Research in Progress

LIQUIDS — ORDERED CHAOS

C. J. Pings studies optical properties of a liquid.

The behavior of gases and solids is quite well known. Theories have been developed which make it possible to predict their behavior under different circumstances.

There are lots of theories about liquids, too. But none are completely successful. Scientists simply do not know why liquids flow, splash, and otherwise behave as they do.

At Caltech, Cornelius J. Pings, associate professor of chemical engineering, has been studying the fundamental behavior of liquids for the past eight years. This work is now being expanded under a new contract with the Air Force Office of Scientific Research. Additional support comes from the Office of Naval Research and the National Science Foundation.

Dr. Pings and his group are attempting to learn more about how atoms and molecules behave in the liquid state at various temperatures and pressures. This involves not only "looking at" atoms and molecules, but also studying the microscopic forces that lace them together in the informal, shifting way that is characteristic of liquids.

"Although the molecules of solids are arranged in orderly rows and those in gases in perfect disorder, the molecules in liquids comprise a moving interlocked mess — a sort of ordered chaos," Dr. Pings explains. "In liquids, each atom is affected by thousands of surrounding atoms whose positions in relation to each other are constantly changing."

This is one good example of a many-body problem, a name given to a number of current problems in physics involving the simultaneous interaction of a large number of particles, atoms, or molecules. The biggest digital computer in existence is not powerful enough to solve these problems by brute-force arithmetic. Although they are currently the focus of much activity by theoretical physicists and chemists, progress is slow, and a general solution to these many-body problems is not yet in sight.

A lack of a good working theory for the behavior of liquids has its frustrating and expensive consequences at the practical level. The modern-day engineer and scientist, for all of his knowledge of atoms and molecules, cannot make a straightforward prediction of the elementary properties of even the simplest liquids. Such things as densities, viscosities, and boiling points — needed for the design and intelligent operation of chemical plants, oil refineries, and liquid-fueled rockets — cannot be reliably estimated from theory and must usually be measured in the laboratory and pilot plant.

It is apparent also that continued lack of full understanding of the behavior of liquids in general, and solutions in particular, will stand as a barrier to full insight to many basic problems in physiology and medicine. Chemical kinetics in the liquid phase is currently at a stalemate, in contrast to the significant gains in gas-phase kinetics in the last decade.
Previous experimental studies have been made of the forces and configurations involved in liquids. However, much is still unknown and the theoretician is frequently stymied by lack of knowledge of what is actually going on at the molecular level in liquids and dense gases. Pings and his co-workers are interested in determining the behavior of very simple liquids at a wide variety of temperatures and pressures. The group hopes to obtain enough data to provide a sound framework for a comprehensive, over-all theory. The team is now enlarging its laboratory space to make observations of molecules and their forces in liquids with several techniques.

The first is x-ray diffraction. It enables investigators to measure the average number of neighboring atoms and the distance they sit from each other. A beam of x-rays is directed at the liquid being studied and the atoms in the fluid diffract the x-rays. The diffracted radiation is detected by scintillation counters. Mathematical analysis of the diffraction data yields direct information about the average configurations in the system of moving liquid molecules.

One set of completed experiments on liquid nitrogen has revealed that each nitrogen molecule on the average is surrounded by a "shell" of 15 neighboring molecules at a distance about 5 percent greater than the shell of nearest neighbors in the crystal lattice.

A current experiment on liquid argon will determine how these configurations change with the temperature and density of the fluid. Mr. S. E. Rodriguez has just completed a set of diffraction studies on liquid gallium for his PhD thesis. Gallium is a metallic element that looks like mercury, although it is less than half as dense. It normally freezes at 29.8°C. However, Rodriguez was successful in supercooling one specimen to 0°C for more than 30 hours while he determined its structure. Tentative conclusion: Unstable supercooled gallium is a normal liquid as far as its molecular-level configuration is concerned.

The second experimental technique is a study of the refractive index of the fluids. This is the measurement of how much a beam of light is bent as it stabs through a liquid. The amount of bending is indicative of the electrical environment in the immediate vicinity of a molecule in the liquid.

These measurements have been made on methane, carbon tetrafluoride, and argon. The argon measurements have been concentrated on the liquid up to 100 atmospheres, but have been included in some studies of both gaseous and solid argon. Of particular interest in this study is the Lorentz-Lorenz theory, which postulates a quite simple relationship between the dielectric constant (or refractive index) and the density of a substance.

The experimental work so far has indicated that the theory seems to be quite good for non-polar gases, liquids, and solids. This may be of some significance, since very few properties can be predicted for all three states of matter by a single theory or model.

The third experimental technique is ultrasonic absorption. Ultrasound pulses disturb the liquid slightly, causing its structure to change. The rate at which the liquid's forces pull its molecules back to their original position could apply to information that may lead to a theory of predicting viscosity and other transport properties.

Much of the investigation is concentrated at the critical region of a liquid, the borderline region between liquid and gas. Theoreticians still have no satisfactory explanation for the very strange behavior of a fluid at its critical state. It is known that very large clumps form in liquids in this region. The clumps often are so large that they cause light to scatter. In some instances an otherwise colorless liquid looks brown from the scattering.

There is considerable theoretical and practical interest in this region. Practically, there is much interest in the fact that heat capacity and thermal conductivity increase as much as ten times. The thermal conductivity properties suggest that liquids in the critical state may provide a very effective heat transfer medium for boilers and chemical processing equipment, and the heat capacity properties may be useful for heat control, as a sort of heat buffer.

On the theoretical side, the critical region seems to be sort of a promised land for the theoretician interested in many-body problems. A key to the critical region might very well also turn the lock of the whole liquid state problem. Two international meetings will be held in the next 12 months on experimental and theoretical problems of the critical state.

Liquids currently under investigation by the Pings group are all relatively simple; they include mercury, carbon tetrafluoride, gallium, nitrogen, and argon. Some substances, such as argon and nitrogen, require cooling down to temperatures of minus 310 degrees F. before they will liquefy.

At present, water is too complex a liquid to investigate. One of its complicating factors is the presence of the unusual hydrogen bond forces between the molecules, resulting in very peculiar behavior.

"I think we will wait a few years," says Dr. Pings, "before we tackle anything as complicated as water."