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Superconductivity in liquid metallic hydrogen

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By solving the Eliashberg equations for the gap function, the superconducting transition temperature of a proposed low-temperature liquid state of metallic hydrogen is found to be comparable to that obtained, with similar approximations, for the solid. This indicates that metallic hydrogen may be a superconducting liquid in the density range $1.6 \geq r_s \geq 1.3$, where the melting point is expected to be fairly low.

It has been predicted that hydrogen becomes metallic at high density,[1-3] the requisite pressures being in the range 1–3 Mbar. At high temperatures the system will be a liquid metal, the protons forming an almost classical liquid[2] but the electrons remaining highly degenerate. At low temperatures the metal is assumed to form a monatomic crystal [possibly fcc (Ref. 3)] and in this state it is also predicted to be a superconductor with transition temperatures T_c calculated[4,5] to be as high as 300 K for densities near the insulator-metal phase transition ($r_s' \approx 1.6$).

Recently, Mon *et al.*[6] determined the internal energy difference between postulated ground-state liquid and crystalline phases of metallic hydrogen over a wide range of densities. These differences, which are small, are given (per proton) in Table I; it seems reasonable to suggest that they will be a direct measure of the melting temperature T_m of the system, and we may therefore infer that T_m is near zero for $r_s \approx 1.6$ and is likely to be only a few hundred degrees at $r_s = 1.2$.

Should these estimates of T_c and T_m be valid, then the possibility arises that solid metallic hydrogen may be a superconductor up to its melting point, at least in a certain range of densities. If we continue this line of argument and assume that superconductivity is *not* greatly inhibited by melting, we must then conclude that metallic hydrogen can become a new state of matter: a superconducting liquid.

TABLE I. Energy difference per particle between liquid and solid metallic hydrogen [according to Mon *et al.* (Ref. 6)] and the superconducting transition temperatures of liquid metallic hydrogen.

r_s	$E_l - E_s$ (K)	T_c^* (K)
1.600	7	87
1.488	189	119
1.360	350	141
1.200	608	40

A liquid differs from a dynamic solid principally in its atomic disorder and lack of static shear strength. From the existence of good amorphous superconductors we know that disorder and superconductivity are not mutally incompatible. Furthermore, we also know that the compressibility of ordinary metals changes little when they melt; so that the longitudinal "phonons," which are very important for superconductivity, may be taken to have roughly the same spectrum in the liquid as in the solid. Thus a superconducting metallic liquid is in principle quite possible, and we need a method for calculating its transition temperature.

We shall compute T_c by solving the Eliashberg equations for the gap function $\Delta(\omega)$ and by finding the temperature at which the gap is suppressed by a vanishingly small pair-breaking field.[7] The input required for this method is the Eliashberg function[8] $\alpha^2F(\omega)$, which in solids is obtained from the spectral weight of the phonon Green's function. In turn this is obtained from methods such as the self-consistent harmonic approximation[3,9] (SCHA). In a highly excited quantum liquid, there does not exist a well-defined phonon spectrum except at very long wavelengths; so $\alpha^2F(\omega)$ must be extracted from a more general description of the ionic-density fluctuations which can be achieved as follows.

Let the exact imaginary-time-ordered propagator of ionic-density fluctuations be denoted by

$$\Pi(\vec{r},\tau) = i\langle T_\tau[\delta\hat{n}(\vec{r},\tau)\,\delta\hat{n}(0,0)]\rangle \ , \tag{1}$$

where T_τ orders imaginary times,[10] the angle brackets denote an equilibrium ensemble average, and $\delta\hat{n}$ is the ionic number density-fluctuation operator. We define the Fourier transform

$$\Pi(\vec{q},i\omega_n)=\int_0^{\beta\hbar}d\tau\int d^3r\,\Pi(\vec{r},\tau)\times\exp[-i(\vec{q}\cdot\vec{r}-\omega_n\tau)]\ , \qquad (2)$$

where ω_n is the Bose-type Matsubara frequency $2\pi n/\beta\hbar$. This function is related to the imaginary part of the real-time density-density response function by[10]

$$\Pi(\vec{q},i\omega_n)=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\chi''(\vec{q},\omega)}{\omega-i\omega_n}=\int_0^{\infty}\frac{d\omega}{\pi}\frac{2\omega\chi''(\vec{q},\omega)}{\omega^2-(i\omega_n)^2}\ , \qquad (3)$$

where we have used the fact that χ'' is odd in frequency. For a crystalline solid, the density fluctuation propagator can be expressed[8] in terms of the phonon Green's function $D_\lambda(\vec{q},i\omega_n)$

$$\Pi(\vec{q},i\omega_n)=\sum_\lambda(\vec{q}\cdot\hat{e}_{\vec{q}\lambda})^2\left(\frac{\hbar n_i}{2M_i\omega^2_{\vec{q}\lambda}}\right)D_\lambda(\vec{q},i\omega_n)\ , \qquad (4)$$

where λ labels polarizations, $\hat{e}_{\vec{q}\lambda}$ and $\omega_{\vec{q}\lambda}$ are the polarization vector and frequency of the mode $\vec{q}\lambda$, and n_i and M_i are the number density and mass of the ions (protons in this case). For wave vectors $\vec{q}$ outside the first Brillouin zone, $\hat{e}_{\vec{q}\lambda}$ and $\omega_{\vec{q}\lambda}$ are found by subtracting a reciprocal-lattice vector from $\vec{q}$ to obtain a vector in the first zone. The Green's function $D_\lambda(\vec{q},i\omega_n)$ is expressed in terms of a spectral density $B_\lambda(\vec{q},\omega)$ via

$$D_\lambda(\vec{q},i\omega_n)=\int_0^{\infty}d\omega\frac{2\omega B_\lambda(\vec{q},\omega)}{\omega^2-(i\omega_n)^2}\ , \qquad (5)$$

where $B_\lambda(\vec{q},\omega)$ is proportional to $\delta(\omega-\omega_{\vec{q}\lambda})$ for a purely harmonic lattice. The Eliashberg function is then related to $B_\lambda(\vec{q},\omega)$ by

$$\alpha^2F(\omega)=N(0)\sum_\lambda\int_0^{2k_F}dq\left(\frac{q}{2k_F^2}\right)|v_{\rm ei}(q)|^2\left(\frac{\hbar n_i}{2M_i\omega^2_{\vec{q}\lambda}}\right)(\vec{q}\cdot\hat{e}_{\vec{q}\lambda})^2B_\lambda(\vec{q},\omega)\ , \qquad (6)$$

where $N(0)$ is the density of states per spin at the Fermi energy and $v_{\rm ei}(q)$ is the effective interaction between electrons and ions, including screening, vertex corrections, and nonlinear effects. For simplicity we have performed an average over a spherical Fermi surface, as would be appropriate for a disordered superconductor. If we substitute (5) into (4), take the frequency integral outside the sum on polarizations, and compare with (3) we obtain an expression for $\chi''(\vec{q},\omega)$ in terms of $B_\lambda(\vec{q},\omega)$. This can be substituted in (6) after taking the polarization sum inside the momentum-transfer integral:

$$\alpha^2F(\omega)=N(0)\int_0^{2k_F}dq\left(\frac{q}{2k_F^2}\right)|v_{\rm ei}(q)|^2\,\frac{\chi''(\vec{q},\omega)}{\pi}\ . \qquad (7)$$

Expressions equivalent to (7) have been derived for amorphous metals[11]; since the response function χ is well defined for both amorphous and liquid metals, we propose that (7) is valid for liquid metals [even though (4) and (5) above are not]. To justify this extension of (7) to a low-temperature liquid metal we give an argument based on diagrammatic perturbation theory in which both electrons *and protons* are treated as interacting Fermi systems. Let us consider the full interaction between two electrons, including all possible polarization insertions involving either protons *or* electrons. A typical term in the expansion for this interaction involves a polarization insertion which can be divided into proper polarization parts, each of which begins and ends with either an electronic- or an ionic- (proton-) density fluctuation. Those terms in which only electronic proper polarization insertions appear can be summed to give the screened Coulomb repulsion. Now consider the set of all diagrams with a given set of ionic proper polarization insertions and a fixed set of electronic polarizations between ionic ones. The electronic polarizations occurring to the left or the right of all the ionic polarizations can be summed to give once again, screened Coulomb interactions at each end of the diagram. In this way the *effective* interaction between electrons may be diagrammatically expressed as shown in Fig. 1, and the Eliashberg function is obtained from this interaction by averaging over the Fermi surface.

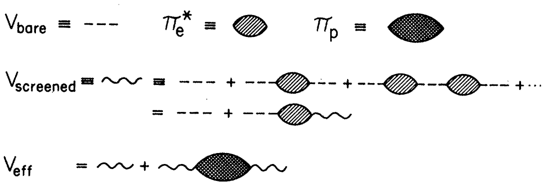

FIG. 1. Structure of screened interactions and the total effective interaction between electrons. Π_e^* is the set of all bubble diagrams beginning and ending with an electron density fluctuation which cannot be separated by cutting one bare-interaction line. Π_p is the set of all diagrams beginning and ending with a proton density fluctuation, separable or not. The second term in $V_{\rm eff}$ gives rise to the expression for $\alpha^2F(\omega)$.

We now give an approximation for the ion density-density response function whose imaginary part appears in (7). A first-principles calculation is likely to be intractable, so we use a phenomenological approach and some results of previous microscopic treatments of solid metallic hydrogen,[6,9,12] the latter being more amenable than the liquid to an *ab initio* theory. We write the response function for the screened interacting protons in terms of a random-phase-approximation- (RPA) like expression involving the noninteracting response function[13] and an effective proton-proton interaction $f(q,\omega)$:

$$\chi(q,\omega)=\frac{\chi^{(0)}(q,\omega)}{1-f(q,\omega)\chi^{(0)}(q,\omega)} \quad . \tag{8}$$

Theories of this form have been proposed[14] for ^{3}He, classical fluids,[15] and the interacting electron gas.[16,17] Our own approximation to this function is based on the requirement that the liquid have the same long-wavelength sound velocity as solid metallic hydrogen at the same density, a quantity calculated by Straus,[9] Mon *et al.*,[6] and others.[12] We also make the ansatz that the effective interaction between protons is independent of frequency and temperature, and that its Fourier transform $\tilde{f}(r)$ has the form of a screened Coulomb interaction for r greater than some r_c, and is constant for $r < r_c$. We then fix r_c by the requirement that $f(q)$ must give the desired sound velocity as $q \rightarrow 0$. This construction is in the same spirit as the polarization potential approach[14] used in ^{3}He, but for liquid metallic hydrogen it is less constrained for lack of experimental information.

When $\chi''(q,\omega)$ is computed from (8) using this $f(q)$, we obtain a density-fluctuation spectrum in the (q,ω) plane that is typical of a neutral Fermi liquid.[18] This is to be expected since the screening of the ions gives an acoustic spectrum instead of an ionic plasmon of frequency $(4\pi ne^2/M_i)^{1/2}$. There is, of course, an electronic plasmon at high frequencies which is not treated explicitly. Its effect is contained in the usual parameter μ^*.

To compute $\alpha^2F(\omega)$ from $\chi''(q,\omega)$ we need to know the effective interaction $v_{\text{ei}}(q)$ between the electrons and protons. The absence of core electrons removes uncertainties encountered in ordinary metals in the choice of a pseudopotential, but a new difficulty appears because linear-response theory for the electron gas begins to break down. This problem is often treated by replacing the screened Coulomb interaction of linear response by an effective electron-ion interaction which incorporates nonlinear effects in some approximation. Carbotte *et al.*[5] have obtained this interaction by a density-functional technique; we approximate their results for the function $v_{\text{ei}}(q)$ [called by them $w(q)$] by a rescaling of the linear-response result, and then fit the scale factors to a polynomial function of r_s in order to extrapolate their results into the density range treated here. The function $\alpha^2F(\omega)$ which results from this procedure is remarkably similar to that found for a crystalline solid. In both cases there is a peak at high frequency coming from the longitudinal phonons. In addition the liquid shows a broad background at lower frequency which comes from the diffusive particle-hole spectrum of the screened protons. This background might be regarded as a remnant of the low-frequency peak which arises in crystals from umklapp processes and is related to transverse phonons.

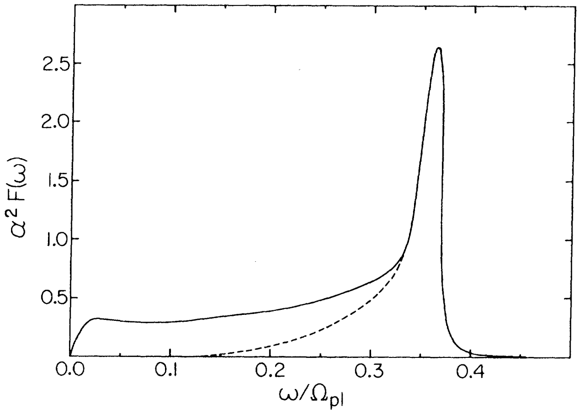

FIG. 2. Eliashberg function $\alpha^2F(\omega)$. The frequency is expressed as a fraction of the ionic plasmon frequency $\Omega_{\text{pl}}=(4\pi n_i e^2/M_i)^{1/2}$. The dashed curve indicates the results expected if there were only a longitudinal sound mode, and no single-ion excitations present.

In computing T_c as a functional of $\alpha^2F(\omega)$, we encounter an interesting self-consistency problem which is not present for solid superconductors. In the liquid case $\alpha^2F(\omega)$ is itself dependent on temperature (which is not the case in a harmonic solid). It follows that $T_c(\alpha^2F(\omega))$ also depends on the assumed temperature of the system. That is, we must compute a function $T_c(T)$ and the true transition temperature is then given by the quantity T_c^* which satisfies

$$T_c^*=T_c(T_c^*) \quad . \tag{9}$$

We have obtained $\alpha^2F(\omega)$ at several densities using reasonable initial guesses for the temperature, and then computed T_c using an Eliashberg equation computer subroutine.[19] This T_c is used to find a new $\alpha^2F(\omega)$, and the procedure is iterated until (9) is satisfied to high accuracy. In practice, about five iterations are found to be sufficient, and the results are given in Table I. The transition temperatures are comparable to those found for solid metallic hydrogen by other authors, and are likely to exceed the melting point in some density range (although at very high densities the system becomes normal again). The assumption of a liquid superconducting state is thus justified (see Table I).

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[19] Kindly provided to us by Dr. D. Rainer.