8. Time-Resolved Spectroscopy of Condensed Matter

Academic Research Staff

Prof. J.D. Litster, Dr. L.C. Kupferberg

Graduate Students

D.E. Cooper, B.D. Larson, L.E. Solomon

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James D. Litster, Brent D. Larson, Lorraine E. Solomon

We are using time-resolved spectroscopy in conjunction with light scattering and x-ray scattering to study the properties of condensed phases (solids, liquids, liquid crystals, and other phases) of matter. Our goal is to understand why large numbers of interacting particles form the phases which they do and why they have the properties which they have; this problem of phase transitions is one of the most important problems of current interest in physics.

The tools we use provide different kinds of information. From x-ray scattering we learn about the mass density fluctuations and structure on length scales as small as 1 Å to as large as 1 µm using high resolution, but we learn nothing about dynamical behavior since it is not possible to measure energy changes in the scattered radiation with sufficient precision. Quasi-elastic light scattering enables us to study the dynamical behavior of fluctuations which alter the refractive index of the material studied; by digital autocorrelation we can measure energy changes in the scattered light of 1 part in 10^{14}. Light scattering, however, restricts us to studying properties on a length scale of half the wavelength of light or longer. The use of time-resolved spectroscopy enables us to study the dynamical behavior of processes as fast as 10^{-12} second and, in addition, it is frequently a local probe of behavior, thus providing information on the same length scale as x rays combined with dynamical information that can be obtained optically.

In the past, we have applied this singular technique to studying phase separation in binary critical mixtures and to studying the microscopic fluid properties of polymer solutions and gel phases. During the past year we have been concentrating on the behavior of surfactant molecules in water solutions with salt. These molecules are amphiphilic, that is, one end prefers to interact with polar materials like water, and the other end prefers an oily environment. In a sufficiently concentrated

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2Assistant Professor, Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts
solution (about $10^{-3}$ molar) they organize themselves into micelles, roughly spherical structures with the oil-loving ends of the molecule in the middle and the polar moiety on the outside. As more surfactant is added to the solution more micelles form, and when about 50% of the volume is occupied by micelles, the micelle-micelle interaction has become so strong that they form an ordered phase. The micelles we have been studying are decylammonium chloride (DACI) and have been found by x-ray scattering to be diskshaped at high concentrations, with a diameter of 60 Å and a thickness of 20 Å. They order first into a phase in which the symmetry axes of the disk align parallel, but without positional ordering. On lowering the temperature, the disks fuse themselves into bilayers with the oil-loving moiety in the interior of the layer. This occurs as a second-order (continuous) transition. New hydrodynamic normal modes appear as a result of this ordering, and we have been studying these by light scattering.

We have been using pulses from a mode-locked dye laser to study the orientational dynamics of the micelles as a function of temperature and surfactant concentrations. This is done in a way quite analogous to using a strobe light to study rotating machinery. By adding a small amount of dye (about one molecule to each micelle) we can monitor the orientation of the micelles by measuring the decay of dichroism following an excitation pulse of light. The reorientation of a single micelle in solution would lead to a dichroism decaying as $e^{-60Dt}$ where the rotary diffusion constant $D$ is given by $D = kT/6\eta V$, where $\eta$ is the viscosity of the water, and $V$ is the volume of the micelle. At low micelle concentrations, the micelles behave as independent particles with a volume that agrees with the x-ray measurements; we find $1/6D \sim 400$ psec at 25°C and scales with the viscosity of water as the temperature is changed. At higher concentrations, when the micelles interact, the reorientation time appears to be temperature-independent, which is a quite unexpected result. We believe the statistical mechanics of how these micelles interact is of fundamental interest and will pursue it vigorously.

Future directions will also include a study of nonradiative energy transfer in micelles; this will yield information on the structure of the micelle, as well as being of some practical importance for building more efficiently pumped dye lasers for some spectral regions. We expect that the elucidation of the behavior these materials, which are lyotropic liquid crystals, will contribute to progress in the field of statistical mechanics. Less broadly, we expect to gain greater insight into the physics of surfactants, and the formation and stability of microemulsions and bilayers, which are the basic structural component of cell walls in biology.

Publications
