4 A Case Study: Hydrogen

The most abundant planetary ingredient is hydrogen. In this chapter we discuss the behavior of this material. However, we will also use this case study as an opportunity to introduce a number of basic ideas involving phase transitions. In reality, even this simplest of elements turns out to be remarkably complicated and the approach described here is inadequate. However, it still serves as a valuable introduction to the general ideas.

4.1 What is the Zero Pressure Ground State of Hydrogen?

In the last chapter, we calculated the energy for a uniform ensemble of hydrogen as protons and electrons. The zero-pressure energy for this state (when computed as carefully as possible; i.e., including correlation and band structure) is about -1.03 or -1.04 Rydbergs per hydrogen (or equivalently, per electron), so it is bound relative to hydrogen atoms (which lie at exactly −1.00 Rydberg). It is not, however, lower than the energy per proton of molecular hydrogen gas, liquid, or solid, where the energy is about -1.15 Ryd. (It takes about 4 eV, or 0.3 Ryd, to bust up a hydrogen molecule.) So hydrogen prefers to form molecules at zero pressure. (This is not true of other first column elements in the periodic table, i.e., Li, Na, K...)

4.2 The Molecular-Metallic Transition in Hydrogen; A Traditional View

We have seen that hydrogen could exist in a metallic state (free-electron-like state) analogous to alkali metals. Recall that hydrogen is in column one of the periodic table. But we know from everyday experience that hydrogen normally exists as diatoms (molecules with bound electrons). At sufficiently high pressures, the metal must win. The reason is that when the molecules are as close to each other as the distance between the protons, then there is no longer benefit from strongly correlating the electrons with the protons. Indeed, the Pauli exclusion effect together with Heisenberg’s uncertainty principle will lead to a very high penalty for clumping the electrons... they will want to be as uniformly distributed as possible. So the energies of the two states (molecular and metallic) must cross.

The energy per proton of the molecular state can be approximated as:

\[ E = -1.15 + \frac{1}{2} [E_{\text{zero point}} + \frac{1}{2} \sum_{i \neq j} \phi(|\vec{r}_i - \vec{r}_j|)] \]  

(4.1)

and obviously depends crucially on \( \phi \), the potential of interaction between the hydrogen molecules. (Since this is the energy per proton, we must divide the zero point energy of a molecule by one half and the other factor of one half comes from the double counting that

\[ \text{This argument is not as straightforward as it seems and might even be wrong in some cases. The problem is that the approach to uniformity in the electron gas does not automatically imply that the material is a metal. The latter requires availability of nearby empty states for the electrons. We can nonetheless compare the energy of the assumed molecular state and the theoretically predicted metallic state and find when the latter is preferred. That’s what we are doing here.} \]
arises from the summing of intermolecular interactions.) In reality, this use of a pair potential is only an approximation to a many body problem. An equivalent way of saying this is that it is not really a pair potential (it depends on the presence of other molecules) and it is not strictly a function of spacing. This is the major problem with doing the calculation, and is a reason why we still do not know the transition pressure.

In order to understand where this transition pressure occurs, we must first review some elementary thermodynamics. At any temperature and specified pressure, we want to find the state with lowest Gibbs energy, where Gibbs energy is defined by

\[ G = E + PV - TS \]

We can easily understand why this must be true by considering a system at the transition pressure (here we focus on the zero temperature case, but a similar argument can be made for finite temperature). If we are at the transition pressure and change a small amount from phase 1 (volume \( V_1 \)) to phase 2 (volume \( V_2 \)), then the energy change is \( E_2 - E_1 \) and the work done by the rest of the material on the part that has changed phase is \( P(V_1 - V_2) \). The net energy cost must be zero in equilibrium, and thus

\[ E_2 - E_1 = P(V_1 - V_2) \quad (4.1) \]

But this is algebraically equivalent to saying that the phases have equal Gibbs energies (at zero \( T \)) at the transition pressure. Therefore, the way to find a phase transition is to look for a crossing of the two Gibbs energy curves as a function of pressure (see figure below). Notice that the high pressure stable phase must have lower \( dG/dP = \text{specific volume} \) (i.e., higher density).

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**Figure 4.1**

Graphically, this can also be done as a Maxwell construction. The Maxwell construction involves finding a common tangent to the two curves for internal energy as a function of specific volume. (At finite temperature, it is done with the Helmholtz free energies.) Below, we see it sketched for hydrogen, together with a sketch of what it looks like in the pressure-volume plane. Note that if you only have P-V data or theory for each phase, then you don’t have enough information to decide on the location of the phase boundary! The reason is that the phase transition is determined by the energy, and a P-V diagram involves only the derivative of energy, not energy itself—phase changes can be observed,
however, as sudden drops in volume during a compression experiment, as long as the phase transition is not kinetically inhibited.

**Figure 4.2**

Below, we see the “actual data” with the metallic hydrogen equation of state superimposed. These constructions are often the best way of understanding whether there should be a phase transition. However, the presence of an offset in two P-V curves does not imply that there must be a phase transition—it might instead simply indicate an inadequate theory. At present, the pressures that appear to be needed for this transition are not achievable by experiments, except at very high temperature. It is possible that this “monatomic” metallic state appears at a pressure of maybe 4 to 6 Megabars (still reached at 70% of the radius of Jupiter), but this remains uncertain and might not even be that important, as explained below.
4.3 What is Really Happening in Hydrogen?

This is still not fully understood, but it is now clear that the simple picture described above is not correct. It is likely that the metallization of hydrogen proceeds through an intermediate phase that still contains molecules and yet is a metal, albeit a poor one. In the context of the band picture of materials, this is a very plausible thing, supported by detailed calculation (and to some extent by experiment). As an example of theory, look at the work of Saumon and Chabrier (e.g. Phys. Rev., v46 p2084, 1994). As an example of the experimental effort, look at any of many papers by Nellis and coworkers. The shock
wave data suggest metallization by band overlap in a semiconductor *without destroying the molecules.*

*Figure 4.4*

This picture appears to be consistent with the electrical conductivity data (next Figure) which shows a rapid decline of resistance with pressure, followed by a “plateau” at a value that is reasonable for a poor metal. For comparison, the resistivity of liquid metallic Fe in Earth’s core is thought to be around $10^{-4}$ ohm-cm, the resistivity of copper at room temperature is a few times $10^{-6}$ ohm-cm, and the resistivity of “water” is perhaps $10^{-3}$ ohm-cm under the high pressure, high temperature conditions appropriate for Uranus or Neptune. The latter is of interest because it is presumably protonic conduction rather than electronic. Thus, the conductivity value measured for hydrogen is only a factor of ten or so above the value that might be explained by protons rather than electrons, leaving open the question of the role of the protons.
Examples of some of the most recent theoretical work on hydrogen and on hydrogen-helium mixtures are to be found at

http://militzer.berkeley.edu/

(the work of Burkhard Militzer at UC Berkeley, and collaborators). In this work, Schroedinger’s equation is solved over and over as the positions of protons in a box are changed (representing all possible configurations in a fluid). Density functional theory is used. This means that one-electron wave-functions are used, but allowing for the exchange appropriate for a non-uniform electron gas. This work does not support the existence of a first order phase transition between molecular and metallic hydrogen but instead shows a gradual and complex change in proton-proton correlation as density and pressure are increased. These results have been incorporated into giant planet models but there are still some problems. We will discuss the extent to which this has been achieved in a later chapter.

Ch. 4 Problems

4.1) In shock wave experiments, it is found that at extreme pressures, the pressure-density relationship becomes nearly vertical (i.e., the pressure increases without bound but the density saturates at a nearly constant value).
Conservation of energy (one of the Rankine-Hugoniot equations) must be satisfied:

\[ E - E_0 = \frac{1}{2} (P + P_o) (\frac{1}{\rho} - \frac{1}{\rho_o}) \]

Here, \( \rho \) is the density of the shocked material, \( \rho_o \) is the density of the unshocked material, \( P \) is the pressure of the shocked material, \( P_o \) is the pressure before shocking; likewise \( E \) and \( E_o \). Assume a strong shock for which \( P_o, E_o \) can be ignored, there is a large density increase, and most of the energy gain goes into temperature increase. Explain what a nearly vertical pressure versus density result implies for the relationship between shock pressure and shock temperature and how this might be reconciled with the equation of state.

**Answer:** If \( E \) becomes mostly thermal then \( E \sim C_v T \sim P/2 \rho_o \) (i.e., ignoring the \( 1/\rho \) term) where \( C_v \) is the specific heat (and might include the effects of dissociation). \( P = 2 \rho_o C_v T \) and therefore \( T \approx P \). From fundamental thermodynamics, i.e., the Maxwell relations, the thermal part of the pressure equals \( \gamma P \), where \( \gamma \) is the a dimensionless number known as the Gruneisen parameter. This is discussed further in a later chapter.) This is compatible with the total pressure if \( \rho/\rho_o \) goes to a constant value at very high \( P \) and \( T \). The non-thermal part of the pressure depends on \( \rho \) and does not increase further, whereas the thermal pressure is unbounded because \( E \) and \( T \) continue to increase as \( P \) increases. Accordingly, a nearly vertical pressure vs. density curve results. [There are many assumptions in this argument and it can only be made vigorous for a dissociating ideal gas, but this argument as presented captures the essential character of the shock data.]

4.2) Suppose we have a material for which the internal energy is given by

\[ E = a/V^3 + b/V^2 + c/V \]

where \( V \) is the specific volume. Assume \( T = 0 \). The volume must be positive and the pressure \( P \) of the material is assumed to be non-negative. Find the criteria involving \( a, b \) and \( c \) such that this equation represents a material that is (i) One stable phase at all physical \( V \) and \( P \); (ii) One stable phase over a finite range of \( V \) and no phase at any other range of physical \( V \); (iii) Exhibits a first order phase transition for physically meaningful choices of \( V \).

**Hint:** A thermodynamically stable material must have a positive bulk modulus. Why?

4.3) Estimate the metallization pressure of helium as follows. Assume the metallic equation of state is obtained as described in the text (i.e., Fermi +Coulomb +Exchange with \( Z = 2 \)). Assume the atomic (i.e., insulating) equation of state takes the form \( P = K \rho^4 \) where \( P \) is in Megabars, \( \rho \) is in g/cc and \( K = 0.1 \) Mbars (so \( P = 1.6 \) Mbar at \( \rho = 2 \) g/cc). One other essential piece of information: The first ionization energy of the helium atom is \( 3.94 \times 10^{-11} \) ergs and the second ionization energy is \( 8.72 \times 10^{-11} \) ergs (i.e., 4 Rydbergs). Everything you do is at
absolute zero temperature. Also estimate the densities (in g/cc) for the two coexisting phases at the phase transition pressure.

The main part of this problem is to understand how to get from this information to what the question requests. The secondary thing is converting among different units, etc, which may seem annoying but you have to be able to do this in science! You will need Avogadro’s number (6 x 10\(^{23}\)), among other things. Here is an intermediate result to check that you’re doing it right: In helium, 1 Ryd/eln is the same as ~6.5 x 10\(^{12}\) erg/g. (but derive this, don’t use my number!) You will probably want to do this problem numerically (i.e., with Mathematica or whatever) but it is not essential to use a computer. Notice that the equation I have given you for atomic helium has no equilibrium density (it wants to expand without limit.) This is a very minor “error” since the binding energy of liquid helium is negligible on the scale of energies considered here). A realistic answer for this approach is tens to hundreds of Megabars. The “true” metallization pressure of helium is tens of megabars but depends on temperature and involves closure of a mobility gap rather than a simple calculation of the type you’ve done here. [For a commentary on the most recent work on this , see D. J. Stevenson, Proc. Natl. Acad. Sci. , vol 105, p11035 (August 12, 2008). But this will not help you do the problem.]

4.4) A popular (but very crude) pair potential is inverse twelfth \(\Phi \sim r^{-12}\) (the repulsive part of the Lennard-Jones potential). Show that this predicts an equation of state of the form \(P \propto \rho^5\). A more realistic potential (for a limited range of interparticle spacings) is \(\Phi \sim \exp(-r/r_1)\) where \(r_1\) is some specified constant. In both cases, assume that only nearest neighbor particles contribute significantly to the total energy (in the sense of equation 4.1). Show that there must be some pressure above which this gives a softer equation of state, where softness is defined by the smallness of \(d^2P/dn^2\). This parameter is 5 for Lennard –Jones at high P and 5/3 for the Fermi gas and ~2 for metallic hydrogen in Jupiter. (In this sense, metallic hydrogen is much softer than a Lennard Jones fluid… that’s why it will be eventually favored at sufficiently high P). The value of \(d^2P/dn^2\) has a crucial role to play in defining the behavior of planets, e.g., their radius-mass relationship.