“Rocks”, “Ices” and “Gases”
The cosmically most abundant elements can be divided into three groups:

“Gases”: those that do not condense (i.e. form solids or liquids) under conditions plausibly reached when planets formed;

“Ices”: those that form volatile compounds and condense but only at low temperatures (beyond the asteroid belt);

“Rocks”: those that condense at high temperatures and provide the building blocks for the terrestrial planets.

It is important to understand that these are labels of convenience; nothing is ever so simple that you could so easily subdivide materials. The quotation marks are there to remind you that what we call an ice is sometimes in the gas or liquid phase, etc. But the subdivision proves nonetheless of great usefulness because of the large differences in behavior and abundances among these groups.

The gases are hydrogen, helium and (to a much lesser extent) the noble gases. [Note: Noble gases on Earth are tiny quantities carried to Earth adsorbed on solid particles; thus neon is of low abundance on Earth despite having much higher cosmic abundance than silicon.] The gases are thus overwhelmingly what the universe is made of, and what the Sun is made of and (as we shall see) what Jupiter is made of. The hydrogen molecule H$_2$ is the low pressure thermodynamic state of H and it interacts with other hydrogen molecules and with helium by a van der Waals interaction, meaning that it is a very weak force except when the molecules are pushed very close together. That’s why condensing hydrogen requires very low temperatures. It’s also why it’s easy to squeeze hydrogen (as a liquid or solid or, of course, as a gas) until you approach densities where the distance between molecules is about the size of a molecule.

The ices are mostly hydrides of the next set of light elements: O, C and N (i.e. water, methane and ammonia respectively). But they also include other
combinations among themselves (e.g. \( \text{N}_2 \), \( \text{CO} \), \( \text{CO}_2 \), HCN....) As we discussed last time, hydrides do not necessarily dominate (they don’t seem to in the interstellar medium) but they are thermodynamically favored when the partial pressure of hydrogen is high and will thus form if temperature or pressure permits reactions to occur. Water is the least volatile of this set because of hydrogen bonding between water molecules (which you can think of loosely as a weak form of ionic bonding arising from the very non-uniform charge distribution around the water molecule). Ammonia also has some hydrogen bonding. Methane and molecular nitrogen rely on van der Waals bonding in the liquid and solid state. CO has a small dipole moment but also interacts mostly by Van der Waals.

“Rocks” include both metallic materials (iron and iron-nickel alloys) as well as what we might usually call rock (oxides and silicates). Here one has strong ionic and covalent bonding. Metallic bonding can be thought of as a special case of ionic bonding (with the electrons providing a spatially distributed charge rather than the discrete charges of an ionic material such as \( \text{NaCl} \)). These materials are much more tightly bound, hence involatile and stiffer. The main constituents are Fe, \( \text{MgSiO}_3 \), \( \text{Mg}_2\text{SiO}_4 \), “FeO” (quotation marks refer to several different oxidation states), but of course Fe can substitute for Mg to a limited extent and form solid solutions, e.g., \( (\text{Mg,Fe})_2\text{SiO}_4 \).

To summarize then, we have:

<table>
<thead>
<tr>
<th>Type of bonding</th>
<th>Examples</th>
<th>Solid Densities at low P</th>
<th>Bulk modulus of solid</th>
<th>Locations found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals</td>
<td>Hydrogen, helium, methane, ( \text{N}_2 )</td>
<td>e.g. hydrogen is (~0.07) g/cc</td>
<td>e.g. hydrogen is a few kilobars</td>
<td>Giant planets (also ( \text{CH}_4 ) &amp; ( \text{N}_2 ) on icy satellites)</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td>Water, ammonia</td>
<td>Around unity</td>
<td>Ten kilobar (roughly)</td>
<td>Giant planets, icy satellites</td>
</tr>
<tr>
<td>Ionic and covalent (including metallic)</td>
<td>“Rocks”, metallic iron</td>
<td>Rocks are around (3)g/cc; iron is near (8) g/cc</td>
<td>Typically of order one megabar</td>
<td>Terrestrial planets, cores of giant planets(?) icy satellites</td>
</tr>
</tbody>
</table>
The type of bonding refers to the low pressure behavior; everything becomes a metal at high pressure. (In Jupiter, the only material that fails to metallize is helium).

The bulk modulus is an important material property:

\[
\text{Adiabatic bulk modulus } K_s \equiv \rho \left( \frac{\partial p}{\partial \rho} \right)_s
\]

\[
\text{Isothermal bulk modulus } K_T \equiv \rho \left( \frac{\partial p}{\partial \rho} \right)_T
\]

\[p = \text{ pressure}\]
\[T = \text{ temperature}\]
\[\rho = \text{ mass density}\]
\[S = \text{ entropy}\]

so bulk modulus has units of pressure. [Reminder: One bar is \(10^6\) dynes/cm\(^2\) or \(10^5\) Pascals; and it is roughly the pressure at Earth’s surface. ]

**So What are the Pressures inside Planets?**

Clearly the bulk modulus is a measure of the strength of interaction among the molecules in the material... soft (weakly bound, volatile) materials compress easily while tightly bound materials are stiff. It is also a guide as to how much density change might arise in a planet due to internal pressure. From the definition of \(K\), \(\Delta \rho/\rho \sim p/K\) (i.e., the fractional change in density between surface and deep interior is roughly the pressure in the deep interior divided by the bulk modulus). If the actual pressure is comparable to the bulk modulus then you might expect the density inside the planet to be considerably larger than at the surface. We can estimate the pressure by assuming that the density is roughly constant; obviously this is only a very rough guide but it gives a “warning” (i.e., tells you whether your assumption was a good one) and actually not too bad an approximation. In the following, \(\bar{\rho}\) with an overbar is the mean density, \(M(r)\) is the mass inside radius \(r\), etc.
Hydrostatic equilibrium ⇒ \( \frac{dp}{dr} = -\rho(r)g(r) \)

\[ g(r) = \frac{GM(r)}{r^2} \approx \frac{4}{3} G\pi \bar{\rho}r \]

\[ p(r) \approx \int_{r}^{R} \frac{4}{3} G\pi \bar{\rho}^3 x dx \]

∴ \( p(r) \approx \frac{2}{3} G\pi \bar{\rho}^2 (R^2 - r^2) \)

\[ P_{center} \approx (1.4 \text{ kilobars}) \left( \frac{\bar{\rho}}{1 \text{ g/cc}} \right)^2 \left( \frac{R}{1000\text{ km}} \right)^2 \]

For the Moon this predicts about the true central pressure (not surprisingly). For Earth, it predicts around 2 Megabars (true value about 3.6). For Jupiter, it predicts around 10Mbar (actual is 40 or more). This crude formula underpredicts the central pressure of differentiated bodies (which is to say, all planets), especially when the core has a density much larger than the mean density.

**How do We Figure out the Behavior of Materials at High Pressure?**

If we want to figure out what goes on in a planet then we need to know how the materials listed above behave at planetary pressures. One approach is experiment. This is extremely important, and we will talk about some experimental constraints in due course. The experimental techniques are of two kinds: shock waves or static compression (e.g. diamond cell). But experimental data alone are not enough for two reasons: (1) Experiments do not usually get to the full range of conditions encountered in planets. For example, pressures deep within Jupiter are unattainable by conventional techniques. (2) Even when experiments reach relevant conditions, they seldom map out enough of the thermodynamic phase space (T, P and composition) to be sufficient for planetary modeling (where one needs a fine grid of parameter values). So it helps greatly to have a theoretical framework to incorporate experimental results and to extrapolate and interpolate.

Here are the theoretical frameworks one can use:
(1) **Parameterizations of convenience.** These are non-physics based, simple recipes, fitted to data. Because they are not based on a real theory they are dangerous. They are extensively used because they are convenient. An example is the Birch-Murnahan equation of state, heavily used in geophysics.

\[ p = \frac{3}{2} K \left( \frac{\rho}{\rho_o} \right)^{5/3} \left[ \left( \frac{\rho}{\rho_o} \right)^{2/3} - 1 \right] \]

where \( K \) is the zero pressure bulk modulus.

(2) **Asymptotic theories.** Here one appeals to the simplifications that arise at very high pressure. The free electron gas approach (below) and Thomas-Fermi-Dirac theory are examples. This is an excellent approach for metallic hydrogen, for example (and for brown and white dwarf stars in general).

(3) **Brute force solution of Schrödinger’s equation.** Often you will find this referred to as *ab initio* calculations. Immense advances in computer power have made this possible for quite complex systems. It is still only really practical for systems that have periodicity (crystals) or for small numbers of atoms (much less than Avogadro’s number!) This is now being extensively done for complex earth materials as well as for more complicated systems.

(4) **Pair potentials** This is the time-honored physical chemists approach of identifying species (atoms, molecules, clusters) and representing the energy as the sum of pairwise interactions among them.

\[ E = \frac{1}{2} \sum_{i<j} \phi |\vec{r}_i - \vec{r}_j| \]

This is often carried out in a **Monte Carlo** or molecular dynamics simulation on a computer.

**Monte Carlo** is a method in which you seek the ground state energy by taking an ensemble of molecules or atoms and then moving one of them at random and deciding probabilistically (like a gambler!) whether to accept the move. A good move is one that lowers the total energy, but even a “bad”
move should be accepted with some finite probability, in accordance with the fundamental rules of statistical mechanics.

*Molecular dynamics* is very simple: You solve $F=ma$ for an ensemble of molecules bouncing off each other, and calculate the total energy.)

An excellent example of the state of the art, incorporating aspects of both (3) and (4) is the work of Chiarotti and colleagues, e.g. “Superionic and metallic states of water and ammonia at giant planet conditions,” Cavazzoni C, Chiarotti GL, Scandolo S, Tosatti E, Bernasconi M, Parrinello M; *Science* **283** 44-46 (Jan 1, 1999). In this work, ab initio calculations are used to find a suitable empirical potential and then molecular dynamics is used to determine the behavior a system interacting classically in accordance with that potential.

**The High Pressure Limit**

It is a good idea to get some physical understanding of why materials resist compression, and one way to do this is to construct a theory that works at very high pressures. This turns out to be an excellent approximation for the deep interior of Jupiter, as well as being pedagogically valuable.

Materials resist compression because of quantum mechanical effects. This is very important! One tends to think of materials as consisting of positive and negative charges, and imagines Coulomb forces as being the reason materials don’t like being squeezed. But a moment’s thought tells you this must be nonsense: Matter is neutral overall, and the assemblage of positive and negative charges is energetically favorable (unlike charges attract). In fact, material would spontaneously collapse if Coulomb forces dominated. The important thing is that from Schroedinger’s equation, electrons do not like to be confined in a small volume. Recall that Schroedinger’s equation takes the form:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) \Psi = E \Psi$$

where $V$ is the potential, $\Psi$ is the wavefunction and $E$ is the energy eigenvalue. The term involving del-squared is the kinetic energy operator
p²/2m [recall that p=−iℏ∇]. If a particle is confined to a region of physical dimensions a then \( \nabla \rightarrow a^{-1} \) (order of magnitude!) so

\[
\frac{-\hbar^2}{2m} \nabla^2 \rightarrow \frac{\hbar^2}{2ma^2}
\]

If \( a \) (the characteristic size of the region in which the electron is confined) is equal to \( a_o = 0.529 \times 10^{-8} \) cm, the first Bohr radius of the hydrogen atom, then this energy is 1 Rydberg (=13.6 eV). You might say: Let the electrons all spread out in the volume of the material, but that still costs energy because you can only have two electrons (of opposite spin) in one eigenstate. Thus the Pauli exclusion principle, relevant to electrons because they are Fermions, guarantees an energy cost like that suggested even if you have “free electrons”. Here’s why:

For free electrons (\( V=0 \) in Schroedinger’s equation), the eigenstates can be chosen to be “plane waves” \( \Psi \sim \exp[i\mathbf{k} \cdot \mathbf{r}] \) and the eigenenergies of each electron are \( \hbar^2 k^2 / 2m \). But the wavefunctions must “fit” in the volume the electrons occupy. Consider a cubic box of side \( L \), then one choice (called periodic boundary conditions) will enforce:

\[
k_x = 2\pi n_x / L; \quad k_y = 2\pi n_y / L; \quad k_z = 2\pi n_z / L;
\]

where \( n_x, n_y, n_z \) are integers. All directions are equally suitable and we will fill energy states starting from the lowest energy until we have accommodated all electrons. Clearly, each state (without regard to spin) occupies a “volume” \( (2\pi/L)^3 \) in phase space and we will occupy states out to some maximum wave vector called the Fermi wavevector \( k_F \). Let \( n \) be the number of free electrons per unit volume, then

\[
\frac{2(4\pi k_F^3 / 3)}{(2\pi / L)^3} = nL^3 \quad \Rightarrow \quad n = k_F^3 / 3\pi^2
\]

The factor of 2 in the numerator comes from the two available spins of the electron. It is convenient to write \( n = 1/(4\pi r_s^3 \ a_o^3) \), so that \( r_s \) is the radius (in atomic units) of the sphere that contains one electron on average. Then \( k_F \).
=1.92/r_s a_0 and the Fermi energy \( E_F = \frac{\hbar^2 k_F^2}{2m} = (50.1\text{eV})/r_s^2 \). In Rydbergs the mean energy in the Fermi sea is \( 2.21/r_s^2 \).

**Summarizing the Fermi Gas**  
If we consider an ensemble of non-interacting electrons, place them in a uniform positive background (so as to assure charge neutrality overall), and assume absolute zero in temperature, then the energy of the ensemble is dictated by the Pauli exclusion principle, according to which a “Fermi sea” is filled, up to an energy called the Fermi energy (and momentum called the Fermi momentum). This model of a uniform positive background is called “jellium”. The resulting mean energy per electron, and pressure are

\[
E_{\text{Fermi}} = \frac{2.21}{r_s^2} \text{ Ryd.}
\]

\[
P_{\text{Fermi}} = -\frac{dE_{\text{Fermi}}}{dV} = \frac{51.6}{r_s^5} \text{ Megabars}
\]

\[(V = \frac{4}{3} \pi r_s^3 \text{ in atomic units})\]

[Note: One Rydberg is the binding energy of the hydrogen atom, namely 13.6 eV. The atomic unit of energy, \( e^2/a_0 \), is 2 Rydbergs. The atomic unit of pressure is \( e^2/a_0^5 \) and is about 294 Megabars]. The parameter \( r_s \) is known as the electron spacing parameter for obvious reasons. The mass density (in g/cc) is related to this through the equation:

\[
\rho \approx \frac{2.69A}{r_s^3 Z}
\]

where \( A \) is the atomic mass and \( Z \) is the nuclear charge. Among light elements, \( A/Z \) is 1 for hydrogen and close to 2 for others.

The Fermi energy is strictly repulsive of course and the resulting pressure is always positive. So the Fermi gas cannot exist as a bound state at zero pressure. [Note: We call it a “gas” because it involves non-interacting particles. But it is dense. Do not make the mistake of thinking that “gas” means low density!]
Does Temperature Matter?

At T=0, every level up to the Fermi level is occupied, and the occupancy of higher levels is exactly zero. In accordance with the rules of Fermi-Dirac statistics, there is finite occupancy of higher levels at T≠0, at the expense of occupancy close to but below the Fermi level:

But here’s the point: For situations of interest to us, the Fermi energy is enormous relative to thermal energies... so the electrons can be well approximated as lying in their zero temperature state. Here’s the quantitative reasoning:

1 electron volt = 1.6 x 10^{-12} ergs  
Boltzmann’s constant = 1.38 x 10^{-16} ergs/degree Kelvin  
kT = 1 eV ⇒ T ≈ 12000 K

So Fermi temperatures \( T_F \), defined to be Fermi energy divided by Boltzmann’s constant, are many tens of thousands of degrees..... higher than actual temperatures in planets. The Fermi temperature in Jupiter is typically around 200 to 300,000K. It is this inequality, \( T << T_F \), that leads us to say that planets are degenerate. Do not confuse this with the issue of “hot” or “cold” in the context of the motions of the atoms (e.g. is it melted?) This is a different issue involving the much lower energies of atomic vibrations and translations, and we will deal with this in due course.

Of course, this is just part of the energy in a system. But it is an important part. Some examples:
<table>
<thead>
<tr>
<th>Metal</th>
<th>Value of $r_s$ (eV)</th>
<th>Fermi Energy (eV)</th>
<th>Free electron Bulk modulus (in Mbar)</th>
<th>Actual Bulk mod. (in Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3.25</td>
<td>4.74</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>Al</td>
<td>2.07</td>
<td>11.7</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>H*</td>
<td>~1</td>
<td>~30</td>
<td>~80</td>
<td>~30</td>
</tr>
</tbody>
</table>

(*typical to the interior of Jupiter).

The free electron bulk modulus listed above is obtained by taking the volume derivative of the Fermi pressure. Since Fermi pressure scales as $(\text{density})^{5/3}$, it is obviously $5/3$ of the pressure.