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Shock-wave studies: modeling the giant planets

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Shock-wave studies: modeling the giant planets

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The giant planets—Jupiter, Saturn, Uranus, and Neptune—are known to differ markedly from the well-studied inner, or terrestrial, planets. Observations of their average density, gravitational moments, and atmospheric composition have enabled researchers to draw some conclusions as to their structure, but efforts have been hampered by a lack of accurate data on the chemical, physical, and thermodynamic properties of constituent materials at the extremely high temperatures and pressures characteristic of planetary interiors. Shock-wave experiments conducted recently at LLNL have enabled us to develop more accurate equations of state for many of these materials, and these equations of state have made models of the giant planets more accurate.

The recent flights of Pioneer and Voyager to Jupiter and Saturn, as well as anticipated visits to Uranus and Neptune, have stimulated a renewed interest in the structure of these giant planets. To construct accurate structural models, we must explain their observed luminosity, radius, oblateness, rotation rate, and gravitational moments in terms of equations of state for the postulated constituent materials. (An equation of state defines the relationship of pressure, density, and temperature for a given material.) The theory linking equations of state to planetary structure is summarized in the box on p. 6.

As shown in Fig. 1, the giant planets are currently thought^{1,2} to consist of three layers: a top layer of molecular hydrogen and helium; a middle layer either of metallic hydrogen and helium (for Jupiter and Saturn) or of icy ammonia, methane, and water (for Uranus

and Neptune)²; and a rocky core of iron, nickel, silicon, and magnesium oxides. Hydrogen and helium are subjected to a very wide range of pressures (e.g., from 0.1 MPa to 4000 GPa in Jupiter) and the ices to pressures between 20 and 600 GPa (100 GPa = 1 Mbar). The rocky core components are subjected to roughly 1000 GPa in Uranus and Neptune and to as much as 10 000 GPa at Jupiter's center. To construct structural models that predict correctly the observed characteristics of the giant planets, we must have accurate equations of state, melting curves, intermolecular potentials, and electrical conductivities for all

Fig. 1 Postulated structural models of Jupiter, Saturn, Uranus (and Neptune), and Earth, showing material compositions and calculated temperatures and pressures. Unlike Earth, which is composed mainly of heavy rock and iron, the giant planets appear to be composed of low-density materials, mostly hydrogen and helium. However, all four do appear to have a rocky core. The pressures and temperatures believed to exist in the giant planets are many times greater than those in the Earth. (Note that 100 GPa = 1 Mbar.)

these materials over an incredibly wide range of physical conditions.

LLNL has a longstanding experimental and theoretical research program that has provided equation-of-state data for many elements and materials over a wide range of pressures and temperatures. Our data and computational techniques, although not originally developed with planetary physics in mind, are now proving very useful in modeling the giant planets.

Shock-wave experiments

There are three types of experiments in which thermodynamic

data on materials at high pressures can be obtained: isothermal-compression experiments (wherein the temperature remains constant), isentropic-compression experiments (wherein the entropy remains constant), and Hugoniot-compression experiments (i.e., shock-wave experiments). Calculated Hugoniot curves, isotherms, and isentropes for liquid hydrogen are shown in Fig. 2 to illustrate the qualitative differences between the three types of data.

Before 1945, almost all high pressure data on fluids were obtained from experiments carried out hydrostatically. The pressure

was generated by a piston pressing down on a liquid sample in a pressure vessel. However, the pressures attainable under such conditions are severely limited by the strength of available pressure vessel materials.

As a result of war-time research, the shock-wave method emerged as a new high-pressure tool. This method relies upon high explosives or a high-velocity gas gun to generate a rapidly moving shock wave, which hits the target, compresses the material, and creates very high pressures momentarily.

Most of the shock-wave data used to model the giant planets

Fig. 2 There are three types of experiments in which thermodynamic data on materials at high pressures can be obtained: isothermal-compression experiments (wherein the temperature remains constant), isentropic-compression experiments (wherein the entropy remains constant), and Hugoniot-compression experiments (i.e., shock-wave experiments). Shown here is a comparison of calculated thermodynamic properties for isothermal, isentropic, and Hugoniot compressions of hydrogen. Isothermal measurements extend only to 2.5 GPa, and isentropic P-V measurements have not been made. Only shock data are available above 2.5 GPa. A considerable variation in the path of the Hugoniot can be achieved by means of reflected-shock experiments (the dashed curves). In these experiments, the temperatures along the Hugoniot are lower (at the same density) than those reached by the principal Hugoniot, tending toward the isentrope. Thus, by carrying out a series of reflected-shock experiments, it is possible to widen the range of our experimental data, and make subsequent theoretical extensions of the data more accurate.

were obtained with the LLNL two-stage gas gun (Fig. 3). This device can accelerate a 20-g metal projectile against a target at velocities up to 7 km/s.³ To achieve conditions comparable to those in the planetary interiors (Fig. 1), H_2 , CH_4 , NH_3 , and H_2O must be shocked from the liquid phase. The first three have boiling points below room temperature, and thus the targets are actually small cryostats.⁴ When the projectile hits the target, it generates a high-pressure shock wave that momentarily compresses and heats the target material (Hugoniot compression) into the pressure-temperature region of interest. The properties of the material must be measured during that brief instant. To obtain even higher pressures, we employ a reflected-shock technique in which the primary shock is passed through the target material and

then reflected off an anvil (e.g., a brass plate). As the reflected shock wave passes back through the target, it further compresses the target material. (See the dashed curves in Fig. 2.)

The thermodynamic properties of interest in our shock-wave experiments are the pressure, volume, and energy of the compressed sample. They are obtained by measuring the projectile velocity, the shock velocity in the target material, and the initial mass densities of the target and projectile materials, and then applying the equations of conservation of momentum, mass, and energy. The temperature of the shocked target material can be computed from the pressure and energy values using an equation of state based on this data.

By conducting a series of shock-wave experiments, all with the

same initial conditions but different projectile velocities, we can obtain a locus of pressure, volume, and energy points (generally following the calculated Hugoniot curve in Fig. 2). By varying the initial density, we can obtain a different set of Hugoniots. However, unless the initial density can be varied considerably, the final Hugoniots will not differ sufficiently to justify the extra effort. A considerable variation in the path of the Hugoniot can be achieved by means of reflected-shock experiments (the dashed curves in Fig. 2). In these experiments, the temperatures along the reflected Hugoniot are lower (at the same density) than those reached by the principal Hugoniot, tending toward the isentrope. Thus, by carrying out a series of reflected-shock experiments, it is possible to widen the range of our experimental data, and make

subsequent theoretical extensions of the curves more accurate.

Using theoretical and experimental techniques, we have explored the thermodynamic properties of the basic constituent elements of the giant planets, thus providing more accurate models of planetary structure.

Thermodynamic properties of hydrogen

The observed low average densities of Jupiter and Saturn (1.3 and 0.7 g/cm³, respectively) indicate that they are composed of about 77% hydrogen by mass. As mentioned above, the pressures at the outer boundary of the rocky core in Jupiter and Saturn (see Fig. 1) have been calculated at about 4000 and 1000 GPa, respectively. A number of static experiments have been conducted to determine the thermodynamic

properties of hydrogen and deuterium at high pressures, but none of them achieved pressures above 5.7 GPa.

We recently conducted single-shock-wave experiments that obtained pressures up to 20 GPa and reflected-shock-wave experiments that reached 80 GPa and 7000 K (Fig. 4). In addition, we have planned two more reflected-shock experiments that will reach pressures between 20 and 80 GPa.

To illustrate the significance of these shock-wave data to planetary modeling, we have compared pressure-temperature plots for computed isentropes of the current models of Jupiter and Saturn¹ with our shock-wave results (Fig. 4). We see that our shock Hugoniot closely follow the paths of the planetary isentropes. Typically, when a Hugoniot and an isentrope originate from the same initial con-

ditions, they progress along different pressure-temperature paths, as in Fig. 2. However, because the planetary isentropes originate at very low (atmospheric) densities and low temperatures, they follow an extended compression range and reach pressures and temperatures comparable to those obtained by the high-density Hugoniot. Thus we can use single-shock and reflected-shock experiments to sample a part of the pressure-temperature region of interest to planetary models.

In principle, we should be able to calculate the forces acting between hydrogen molecules and thus extend our understanding of the thermodynamic properties of hydrogen far beyond the experimental data. However, this method is very complex, and the results are uncertain. As an alternative to theoretical rigor, we can, by a combination of theory and experiment, determine an effective intermolecular potential for hydrogen which, when used with statistical mechanical models, will reproduce experimental data. These models can then be used to extend the thermodynamic data on hydrogen over the range of

Fig. 4 Comparison of our experimental shock-wave results with the isentropes for Jupiter and Saturn and the calculated hydrogen phase diagram. Single-shock data points up to 21 GPa and reflected-shock points up to nearly 80 GPa are shown as solid circles; planned reflected-shock experiments are shown as open circles. Colored shading and dashed lines are used to denote the speculative regions of the hydrogen phase diagram.

pressure-temperature conditions in the giant planets.

To do this, we started with the intermolecular potential for hydrogen given by Silvera and Goldman,⁵ who used a very accurate model for molecular solids to determine a hydrogen pair potential that fits the solid (4 K) hydrogen and deuterium data to 2.5 GPa. We tested their intermolecular potential with an accurate theory for compressed hydrogen fluid and were able to predict the experimental fluid isotherms from 0 to 2 GPa and from 75 to 300 K, as well as the hydrogen melting curve to 5.7 GPa.

However, to correctly calculate our shock-wave data, we had to modify the Silvera-Goldman potential at small intermolecular separations. Their potential had been fitted to low-temperature solid-hydrogen data below 2.5 GPa, and does not extrapolate correctly beyond that region. However, shock-wave data represent a much higher temperature phenomenon, wherein the important interactions occur at small intermolecular separations. The modified potential, combined with our fluid theory of hydrogen, fits the range of conditions from the lower temperature static isotherms used by Goldman and Silvera to the shock-wave data at about 80 GPa and 7000 K. Using this modified potential, we found that the high temperatures

generated in the shock process make it possible to determine the potential at intermolecular spacings comparable to those found in the molecular hydrogen solid at densities believed to be near the metallic transition of hydrogen.

Using theories of the solid and fluid, we extended the melting curve of molecular hydrogen (H₂)

to pressures of a few hundred gigapascals and then computed the molecular-metallic phase transition using a previously calculated equation of state for hydrogen metal. We estimate that the metallic phase transition of molecular hydrogen ranges from pressures of 200 to 500 GPa.⁶ These results are shown in Fig. 4, together with our

Static model of planetary structure

The basic assumption in this model is that the planet is in hydrostatic equilibrium. This implies that the evolutionary time scale greatly exceeds response times in the planet's interior.

If the planet is rotating, the relationship between pressure and depth is

$$\frac{dP}{ds} = \frac{GM(s)\rho(s)}{s^2} + \frac{2}{3}\omega^2 s \rho(s). \quad (1)$$

This equation, which is a form of Newton's law of gravitation, says that $M(s)$, the mass interior to the planet at a radius s , pulls matter located at radius s (having a density $\rho(s)$) toward the center of the planet; this pull is countered by the material pressure P and (to a small extent) by the planet's rotation rate ω . (G is the gravitational constant.) The resisting pressure depends on the pressure-density relationship of the planetary material and is related to the density and temperature by the equation of state,

$$P = P(\rho, T, x), \quad (2)$$

where $x = x_i(s)$ are the fractional abundances of the various planetary materials.

The giant planets are believed to be in convective equilibrium, and their temperature gradients are thought to be isentropic. That is, the gravitational force acts as a piston, compressing the planetary fluid reversibly and isentropically (i.e., at constant entropy). Thus the entropy is a constant within the planet, from its outer atmosphere to its inner core, and Eqs. 1 and 2 must be solved with this constraint.

This static model can be extended to the study of planetary evolution by introducing energy transport equations and permitting ω (the planetary rotation rate) to change consistent with the conservation of angular momentum.

experimental Hugoniot and planetary isentropes. The phase transition at 200 GPa, is not abrupt, but, in reality, is probably gradually, occurring between 200 and 500 GPa. The actual phase transition may resemble that observed in diatomic iodine: as the pressure is increased, the valence electrons in the molecule gradually occupy states in the unfilled conduction band, resulting in a phase transition that is continuous in density and pressure.

Investigating this possibility, we developed a phase diagram in which molecular hydrogen is first converted to an electrically conducting form of the molecule and then, at some higher pressure, into a monatomic metal. The results of Sharma *et al.*⁷ suggest that this might occur. They measured the molecular vibrational frequency using Raman spectroscopy at pressures up to 60 GPa and found that over the first part of that pressure range, the vibrational frequency increased with increasing pressure as expected. However, above 30 GPa, the frequency began to decrease. This decrease could be interpreted as the gradual onset of intermolecular bonding. Even if a molecular conducting phase does not appear at low temperature and high pressure, the electron energy gap may have narrowed sufficiently to permit thermal excitation of a significant number of electrons into the conduction band at planetary temperatures of 10 000 K. Thus we could expect the electrical conductivity along the isentropes to increase from insulator to semiconductor to semi-metal and then to metallic as indicated in Fig. 4.

Thermodynamic properties of helium

It is believed that helium accounts for about 21% of the total mass of Jupiter and Saturn. Thus, thermodynamic data on helium similar to those obtained for hydrogen are needed if we are to model the planetary interior accurately. Static solid and fluid data for helium are available, including a 4-K, 2.5-GPa solid isotherm, fluid isotherms to 300 K and 2 GPa, and a melting curve up to 11.5 GPa at room temperature. In addition, there are high-energy molecular-beam data for helium that provide information on very-short-range molecular pair interactions.

However, no shock-wave data exist for helium; for a mixture of hydrogen and helium, the mixture of interest to the study of the giant planets, the only data available are at low pressures (below 1 GPa). Because hydrogen and helium have highly disparate boiling points (hydrogen boils at 20 K and helium at 4 K, a factor-of-five difference), this mixture cannot be easily made for shock-wave experiments. As a result, it is unlikely that these experiments will be conducted in the foreseeable future.

However, shock-wave experiments with helium alone are possible. In fact, we hope to conduct both single-shock and reflected-shock experiments on helium. In these experiments, we should be able to reach pressures up to 70 GPa and temperatures up to 20 000 K. As can be seen in Fig. 1, these conditions are similar to those in the interiors of the giant

planets. The very high temperatures obtained in these shock-wave experiments will also enable us to determine the pair potential between helium atoms. From this, reasonable estimates of the hydrogen-helium pair interaction potential can be made, providing essential insights into the behavior of the molecular mixture.

Thermodynamic properties of the ices

Water, ammonia, and methane form the middle ice layer in the three-layer models of Uranus and Neptune (see Fig. 1). The calculated pressures and temperatures for this layer range from about 600 GPa and 7000 K at the inner core/ice boundary, to about 20 GPa and 2000 K at the outer ice/hydrogen-helium boundary.

Shock-wave data on these molecules, including electrical conductivities for water and ammonia and temperatures for water, have been measured at LLNL over part of this pressure-temperature range. Liquid water has been compressed up to 82 GPa in a single-shock experiment and up to 230 GPa in a reflected-shock-wave experiment. In a separate set of experiments on water, temperature was measured with an optical pyrometer⁸ at pressures up to 82 GPa. With these new data, an equation of state was developed that is considerably "softer" (i.e., that has a less steep pressure-volume curve) than previous ones.

Using this new equation of state, researchers produced evolutionary and structural planetary models for Uranus and Neptune that agree with the observed data, assuming only approximate solar abundances of ice and rock.² Figure 5 compares the shock-wave data for the ices to the calculated planetary entropies for Uranus and Neptune, demonstrating the great relevance of these data to the theoretical modeling of these planets.

Electrical conductivity data on these ices are of great interest because they can lead to an explanation or prediction of a magnetic field. The motion of charged particles trapped in such magnetic fields generates radio waves. At present, there is one report of possible radio signals from Uranus, and there have been no similar reports from Neptune. Electrical conductivities in shock-compressed water were first

measured up to 13.3 GPa (1.7 g/cm^3) and 1100 K.⁹ Recently, we extended these measurements to 59 GPa and 4200 K.¹⁰ These data show that above about 20 GPa, the conductivities become constant at about 20 to 30 mho/cm (see Fig. 6).

From Fig. 6, it is evident that the processes leading to electrical conductivity (i.e., molecular ionization) have become fully saturated. These results are predicted from an analysis of lower pressure data,¹⁰ in which researchers concluded that above 15 to 20 GPa, water becomes fully ionized to H_3O^+ and OH^- and is essentially a molten salt isoelectric with NH_4F and NaOH .

For ammonia, similar results have been observed as shown in Fig. 6. Using explosively driven shock waves, we investigated the Hugoniot and electrical conductivity of liquid ammonia from 4.5 to 28.2 GPa and from 600 to 2300 K. With the two-stage gun, we recently

extended this pressure range to 63 GPa. As expected, the electrical conductivity of ammonia is always less than the conductivity of water because the dissociation constant of ammonia is much smaller than that for water. However, at very high pressure (i.e., planetary pressures), the conductivities of ammonia and water will probably converge.

For methane, the experimental data consist of a principal Hugoniot up to 45 GPa, plus one data point from a reflected-shock-wave experiment at 23 to 91 GPa. No electrical conductivity measurements are available. We have found that the theoretical Hugoniot predictions agree with the experimental shock data up to 23 GPa at 2300 K, but are too high above this pressure.

Chemical equilibria calculations indicate that above 20 GPa and 2000 K, methane is converted into elemental carbon (probably amorphous carbon or diamond) and molecular hydrogen. Recent theoretical calculations on Hugoniot of many hydrocarbons indicate that shock heating induces breaking of the C-H bonds, and that shock compression encourages condensation of the dissociated carbon atoms into some sort of residue.¹¹ If we assume that the hydrocarbons have been completely converted into a mixture of condensed carbon and molecular hydrogen, we can use known equations of state for each of these materials to compute high-density Hugoniot that are in excellent agreement with the experimental data. The results of similar calculations for molecular methane are also in agreement with the experimental data. Under planetary conditions of pressure and temperature, diamond or carbon

residues should be conducting liquid metals. In addition, they may be insoluble and could form a separate phase or possibly even a fourth layer. The significance of a conducting layer of carbon may be very great since it is estimated that the mass of available carbon in Uranus and Neptune is 17% of the total planetary mass.²

To summarize, shock-wave results indicate that the ice layer of Uranus and Neptune consists of material that is highly ionized and almost completely dissociated. It has an electrical conductivity on the order of 30 mho/cm. If appreciable amounts of liquid carbon aggregates are indeed present, the electrical conductivity of these ices would be even higher.

Thermodynamic properties of the rocky core

All of the giant planets are believed to contain a rocky core of iron, silicon, nickel, and magnesium and their oxides on the order of twenty earth masses. Because it is in greatest abundance, the properties of iron, particularly its melting curve and electrical properties at high pressure, are of continuing interest. The equation of state and the electrical conductivities have been studied by shock-wave methods.

However, all efforts to detect melting have failed because the thermodynamic properties of iron at pressures of several hundred gigapascals do not change much in the transition from solid to liquid. Recently, however, researchers at Los Alamos National Laboratory¹² made measurements of the sound velocity in iron to detect changes they believed must be due to

melting. By their measurements, iron melts at a pressure of 250 ± 20 GPa at a calculated temperature of about 5500 K.

We have extrapolated these melting predictions to the core boundary temperatures of Uranus, Neptune, and Saturn. (An extrapolation to Jupiter was con-

sidered too extensive to be reliable.) We found that in Uranus and Neptune, all iron in the core is clearly in solid phase. For Saturn, iron is very close to the melting line and may be liquid. Freezing of the iron into a solid core could provide an evolutionary cooling mechanism that accounts for the

additional energy release characteristic of Saturn and currently attributed to hydrogen-helium immiscibility.

The modeling of candidate rock-core components is more essential for the smaller outer-solar-system bodies than for the giant planets. For example, the rock fraction of Jupiter accounts for about 2% of its total mass, whereas the rock fraction of Io, one of Jupiter's moons, is almost 100% of the total mass. Most planetary structural studies use theoretical models to compute the thermodynamic properties of the rock mixture. However, researchers have recently shown that these models disagree completely with shock-wave data for water, and this will apply to all rock-ice systems. New high-pressure shock-wave data for iron, nickel, magnesium oxide, and silicon oxide have been used to develop revised empirical equation-of-state models for rock mixtures.¹³ These studies show that the experimentally based equation-of-state models are in much better agreement with the planetary structural models than are the theoretical equation-of-state models.

Conclusion

The giant planets—Jupiter, Saturn, Uranus, and Neptune—are known to differ markedly from the well-studied inner, or terrestrial,

planets. Observations of their average density, gravitational moments, and atmospheric composition, have enabled researchers to draw some conclusions as to their structure, but efforts have been hampered by the lack of accurate data on the chemical, physical, and thermodynamic properties of the constituent materials at the extremely high temperatures and pressures common in the planetary interiors. Shock-wave experiments conducted recently at LLNL have enabled us to develop more accurate equations of state for many of these materials, and these equations of state, together with other data, have permitted the construction of more accurate models of the giant planets.

Using new equations of state based on shock-wave experiments, we can model the internal structure of Jupiter in such a way as to explain all of its observed properties, while retaining the same proportions of constituent elements as existed in the sun when it was formed. (It is assumed that the sun and the planets were formed from the same primordial cloud and that they must have been, at least in the beginning, similar in overall composition.) The characteristics of Uranus and Neptune can also be reconciled under the assumption of a solar composition of ice and rocky components. Only Saturn remains anomalous, and investigations of the thermodynamics and solubility of hydrogen-helium mixtures may provide the solution to this discrepancy. There is an emerging consensus, arising from the use of improved equations of

state, that a generally similar rocky core on the order of 14 to 21 earth masses exists in all four giant planets.

Before more accurate models of the giant planets can be devised, theoretical research is needed on the metallic phase transition of hydrogen, the thermodynamics of dense hydrogen and dense hydrogen-helium mixtures (including the solubility of helium in hydrogen), the opacity of dense hydrogen, and the chemistry of ice and rocky-core components at high pressures and temperatures. Experimental work currently being planned and conducted at LLNL will aid planetary theoreticians and physicists in understanding these phenomena.

Key words: electrical conductivity; equation of state; giant planets; helium; Hugoniot; hydrogen; intermolecular potential; Jupiter; Neptune; planetary modeling; Saturn; Uranus.

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Modeling of solid-state materials for solar cells

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One promising method of converting solar energy into electricity is with solar cells. However, the cost per watt of electrical energy delivered is quite high compared with that associated with more conventional ways of generating electricity. New potential solar cell materials are being developed that might make photovoltaic conversion more competitive by decreasing the cost per cell or by increasing a cell's efficiency, but evaluating each material experimentally (without theoretical assistance) would be a monumental task. To facilitate the evaluation of emerging materials, we have developed, under the auspices of the Solar Energy Research Institute, a computer model that can predict their optical and transport properties and evaluate the performance of solar cells made from them. The model enables us to evaluate potential solar-cell materials quickly at a modest cost.

The sun is our one essentially unlimited energy source, and, in fact, most existing energy sources can be traced back to the sun via one path or another. Oil, coal, and other biological energy sources originated as plants that converted solar energy into chemical energy. The rain water that fills lakes and reservoirs receives its original lift into the sky from the heat of the sun. Even nuclear power owes its existence to the creation of heavy elements in the exploding heart of some primordial sun.

With the rising cost of fossil fuels, considerable attention has been focused on effective methods of exploiting solar energy. While solar power would be attractive because of its wide availability and minimal impact on the environment, converting it into a usable form (i.e., into electricity) is presently difficult and expensive.

The two main methods of converting sunlight to electricity rely upon thermal and photovoltaic processes. Thermal conversion usually involves large moving mirror arrays that concentrate the sun's rays on a boiler to generate steam, which is then used to turn a turbine that generates electricity. Photovoltaic conversion involves the direct stimulation of charge carriers (in solid semiconductors), which can then be collected as usable current. Under the auspices of the Solar Energy Research Institute, we have been working to improve the efficiency and decrease the cost of solar photovoltaic cells.

A solar cell consists of a piece of thin, light-absorbing semiconductor material that behaves electrically like a diode. A diode is essentially a one-way valve for electricity. Its junction region (Fig. 1) represents a potential hill for charge carriers. Those going in one direction must climb the hill (a hard task) while those going in the other direction slide down (an easy task). Because of this hill, electricity can flow through the diode more easily in one direction than in the other. To achieve a diode effect, we either

selectively dope a part of the semiconductor with other atoms (forming a homojunction solar cell) or sandwich two different semiconductors together (forming a heterojunction solar cell).

Semiconducting materials have conductivities intermediate between those of metals and insulators. Their properties are best understood in terms of energy-level diagrams like those that will be described later in Fig. 2. Electrons in semiconducting materials can occupy energy levels in either the

valence band or the conduction band, but not in the gap (the forbidden band) that separates them.

In a semiconducting material, there are two types of charge carriers: electrons and "holes." When an electron is lifted into the conduction band, it leaves behind a hole (where it used to be) in the valence band. Both electrons in the conduction band and holes in the valence band are available as mobile charge carriers. Holes behave as if they were positively charged electrons.

Fig. 1 Band structure and solar cell operation. (a) At the junction between p-type and n-type semiconductors, there is a potential hill for electrons (e^-) and holes (h^+) that determines the direction in which they will move if released in the junction region. Such junctions are created either by placing the two semiconducting materials in intimate contact (a heterojunction) or by creating two adjacent doping concentrations in a single semiconducting material (a homojunction). (b) In a solar cell, light absorbed in the junction region causes

electrons to jump from the valence band into the conduction band. As electrons are removed from the valence band, they leave behind "holes" that act like positive electrons. Because of the potential hill, electrons and holes collect on opposite sides of the junction, creating a usable current and voltage. (c) Traps in the junction region (created by impurities or crystal defects) can capture mobile electrons (or holes), impeding the operation of a solar cell.

Depending on the doping (the impurities purposely added to the material), electrons and holes in a semiconductor are classified as majority or minority charge carriers. In n-type material, electrons are the majority carriers, and holes are the minority carriers. In p-type material, the roles are reversed. Near a junction between n-type and p-type materials, electrons from the p-type material (the minority carriers) and holes from the n-type material (also minority carriers) approach the potential hill in the easy direction (down the hill for electrons and up the hill for holes).

If we inject a minority carrier into a uniform slab of semiconductor material, it will move about at random until it is reabsorbed. If we inject many minority carriers into the same material, the net result of their random motions is zero current. If, on the other hand, we inject minority carriers into a junction region, and they survive long enough to cross it, their guided motion will generate a current, and hence a voltage, across the junction.

One way of generating minority carriers inside a semiconducting material is to expose it to light. When a bound electron in a solid semiconductor absorbs a photon that is energetic enough, it can break its band, become a mobile (minority or majority) charge carrier and leave behind a hole. As a rule, the hole is also mobile because the atoms in a solid share electrons, and when an electron

from another atom moves over and fills the first hole, it leaves another hole behind. From a macroscopic point of view, this alternate creating and filling of holes appears to be a single hole moving through the crystal lattice in a direction opposite to that taken by the electrons. The motion involved can be likened to that of a bubble of air as it "falls" upward through a glass of water.

The operation of a solar cell may seem like a straightforward process. Minority carriers are generated near the junction and slide down the potential hill. The preferential motion creates a current through the junction and a voltage across the junction; if we add wires, the electricity should flow to an external load. Unfortunately, the situation is not quite this simple; several processes limit the operation.

One of the most important mechanisms limiting the conversion efficiency of a solar cell is the ability of the material to absorb the available solar photons. If the material lacks this ability—that is, if it is too transparent (like glass)—then the photons will pass through, creating few mobile charge carriers, without which no current will be generated.

We must also consider the ability of charge carriers to move through

the crystal lattice. Unlike an electron in free space, an electron in a semiconductor must wind its way through a crystal lattice. As it collides with one atom after another, it loses energy and slows down. If it slows down too much, it may recombine with a hole, and thus neither the electron nor the hole ever reaches the cell's electrodes, where it would contribute to a usable current.

Another important consideration is the time period during which the charge carriers remain free (before being reabsorbed by the material). As they move through the material, the charge carriers can become unavailable for conduction as a result of a variety of mechanisms. Interactions with holes and traps are important in this regard. A trap is a charge center (caused by an impurity or crystal defect) that creates localized electron energy levels inside the forbidden band. An electron that drops into one of these energy levels is trapped (Fig. 1c).

The effects of the above processes in a semiconductor are described by several material parameters. These are: the absorption coefficient, the carrier mobility,

and the carrier lifetime. Since optical absorption is strongly dependent on the photon energy (or color) of the incident light, it is best described as a plot of the absorption coefficient vs energy. The mobility and lifetime are measures of the charge carrier's ability to move and to survive as a free carrier.

Not every semiconducting material will make a good solar cell. Candidate materials must have a large absorption coefficient for photon energies in the range of the solar spectrum. In other words, they must first be able to absorb strongly the incoming solar photons near the thin junction region of the solar cell. Secondly

they must have a large carrier mobility and a long carrier lifetime. This allows a charge carrier generated near the junction region to survive long enough and move far enough to cross the junction and be collected as usable current. If the solar photons are not absorbed or if the generated charge carriers disappear too soon, then

Fig. 2 The energy band structure of zinc tin phosphide (ZnSnP_2). This diagram shows the allowed electron energy levels for various values of the electron's momentum. The momentum values start at zero (Γ) and extend in the X and Z directions to the edge of the Brillouin zone (a geometric object in momentum space). Note the separation of the allowed energy levels into the

valence band, the forbidden band, and the conduction band. Since the maximum of the valence bands is directly below the minimum of the conduction bands, this is a direct gap material. The separation between the bottom of the conduction band and the top of the valence band is known as the energy gap (E_G).

the solar cell may be so inefficient as to be useless. It is these mechanisms that tend to reduce a solar cell's efficiency and its effectiveness as a power source.

Calculations

There are many candidate materials from which we might make solar cells. Several of these (e.g., CdSiAs_2 , BaZn , ZnSiAs_2 , Zn_3P_2 , ZnSnP_2), which we refer to as "emerging materials," are being investigated by the Solar Energy Research Institute. However, few of them have been highly purified yet, and little is known about their material properties. Experimental programs designed to investigate these properties systematically without theoretical help would take years and cost millions of dollars per material.

To help researchers focus on the materials most likely to yield good solar cells, we have investigated theoretically the properties of the emerging materials and of solar cells made with them. We have also evaluated the adjustable parameters of solar cell design to determine how sensitive the efficiency of a solar cell made from one of these materials would be to such things as doping, junction width, grain size, etc.

Band structure. The first step in calculating the physical properties of a semiconductor is to calculate its energy band structure. The energy band structure (Fig. 2) shows the allowed energy and momentum values for an electron in the solid. To generate this

diagram, we must solve Schrodinger's equation of motion for the crystalline solid.

A solid contains about 10^{23} atoms per cubic centimetre, and thus it is almost impossible to solve Schrodinger's equation exactly. Instead, we must use an approximation, which involves reducing the many-body problem to a one-electron problem and then solving the one-electron equation of motion.¹

To solve the one-electron equation of motion, we expand the wave function as a sum of plane wave solutions and continue expanding it until we get good convergence for a given potential. For a real potential like that shown in Fig. 3a (with its rapid change in potential near the atomic nuclei), this could take many hundreds of terms and make the equation practically unsolvable.

To circumvent this problem, we assume that the inner electrons are all localized and note that we are interested only in the valence electrons and the free mobile electrons in the solid. (These electrons spend most of their time away from the nucleus, and hence the shape of the potential near the nucleus affects them only slightly.) This assumption allows us to smooth out the potential in the region of

the nucleus, as long as we are careful to keep from changing the free-atom energy levels of the valence electrons.

Figure 3b shows this smoothing, which considerably reduces the number of terms required in the expansions. This technique, known as the pseudopotential method,² was first used with considerable success in metal physics, and has proved accurate enough for semiconductor-band-structure computations.

The result of the above expansions and assumptions is a matrix eigenvalue equation, which we solve using standard techniques. To achieve adequate convergence, even with the above assumptions, we have had to solve matrices that range in size from 60×60 to 200×200 terms. (We have even effectively solved 1000×1000 matrices by first using perturbation theory to reduce them to less than 200×200 and then solving the smaller matrix.) These calculations give an energy band structure separated into a valence band, a conduction band, and a forbidden band as shown in Fig. 2 (a plot of the allowed energy levels vs the electron momentum).

An electron in the valence band is bound to the crystal lattice and cannot move beyond a restricted region. To become a mobile electron, it must gain enough energy to cross the forbidden band in one jump and move into the conduction band. Electrons in the conduction band are free to move throughout the crystal. When an electron moves into the conduction band, it leaves behind a vacancy or hole in the valence band that can also move in the crystal.

An important feature of these plots is the location of the top of the valence band in relation to the bottom of the conduction band. The difference in energy between these two points defines the energy of the lowest energy or longest wavelength photon that can be absorbed and cause an electron to move from the valence band to the conduction band. This energy difference, known as the energy gap (E_G), determines the location of the absorption edge in a plot of the absorption coefficient. The absorption edge is the point in the optical absorption spectrum where the absorption increases rapidly from near zero to a high value.

The separation of the top of the valence band and the bottom of the conduction band along the momentum axis determines whether this material has a direct or

indirect gap. As shown in Fig. 4, the top of the valence band may either be directly below the bottom of the conduction band, as it is in a direct-gap material, or off to one side, as it is in an indirect-gap material.

Direct-gap materials generally have higher absorption coefficients than indirect-gap materials. In direct-gap materials, an electron need only absorb a photon to gain the energy required to move into the conduction band. In an indirect-gap material, on the other hand, moving an electron into the conduction band is a two-step process. The electron must absorb a photon and either absorb or emit a phonon (a quantized unit of lattice vibration analogous to the photon of electromagnetic theory) to gain the energy and momentum required to make the transition. Since a two-component absorption is much less probable than a single-component absorption, the probability of an absorption in an indirect-gap material will be less than that in a direct-gap material.

Figure 4c shows an ideal band structure for a solar cell. The material has an indirect gap, but the indirect part of the gap is only slightly lower than the direct gap. Hence, only those photons with energies between the indirect-band gap (the lowest energy photon that can be absorbed) and the direct-band gap (the lowest energy photon that does not require a two-step absorption) must be absorbed with the difficult, indirect-gap

absorption. Slightly more energetic photons can induce direct-gap absorptions as in direct-gap semiconductors.

With this energy band structure, the material can absorb a photon that kicks an electron across the direct gap into the conduction band. The electron will then seek

the lowest point in the conduction band, which is at the indirect gap. To return to the valence band, this electron must then emit a photon and either emit or absorb a phonon. Since this combined process is less likely than photon emission alone (from the direct gap), the electron will linger longer

in the conduction band. In effect, this indirect gap has increased the lifetime of the free carrier without significantly lowering the absorption coefficient of the material.

Absorption coefficient. In most compounds the absorption coefficient is known only over the relatively narrow range of energies

Fig. 4 Classification of semiconducting materials, which depends on the alignment of the top of the valence band (green) with respect to the bottom of the conduction band (tan). (a) A direct-gap material, in which the bands line up. Electrons in direct-gap material need only absorb a photon to move into the conduction band. However, they can just as easily then de-excite back to the valence band. Thus, such materials have high absorption coefficients but short carrier lifetimes. (b) An indirect-gap material, in which the top of the valence band is out of line with the bottom of the conduction band. Electrons in

indirect-gap materials must absorb a photon and a phonon to get into the conduction band. Therefore these materials tend to be more transparent but to have longer carrier lifetimes. (c) An ideal band structure for a solar cell. The gap is slightly indirect, but not enough to decrease the absorption coefficient significantly. Once an electron has crossed the forbidden zone, it will slide down to the lowest point of the conduction band, where it must now undergo a less probable two-step process (photon and phonon) to be de-excited.

Fig. 5 Calculated and experimental absorption spectra for materials with direct and indirect gaps. (a) A direct-gap material, cadmium telluride (CdTe). Note the sudden increase in the absorption coefficient at the absorption edge, and the good agreement between the experimental results and our calculated curve. (b) An indirect-gap material, boron arsenide (BAs). The increase in absorption coefficient is slow, extending over a range of several eV, before direct-gap absorption takes over at about 4 eV. (c) Spectral distribution of solar energy. The sun's radiation output is approximately equivalent to that of a blackbody

with a temperature of 5750 K, as shown by the irradiance at the outside of the earth's atmosphere (green). However, the usable energy at the earth's surface (purple) is considerably decreased from this because of absorption by the atmosphere. It is useful to compare this available energy with the different materials' ability to absorb that energy in (a) and (b). Note how, in this case, the indirect-gap material's absorption (b) remains low well beyond the solar spectrum. As a result, this material is a poor absorber of solar photons. The sharp decreases in sea-level intensity near 1 eV are due to absorption by water vapor and CO_2 .

near the absorption edge (Fig. 5a). This point defines the lowest energy photon that the material will absorb strongly. For solar cell applications, we need to know the absorption coefficient over the whole usable portion of the solar spec-

trum (from about 1 to 3 eV, as shown in Fig. 5c).

Calculation of the absorption coefficient follows rather easily once we have completely determined the band structure. The band structure defines the

minimum energy a photon must have for absorption by the material. Summing over these available energies with suitable constants and probability weighting factors produce a plot of the absorption coefficient like those shown in Fig. 5. Note the good agreement of the calculated values with experimental results in Fig. 5a.^{3,4}

Other optical parameters.

Once we have determined the energy band structure and its associated wave functions, we can calculate such other optical parameters as the complex dielectric constant, the index of refraction, the reflection coefficient, and the transmission coefficient. From the band structure, we can also calculate the band gap and the reduced masses of the carriers (the apparent masses of the electrons and holes due to their being in a crystal rather than in free space).⁵

When all these factors are known, it is a straightforward process to calculate the other material parameters and to model the solar cell. Figure 6 shows the flow of data and calculations.

Solar cell modeling. The final calculation is to model the solar cell and solve for such characteristics as its spectral response, its current-vs-voltage curve, its fill factor, and its efficiency. At this point, we also study how the cell's characteristics

Fig. 6 A computational flow chart showing the array of subroutines we used in calculating material parameters of new semiconducting materials and the performance of solar cells made from them.

react to changes in such adjustable input parameters as doping, geometry, resistivity, interface and surface recombination velocities, and grain size.

Figure 7 contains some of the results of our theoretical calculations for a cadmium-silicon-arsenide homojunction solar cell. Figure 7a shows the current-voltage characteristics for three possible values of the diffusion length (a measure of how far a charge carrier can be expected to move through the material before being absorbed). Each of these curves encloses an approximately rectangular area in the upper-left corner of the figure. The larger this

area and the sharper its lower-right corner, the more power can be extracted from the cell.

Many current solar cell designs consist of thin films laid down one on top of the other. This thin-film design is much less expensive to produce than cells created from slices of semiconductor crystals and could induce significant savings for the solar cell user. However, the efficiency obtained has typically been much lower than that associated with single-crystal designs. These thin films, far from being single crystals, consist of many smaller crystals or grains.

Each interface between the grains is a strong trapping center,

whose strength is described by the interface recombination velocity (v). Figure 7b is a plot of short-circuit current vs grain size for two values of the interface recombination velocity. This is a measure of the maximum amount of current that the solar cell can produce.

Figure 7c is a plot of solar cell efficiency vs grain size for two values of the interface recombination velocity. These theoretical efficiencies are quite comparable with the 15% obtainable with single-crystal silicon cells. If such efficiency can be achieved in practice, the lower cost of thin-film cells could make them highly competitive with present solar cells.

Fig. 7 Theoretical characteristics of a cadmium-silicon-arsenide (CdSiAs_2) homojunction solar cell. (a) The predicted current-voltage characteristics for three possible diffusion lengths. Both the area enclosed by each of these curves and the sharpness of the corner where the current suddenly increases are important in determining the power output of a solar cell. (b) How grain size affects the short-circuit current for two different interface

recombination velocities. (c) How grain size affects the solar cell efficiency, plotted for two different interface recombination velocities. This theoretical efficiency is comparable to that of present single-crystal silicon solar cells (efficiency 15%). If similar performance can be achieved in practice, the lower cost of these thin-film cells could make them very competitive.

Conclusion

The theoretical evaluation of solid-state materials parameters for solar-cell applications is an important and complex problem in theoretical and computational physics. We have spent a considerable amount of time and effort developing the complex models and codes that model the solid-state materials and solar cells.⁶⁻⁹ However, the time cost substantially less than a direct experimental program for each.

We have developed a series of computer codes that, from first principles and basic crystalline parameters, calculate the complex energy band structure and wave vector for a semiconducting material. Using these outputs, we perform a complex integration over the band structure to determine the absorption coefficient and the related quantities of dielectric constant, index of refraction, reflection coefficient, and transmission coefficient. At this point, we are also able to determine the transport properties such as mobility, lifetime, and effective masses.

Once the material parameters have been determined, we can use them in another set of codes that model the operations of solar cells. These codes give us the current-voltage characteristics, short-circuit current, efficiency, and fill factor, related to geometry, grain size, and interface recombination velocities.

The results of all of our calculations have been accurate enough

to allow quick and inexpensive evaluations of materials as candidates for solar cells.

Key words: band structure; mathematical models; semiconductor; solar cells.

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Flame quenching in internal combustion engines

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Computer models are being used at LLNL to pinpoint the origins of unburned hydrocarbons emitted by internal combustion engines. Model calculations show that, contrary to prevailing assumptions, these pollutant emissions do not result primarily from flame quenching on the metal walls of the combustion chamber. Instead, flame quenching in other areas—piston ring crevices, valve seat crevices, and spark plug threads—may be responsible.

The transportation needs of the United States are met in large part by private automobiles powered by internal combustion engines. Essential business and social structures depend on the flexibility and convenience that private automobiles provide, and this dependence is not likely to change in the foreseeable future.¹ Internal-combustion-engine vehicles account for more than half of our oil consumption, and almost half of the oil that we burn is imported. Thus, the internal combustion engine is at the heart of many of our economic, political, and environmental concerns.

Engines and pollutant emissions

Current economic and environmental problems have led to simultaneous demands for high automobile fuel efficiency and low pollutant emissions. These demands are often contradictory. For example, conventional methods of reducing emissions of nitrogen oxides and other pollutants necessarily reduce fuel efficiency. Conversely, many available means of increasing fuel efficiency also increase pollutant emissions. The application of computer models of engine combustion processes

provides a more detailed view of some of these problems.²

Among the chemical pollutants emitted from typical internal combustion engines are unburned hydrocarbon species (UHCs), which have diverse environmental effects. Some are benign; others are toxic, even in small amounts; and still others, including the polycyclic aromatic hydrocarbons (PAHs), are known carcinogens.

The presence of UHC emissions indicates that not all the chemical energy in the fuel is being converted into useful engine work. Furthermore, the current method of reducing such emissions involves the insertion of a catalytic conversion unit in the exhaust stream, which creates a retarding backpressure that further reduces engine fuel efficiency.

Currently, the U.S. Environmental Protection Agency limits UHC emissions from an internal combustion engine to 0.41 g/mi, and California limits them to 0.39 g/mi. Moreover, as shown in Fig. 1, this limit has been significantly lowered over the past decade and may be lowered again. It is possible, therefore, that further reductions in engine fuel efficiency are in the offing.

An alternative approach to reducing UHC emissions—one that may actually increase engine fuel efficiency—involves identifying the physical and chemical

processes that are actually responsible for incomplete combustion. Once these processes are well understood, strategies can be developed to reduce the quantity of UHCs produced. Computer simulations, like those being carried out at LLNL, are particularly well suited to this approach.

Flame quenching

For many years, it has been assumed that a major fraction of UHC emissions is caused by flame quenching on the metal surfaces of the engine combustion chamber (see Fig. 2). Because the temperatures produced by fuel-air combustion are very high (in excess of 2000 K), the metal components of the engine must be cooled to prevent rapid deterioration. Thus, the walls of an engine combustion chamber remain below 500 K. Rapid heat transfer occurs from the

burning hot gases in the chamber to the cool walls, producing a thin layer of unburned gas along the engine chamber walls that also remains cool. Under typical engine operating conditions, this layer of gas is approximately 0.1 mm thick. Because the chemical reactions that keep the fuel burning are very strongly temperature-dependent, the flame cannot penetrate this boundary layer and burn the cold gas.

Schlieren photographs of flame propagation in both internal combustion engines and laboratory combustion chambers have confirmed the existence of this so-called quench layer of unburned, cold gas. Measurements of the thickness of this layer agree very well with theoretical predictions. If it is assumed that none of the fuel in this quench layer is burned, the contributions from all exposed sur-

faces in the engine combustion chamber can be added up to obtain an estimate of the overall UHC emission rate. This estimate agrees rather well with observed emission levels, in apparent confirmation of relationship between flame quenching and UHC emissions.

When we began to use computer models to analyze the flame-quenching process (in collaboration with research engineers from Ford Motor Company),³ our expectation was that some way might be found to reduce residual UHC levels. However, much to our surprise, the modeling results contradicted many long-held views about the flame-quenching process. Subsequent experiments were carried out to address the problems identified, and these experimental results support our modeling results.

Computer modeling of flame quenching

In the calculational study, we used a computer model that solves the equations of fluid mechanics and chemical kinetics simultaneously.⁴ The flame-quenching event is visualized as shown in Fig. 3. The flame approaches the flat combustion-chamber wall at normal incidence, with hot combustion products behind the flame and cold, unburned fuel and air between the flame and the wall. Although the flame is highly turbulent throughout most of the combustion chamber, viscous effects near the wall make it very

Fig. 2 Schematic diagram of a typical engine combustion chamber and piston. Because the temperatures produced by fuel-air combustion are very high (in excess of 2000 K), the metal components of the engine must be cooled to prevent rapid deterioration. Thus, the walls of an engine combustion chamber remain below 500 K. Rapid heat transfer occurs from the burning hot gases in the chamber to the cool walls, producing a thin layer of gas along the engine chamber walls that also remains cool. Under typical engine operating conditions, this layer of gas is approximately 0.1 mm thick. Because the chemical reactions that keep the fuel burning are very strongly temperature-dependent, it has been assumed that flame quenching on the inner metal walls of the combustion chamber is responsible for unburned hydrocarbon emissions.

nearly laminar there. This laminar behavior greatly simplifies our computational task, since we have considerable experience modeling laminar flames, but little with turbulent flames (because no adequate models for such flames exist yet).

In our computer simulation,³ the flame propagates normally as long as it remains at a considerable distance from the cold wall of the combustion chamber. Since the dominant factor in flame propagation is heat transport ahead of the flame into the cold unreacted gas, the relevant distance scale for these flames is L_t , the thermal diffusion length (defined by the propagation coefficient of thermal conductivity). When the flame gets within several thermal diffusion lengths of the chamber wall (e.g., within about 0.1 mm for a typical engine), the cold boundary layer begins to affect flame chemistry.

The energy that diffuses ahead of a normal flame heats up the unburned gases gradually until they begin to react, slowly at first but at a rate that increases exponentially with time. Highly reactive free radical species, such as unpaired hydrogen and oxygen atoms and hydroxyl radicals, also diffuse ahead of the flame. In the region in front of the flame, which is steadily being heated, these radical species accelerate the first stages of fuel reaction by breaking up the fuel and oxygen molecules into smaller fragments, which can then react very rapidly to release most of the heat of reaction.

This sequence of events is disturbed when the flame encounters the thermal boundary layer at the cold wall. First, the heat sink represented by the wall saps the energy that diffuses ahead of the

Fig. 3 Schematic description of flame quenching near the cold metal wall of the combustion chamber of an automobile engine. The flame propagates normally and burns the hydrocarbon fuel completely until it nears the wall of the combustion chamber. The wall cools the unburned fuel-air mixture near it, preventing the flame from burning the mixture. Thus, a layer of unburned fuel

remains on the chamber wall. Until now, it has been assumed that most unburned-hydrocarbon emissions were produced by this process. However, computer calculations show that there is ample time in conventional engines for the mixture near the wall to diffuse outward into the high-temperature region, where it is consumed very rapidly.

flame. Thus the boundary layer does not heat up exponentially, as it would in the absence of the cold wall. Because the preflame region remains cooler, the chemical reactions ahead of the flame are strongly affected.

The chemical reactions of the free radical species can be divided into two classes (see the box on this page). The first consists of those reactions involving fuel and oxygen molecules. These chain-propagation and chain-branching reactions are essential in maintaining a vigorous flame and releasing energy. They are also temperature-dependent, proceeding very slowly at low temperatures and much more rapidly at high temperatures.

The second class of free radical reactions consists of chain-terminating (radical recombination) reactions between pairs of free radicals. These reactions remove free radicals from the flame and tend to extinguish the burning. These radical recombination reactions have almost no temperature dependence and, at normal combustion temperatures, proceed at much slower rates than the chain-propagation reactions. However, in the cold boundary layer resulting from heat transfer to the cold wall, the temperature-dependent propagation reactions are artificially suppressed, and the termination reactions predominate.

The macroscopic effect of the molecular reactions is that the flame is unable to propagate all the way to the wall. Instead, it stagnates

at a distance from the wall approximately equal to the thermal diffusion length L_1 , leaving a layer of unburned fuel.

Up to this point, the computer-modeled properties of thermal flame quenching agree with the traditional picture. However, examination of the subsequent evolution of this quench layer provides important, and somewhat surprising, results.

Although heat is continuously being lost to the wall, the gases in the combustion chamber remain very hot except for the cold boundary layer. The fuel trapped in this

layer begins to diffuse out toward the high-temperature region. Once this fuel reaches the hot gases where the temperature is high and there are large concentrations of free radicals, it is consumed very rapidly. For a typical quench layer thickness of 0.1 mm, the time scale for this burning is approximately 0.1 ms.

The environment in which flame quenching occurs in an operating internal combustion engine is, of course, very dynamic. Superimposed on the flame behavior and fuel consumption is the motion of the piston in the cylinder. Most

Hydrocarbon oxidation

The oxidation (burning) of hydrocarbon fuels involves two general types of reactions: flame-promoting reactions and flame-retarding reactions. There are three types of flame-promoting reactions, illustrated below for the case of methanol oxidation (CH_3OH).

1. Chain-initiation reactions

One or two stable molecules, such as CH_3OH and O_2 , react to produce radical (highly reactive) species, such as $\text{CH}_3\cdot$, $\text{CH}_2\text{OH}\cdot$, $\text{OH}\cdot$, and $\text{HO}_2\cdot$ (the dot denotes a radical). Chain-initiation reactions are highly temperature-dependent.

2. Chain-propagation reactions

The number of radical species remains constant. Chain-propagation reactions are only slightly temperature-dependent.

combustion in the engine chamber takes place fairly close to the time of maximum compression when the piston is at the top of its stroke. The rapid expansion of the burning gases that accompanies the subsequent piston downstroke cools the gases rapidly and effectively ends the overall combustion reaction. If expansion of the reacting gases due to piston motion takes place before the fuel in the quench layer diffuses out to the stagnant flame and is burned, then this fuel will be exhausted as UHCs. However, at typical engine speeds, the combustion chamber is highly compressed

for nearly 10 ms, ample time for the fuel in the quench layer to diffuse and burn completely. From our calculations, it appears that only at engine speeds of 30 000 rpm or higher (a level 10 times greater than that normally experienced in production engines) would flame quenching at the combustion-chamber walls provide the majority of the observed UHC emissions.

This means that, contrary to the long-held assumption, flame quenching on the walls of the combustion chamber is probably not responsible for the majority of

UHC emissions in conventional internal combustion engines. Our computer modeling study, originally intended to develop strategies for reducing UHC emissions due to wall flame quenching, led us to the somewhat surprising conclusion that we needed to look elsewhere for the principal sources of these emissions.

Alternative sources of unburned-hydrocarbon emissions

Hydrocarbon emissions are known to result from other processes in internal combustion engines. Research into the details of these processes has been inhibited in the past by the general consensus that flame quenching on combustion-chamber walls is the primary source of UHC emissions. However, as a result of our computer modeling study, greater attention is now being given to other possible sources of UHC emissions, including flame quenching on the threads of spark plugs, on imperfections in valve seats, and in piston ring crevices (all spaces small enough to prevent entry of the flame). Currently, considerable evidence points to the piston ring crevices as the primary source of UHC emissions.

3. Chain-branching reactions

In chain-branching reactions, the number of radical species increases. Chain-branching reactions are moderately temperature-dependent, less so than chain-initiation reactions, but more so than the chain-propagation reactions.

Flame-retarding reactions would include the following:

The number of radical species is reduced. These reactions are nearly independent of temperature.

A conventional combustion chamber with its moving piston is sealed by several (usually three) piston rings (see Fig. 4). The top two compression rings maintain combustion-chamber pressure, while the third and lowest ring keeps engine oil out of the combustion chamber. Unburned fuel-air mixture is free to enter the crevice between the chamber wall and the piston above the first piston ring (a space 0.25 in. long by 0.019 in. wide in one engine⁵). In addition, some unburned mixture can get beyond the piston ring and occupy the space between the rings. These crevices are so thin that the flame cannot enter, but the total volume is sufficient to produce the UHCs observed in the exhaust.

One experiment⁵ showed that moving the top piston ring closer to the main combustion chamber and narrowing the space between the piston and the cylinder wall reduced UHC emissions by up to 74%. Unfortunately this design was

not practical for production engines.

In another study,⁶ the piston was removed, and the engine combustion chamber sealed (completely eliminating the ring crevice). The

resulting UHC emissions were negligible. When the piston ring crevice was restored to this combustion chamber, high levels of unburned hydrocarbon emissions were again observed.

Fig. 4 For many years the general scientific consensus has been that flame quenching on the inner metal walls of the combustion chamber is responsible for unburned-hydrocarbon (UHC) emissions. Recently, however, it has been shown that substantial amounts of unburned fuel are trapped in gaps between the chamber wall and the piston and around the piston rings. This appears to be a far more significant source of UHC pollutant emissions.

Oil from the engine lubrication system often contaminates an engine combustion chamber and forms a thin layer on the cylinder walls. Recent studies⁷ indicate that fuel absorption in these oil layers may also contribute to UHC emissions.

Summary

Our computer modeling studies have shown that flame quenching in the cold boundary layers on the walls of engine combustion chambers does indeed occur. However, the fuel trapped in the quench layer rapidly diffuses away from the walls and into the high-temperature region in the center of the chamber where it is consumed. The time required for this fuel diffusion and consumption is very short compared to typical combustion-chamber compression times. Therefore, flame quenching on the combustion-chamber walls is probably not responsible for the majority of observed unburned hydrocarbon emissions from typical internal combustion engines. Instead, recent experiments suggest that flame quenching in piston ring crevices is a more important source of unburned hydrocarbons.

Key words: air pollution; automobiles—exhaust gases; combustion modeling; exhaust gases; flame quenching; unburned hydrocarbons.

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LLNL RESEARCH

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