2.35	0.7	2.25	0.000118	12.54	0.0	1.159 ± 0.004	0.9629 ± 0.004	1.545 ± 0.007
	2.2	2.15	0.75	2.60	0.000118	12.54	4.0	1.1427 ± 0.002	0.87025 ± 0.0013	1.3943 ± 0.002
1.36	2.9	1.85	0.7	2.5	0.00054	12.0	0.0	1.7299 ± 0.007	1.9332 ± 0.002	3.097 ± 0.0034
	2.0	1.85	0.7	2.5	0.00054	12.0	9.0	1.6997 ± 0.0023	1.6784 ± 0.001	2.689 ± 0.0017
1.20	2.6	1.9	0.7	2.4	0.00176	12.54	0.0	2.8312 ± 0.004	4.0812 ± 0.004	6.538 ± 0.006
	1.6	1.9	0.7	2.2	0.00176	12.54	13.0	2.77874 ± 0.001	3.7689 ± 0.008	6.0385 ± 0.0125
0.8	1.3	2.0	0.5	2.0	0.3279	12.0	0.0	10.8047 ± 0.05	46.607 ± 0.026	74.666 ± 0.042
	0.8	2.0	0.5	2.0	0.3279	12.0	40.0	10.5682 ± 0.03	45.2928 ± 0.045	72.5678 ± 0.072
1.36	(Same as above for liquid phase)							1.7352 ± 0.003	1.932 ± 0.004	3.095 ± 0.006
	(Same as above for solid phase)							1.7030 ± 0.002	1.6795 ± 0.0015	2.69 ± 0.0025

TABLE II. Results of the variational calculations of the structural energy E and pressure P for mass 2. The variational parameters are defined in Eqs. (3) and (4); α, β, and ξ are dimensionless. The results are for 108 particles.

r_s	A (Å)	α	a (Å$^{-\beta}$)	β	b (Å$^{-\xi}$)	ξ	c (Å^{-2})	E (eV)	P (eV/Å^3)	P (Mbar)
1.6	2.45	2.5	0.7	2.5	0.000079	12.0	0.0	0.7597 ± 0.002	0.5538 ± 0.0025	0.8584 ± 0.004
	2.3	2.5	0.7	2.5	0.000079	12.0	4.5	0.7627 ± 0.002	0.39044 ± 0.0012	0.62556 ± 0.002
1.488	2.8	2.15	0.75	2.60	0.000118	12.54	0.0	1.0977 ± 0.002	0.9400 ± 0.0025	1.506 ± 0.004
	2.4	2.15	0.75	2.60	0.000118	12.54	5.0	1.0904 ± 0.001	0.7923 ± 0.001	1.269 ± 0.0015
1.36	3.2	1.75	0.7	4.0	0.00054	12.0	0.0	1.6494 ± 0.001	1.7694 ± 0.001	2.8346 ± 0.014
	2.7	1.85	0.7	2.5	0.00054	12.0	9.0	1.6325 ± 0.003	1.5668 ± 0.004	2.510 ± 0.006
1.2	3.2	1.9	0.7	2.2	0.00176	12.54	0.0	2.7246 ± 0.003	4.02083 ± 0.04	6.4415 ± 0.067
	2.1	1.9	0.7	2.4	0.00176	12.54	21.0	2.6871 ± 0.0036	3.4375 ± 0.003	5.507 ± 0.005
0.8	1.6	2.6	0.5	1.6	0.3279	12.0	0.0	10.5140 ± 0.024	45.8317 ± 0.05	73.424 ± 0.08
	1.0	2.6	0.5	1.6	0.3279	12.0	60.0	10.266 ± 0.0056	43.3743 ± 0.016	72.546 ± 0.025

TABLE III. Results of the variational calculations of the Lindemann ratio for mass-1 and mass-2 systems.

r_s	Mass	Lindemann's ratio (γ)
1.6	1	0.18
	2	0.167
1.488	1	0.189
	2	0.168
1.36	1	0.169
	2	0.154
1.2	1	0.168
	2	0.131
0.8	1	0.158
	2	0.119

figurations were used in the evaluation of the integrals. The simulation results for a 256-particle system have errors within those of a 108-particle system, and we can conclude that there is negligible size dependence in the results. Many of the Monte Carlo runs were extended to 0.5×10^6 configurations, and in combination with careful block averaging (up to 15 blocks), we achieved the errors quoted in Tables II and III.

Table II also gives the corresponding results for deuterium. The calculations were performed with the same Hamiltonian except that the system has mass 2. Again, the crystal is preferred at $r_s = 0.8$, 1.2, 1.36, and 1.488.

We turn now to the question of quantum statistics. Metallic hydrogen is a Fermi system, but the trial states used do not reflect this. On the other hand, it is clear from the tables that in the *crystalline* phase the particles are very well localized and show no tendency to exchange positions. Under such circumstances it must make a negligible difference to use an equally well-localized but *fully* antisymmetric wave function. Since the protons *are* well localized, nearly all the physical properties of the system will be independent of statistics, and can therefore be determined using trial states (such as ours) that are neither symmetrical nor antisymmetrical. The difference in energy between fermion and boson mass 1 systems is of the order of magnitude of the two-particle exchange energy and this, according to Guyer,[12] can be estimated as

$$J \sim -\left(\frac{3\hbar^2 c}{2m}\right) I_0 , \tag{7}$$

where

$$I_0 = \frac{2}{\pi}(c\sigma^2)^{1/2}\exp[-c(\sigma^2+\Delta^2)] .$$

Here c is the localization parameter discussed above, and Δ is the nearest-neighbor separation. The quantity σ is the effective hard-sphere radius of the pseudopotential $U(r_{ij})$ in the Jastrow function. Using the optimum value of c in our variational search at $r_s = 1.36$ ($c = 9.0$ Å^{-2}), and with $\Delta = 1.3$ Å we find (for mass 1) $I_0 \sim 10^{-10}$ for $\sigma = 1$ Å, and $I_0 \sim 10^{-7}$ for $\sigma = 0$. Accordingly, the two-particle exchange energy is seven orders of magnitude smaller than the localization energy $(3\hbar^2 c/2m)$ which, in turn, is only about 4% of the total structure-dependent energy. By way of comparison[12] the value of I_0 for He^3 is 10^{-4} (here $\Delta = 3.77$ Å, $\sigma = 0$, and $c = 0.65$ Å^{-2}).

We turn now to the energy of a ground-state liquid phase of hydrogen. The variational energy of the Fermi system must lie higher than the corresponding energy of the boson system. This follows because the imposition of the requirement of antisymmetry on the variational wave function can be regarded as a constraint which must raise the variational estimate[13]. Since the liquid-phase energy of the "boson" fluid is found at four densities to be higher than the crystal phase, we may conclude that the energy of the true fermion system will be even higher. But we have argued that in the crystalline phase the choice of statistics has negligible effect. Thus, at the four densities ($r_s = 0.8$, 1.2, 1.36, and 1.488), the liquid phase for the fermion system will have an energy in excess of that for a crystal.

This prediction of crystallinity (for either hydrogen or deuterium) is further supported by an application of the quantum law of corresponding states[14]. We have observed that at high densities ($r_s \lesssim 1.4$) and in the vicinity of the nearest-neighbor separation between protons (or deuterons) the pair potentials of Fig. 1 can be quite well approximated (to within additive constants) by a Yukawa form[7]

$$\Phi = \frac{\epsilon}{\lambda r} e^{-\lambda r} .$$

We also note that the nearest-neighbor separation is *not* close to the first minimum of Φ, again in contrast to the situation commonly prevailing in simple solids.

Now a quantum system described by a Yukawa potential is completely characterized by the reduced quantities

$$\Lambda^* = \frac{h\lambda}{(m\epsilon)^{1/2}}$$

and

$$K^* = \lambda\rho^{-1/3} ,$$

where ρ is the number density. The ground-state phase diagram for these Yukawa systems has been determined by Ceperley *et al.*[15,17] over a wide range of values for Λ^* and K^*, and for both boson and fermion systems. We can therefore use these

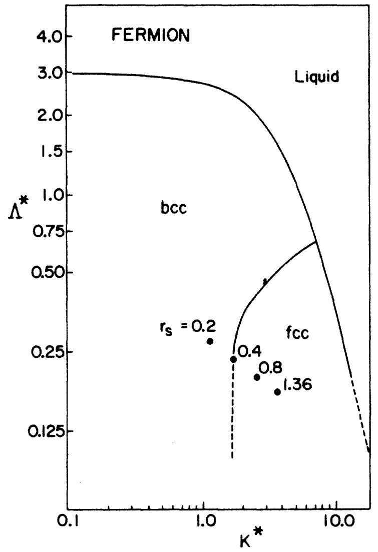

FIG. 2. Phase diagrams taken from Ref. 15 for a system of fermions interacting with Yukawa potentials. Points for metallic hydrogen (mass 1) are obtained from the quantum law of corresponding states.

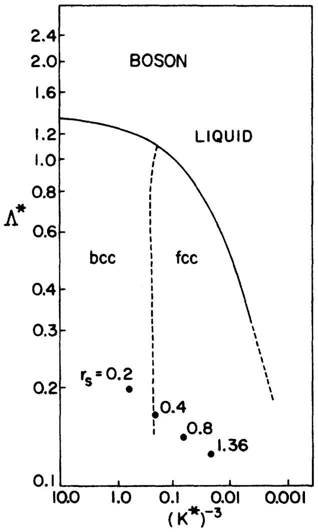

FIG. 3. Phase diagrams taken from Ref. 17 for a system of bosons interacting with Yukawa potentials. Points for metallic deuterium (mass 2) are obtained from the quantum law of corresponding states.

results for hydrogen and deuterium by a simple application of scaling. At $r_s = 1.36$, 0.8, 0.4, and 0.2, the potentials Φ map onto Yukawa functions with $K^* = 3.49$, 2.43, 1.66, and 1.15, respectively. For mass 1 the corresponding values of Λ^* are 0.18, 0.20, 0.23, and 0.28; for mass 2 they are 0.12, 0.14, 0.16, and 0.20, respectively. For mass 1 the ground-state phase diagram of Ceperley *et al.*[15] (Fig. 2) shows that not only is the crystal strongly preferred for the fermion system, but that metallic hydrogen will exist in a face-centered-cubic form for $r_s > 0.4$ and in a body-centered-cubic form for $r_s < 0.4$. We also find that pressure-induced melting has not occurred at the smallest value of r_s considered ($r_s = 0.2$). This is consistent with the recent estimate[16] that pressure-induced melting may not occur until very much higher densities are reached. From the mapping for deuterium and the boson phase diagram of Ceperley *et al.*,[17] we again find that a crystalline phase is preferred, with fcc at $r_s > 0.4$ and bcc for $r_s < 0.4$ (Fig. 3).

We conclude with a brief analysis of the applicability of the quantum law of corresponding states to this problem. Let E be the energy of the system calculated variationally for pair potential Φ. Let E_y and Φ_y be the energy and pair potential of the corresponding Yukawa system. Then to first order

$$E_y = E + \sum_{i<j} \frac{1}{N} \int d\tau \, |\psi_T|^2 [\Phi_y(r_{ij}) - \Phi(r_{ij})] \Big/ \int d\tau \, |\psi_T|^2 , \tag{8}$$

where ψ_T is the trial wave function for either liquid or solid. Notice that since the short-range repulsive part of the potential (which is well accounted for by the Yukawa form) dominates the determination of structural properties,[18] it is convenient to separate (8) as

$$\begin{aligned} \Delta E &= E_y - E \\ &= \Delta E_n + \Delta E_l \\ &= \Bigg(\sum_{\substack{i<j \\ r_{ij} < r_{\min}}} \frac{1}{N} \int d\tau \, |\psi_T|^2 [\Phi_y(r_{ij}) - \Phi(r_{ij})] + \sum_{\substack{i<j \\ r_{ij} > r_{\min}}} \frac{1}{N} \int d\tau \, |\psi_T|^2 [\Phi_y(r_{ij}) - \Phi(r_{ij})] \Bigg) \Big/ \int d\tau \, |\psi_T|^2 , \end{aligned}$$

where $r_{\min}$ in the liquid phase is the first minimum beyond the nearest-neighbor peak of the pair-distribution function, and in the solid phase is the equivalent average separation so chosen to completely include the first coordination shell. In this way ΔE_n accounts for the nearest-neighbor contributions to the difference ΔE arising from the corresponding difference $\Phi_y - \Phi$. In a similar way

TABLE IV. First-order corrections (mass 1) to the energy when the pair potential is approximated by a Yukawa form. ΔE_n represents the nearest-neighbor contributions, ΔE_l the long-range contributions, and ΔE the total energy difference [see Eq. (9)]. Numbers in parentheses give fractions of *total* structural energy E.

r_s		ΔE_n (eV)	ΔE_l (eV)	ΔE (eV)
1.36	liquid	0.117 (0.07)	0.177	0.294 (0.17)
	solid	0.079 (0.046)	0.194	0.273 (0.16)
0.8	liquid	0.078 (0.007)	0.574	0.652 (0.06)
	solid	0.099 (0.009)	0.186	0.285 (0.027)

ΔE_l accounts for the longer-ranged effects. Table IV records these differences, and also expresses them as a fraction of the *total* structural energy E. As expected, the replacement of Φ by Φ_y is much more accurate at high density, but even at $r_s = 1.36$ the approximation is seen to be relatively satisfactory.

In summary, our variational calculation shows that metallic hydrogen and metallic deuterium can both exist in high-density monatomic forms at absolute zero. For densities such that $r_s \leq 1.488$, we find that liquid phases always have higher energies. At $r_s = 1.6$ liquid and solids have energies that are almost indistinguishable within the accuracy of our calculations. It is worth noting, however, that variational calculations of this kind usually provide better estimates of the energy of the solid than of the fluid. This is because the configuration space of the solid is much simpler than that of the fluid, and as a consequence it is possible to construct a better variational wave function for the solid phase. It follows that by using a wider class of variational wave functions, it may be possible to lower the energy of the fluid phases still further. On the other hand, the mapping of the problem onto the Yukawa potential system suggests that at high densities metallic hydrogen and deuterium lie deep within the crystalline phases.

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