Cell Model of hydrogen Liquid at Megabar Pressures

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The phase diagram of dense hydrogen has been constrained by a combination of techniques. [after Goncharov and Crowhurst, Phase Trans. (2007)]
Рис. 1. Влияние квантовых эффектов на кривую плавления: (а) случай кулоновского взаимодействия; (б) случай короткодействующего отталкивания.

Д. А. Киржниц
С. М. Стишов, УФН , 171, №3, 2001
Cold curve for Hydrogen

- Davis
- Kagan
- our appx.
- exp. Boriskov

Calc. Redmer T=3000 K

P, GPa vs. v, Å³
Температура $T = 0$; 

$N = (0.05 \div 10) \cdot 10^{24} \text{ см}^{-3}$;

Среднее расстояние $R = (0.3 \div 1.7) \cdot 10^{-8} \text{ см}^{-3}$

$\alpha_0 = 0.53 \cdot 10^{-8} \text{ см}^{-3}$

Давления $(100 \div 600) \text{ ГПа}$
Cell model of quantum liquid

Every ion localizes in the W-Z cell

$$R = \left( \frac{3}{4\pi} \right)^{1/3} \frac{1}{N^{1/3}}$$

Electron density in the cell

$$n(r) = n_b(r) + n_f$$

Density of localized states is

$$N_b(r, T, \mu) = \frac{1}{\pi} \frac{\exp(-2r)}{1 + \exp[-(E - \mu)/T]}$$

The cell is neutral, there are continuous states over the cell, distributed uniformly over the cell, their density equals

$$N_f(T, \mu) = \frac{(2T)^{3/2}}{2\pi^2} I_{1/2} \left( \frac{\mu}{T} \right)$$

$$I_{1/2}(x) = \int_0^\infty y^{1/2} dy / \left( 1 + e^{(y-x)/T} \right)$$
Cell is electrically neutral

\[ 4\pi \int_0^R r^2 \, dr \left[ n_b(r) + n_f \right] = 1 \]

\[
1 - e^{-2R} \left(1 + 2R + 2R^2\right) + \frac{(2T)^{3/2}}{2\pi^2 n} I_{1/2} \left(\mu / T\right) = x_b + x_f = 1
\]

\[ T \to 0 \]

\[ N_b(r) = e^{-2r} / \pi \quad ; \quad N_f = e^{-2R} \left(1 + 2R + 2R^2\right)n \]

\[ x_b = 1 - e^{-2R} \left(1 + 2R + 2R^2\right) \quad ; \quad x_f = e^{-2R} \left(1 + 2R + 2R^2\right) \]

\[ \mu = \frac{p_F^2}{2} = \frac{(3\pi^2)^{2/3}}{2} (x_f \, n)^{2/3} \]
**Kinetic energy of localized electrons**

\[ T_b = \left( \frac{p^2}{2} \right) = 4\pi \int_0^R r^2 dr R_{10}(r) \nabla^2 R_{10}(r) = -4\int_0^R r^2 dr e^{-r} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} e^{-r} \right) = \]

\[ = \left[ 1 - e^{-2R} \left( 1 + 2R + 2R^2 \right) \right] \]

**Kinetic energy of delocalized electrons**

\[ T_f = \left( \frac{3\pi^2}{5} \right)^{2/3} \frac{3n_f^{5/3}}{4\pi} \int_0^R r^2 dr = \left( \frac{3\pi^2}{5} \right)^{2/3} \frac{3N^{2/3}}{5} \left[ e^{-2R} \left( 1 + 2R + 2R^2 \right) \right]^{5/3} \]

**Electron-ion energy of interaction**

\[ U_{ei} = -4\pi \cdot 2 \int_0^R r^2 dr \frac{n(r)}{r} = -2 \left[ 1 - e^{-2R} \left( 1 + 2R \right) \right] \]

\[ U_f = -4\pi \cdot 2 \int_0^R r^2 dr \frac{N_f(r)}{r} = -4\pi \left( \frac{3}{4\pi} \right)^{2/3} x_f n^{1/3} \]

\[ I = T_b + U_b = -1 + e^{-2R} \left( 1 + 2R + 2R^2 \right) \]
Electron-electron and exchange interactions

Self-consistent potential, formed by all charge particles

\[ \Phi(r) = \frac{1}{r} - \int \frac{n(r')r'^2 dr'd\Omega'}{|r-r'|} \]

\[ \Phi(r) = \frac{1}{r} - 4\pi \cdot \left[ \frac{1}{r} \int_0^r r'^2 dr'n(r') + \int_r^R r'n(r')dr' \right] = \frac{1}{r} - V_b(r) - V_f(r) \]

Middle electron interaction energy

\[ U_{ee} = -4\pi \int_0^R \left[ V_b(r) + V_f(r) \right] n(r)r^2 dr \]

Exchange addition to potential

\[ \Phi_{ex}(r) = \left( \frac{3}{\pi} \right)^{1/3} n(r)^{1/3} \]

Exchange potential energy

\[ \alpha = 1.15 \quad \text{Is fitting parameter} \]

\[ U_{ex} = 8\pi \alpha \left( \frac{3}{\pi} \right)^{1/3} \int_0^R r^2 drn(r)^{4/3} \]
\[ R = U_{ee} + U_{ex} = W = 4\pi \int_0^\infty [V_b(r) + V_f(r)]N(r)r^2 dr - 8\pi a \left( \frac{3}{\pi} \right)^{1/3} \int_0^\infty r^2 dr N(r)^{4/3} \]

In the limit \( N \to 0, \ R \to \infty, \ U_{ex} + U_{ee} \to 0 \) Like as in hydrogen atom

**Total Energy**

\[ E = I + R + T_f + U_f \]

\[ E = I(n) + R + \left( \frac{3\pi^2}{5} \right)^{2/3} \frac{3}{n^{2/3}} x_f^{5/3} - \alpha(n)n^{1/3} \]

\[ \alpha(n) = (36\pi)^{1/3} x_f \quad (\ast) \]
Contribution of different terms in full cell energy

Energy vs. \( n \)

- \( T_f \)
- \( R \)
- \( E \)
- \( U_f \)

\( n \) ranges from 0.0 to 1.0.
Proton contribution

Both electrons and protons are degenerate at $T = 0$. Their wave length in this limit is:

$$\lambda = \frac{\hbar}{p_F} = 1/(3\pi^2)^{1/3} n^{1/3}$$

The relation of this wave length to the cell radius equals to:

$$\frac{\lambda}{R} = \frac{1}{(3\pi^2)^{1/3} n^{1/3}} \left(\frac{4\pi}{3}\right)^{1/3} n^{1/3} = \left(\frac{4}{9\pi}\right)^{1/3} \approx 0.52$$

This constant does not depend on density. The proton wave length and the relation at finite temperature are and (here $T$ and $n$ are expressed in $K$ and Å$^{-3}$ correspondingly). The latter relation equals to $\sim 0.42$ at $n = 0.1$ and $T = 1000$ K. So we have degenerate protons over the entire domain of our consideration.

This atomic – like structure of diameter $2Ra$ and mass $M$ (proton) is confined to move in a space with characteristic dimension

$$\Delta(n) = 2R(1 - 4\pi nR_a^3 / 3)$$

, the mean – proton spacing with the correction due to the own size of the atomic-like structure
The free energy of degenerate proton gas at low temperatures can be presented as

\[ F_p = \frac{(3\pi^2)^{2/3}}{5} \frac{3m}{M} \frac{1}{\Delta(n)^2} - \left( \frac{\pi}{3} \right)^{2/3} \frac{M}{4m} \Delta(n)^2 T^2 ; \text{Ry} \]

**COMPARISON MS AND AS FREE ENERGIES AT T = 0**

\[ E' = I + R + T_f + U_f + 2 + \frac{D}{2} \]

\( D \) is the energy of dissociation of the molecule (0.165 Ry/atom)
Comparison of MS and ML free energies at $T=0$

$\nu_1 = 4.76$
$\nu_s = 8.2$
$p = 382$ GPa
Conclusion

If it is possible to get a quantum metastable hydrogen liquid as molecular hydrogen solid is subjected to melting at megabar pressure

Reference