A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR -89-2105

LA-UR--89-2105

DE89 014228

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE **ISSUES AND FUTURE DIRECTIONS IN SUBSECOND THERMOPHYSICS**

AUTHOR(S) J. W. SHANER

SUBMITTED TO FOR PUBLICATION IN PROCEEDURES OF THE 10TH SYMPOSIUM ON THERMOPHYSICAL PROPERTIES, NBS, GAITHERSBURG, MD JUNE 20-23, 1988

DISCLAIMER

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ISSUES AND FUTURE DIRECTIONS IN SUBSECOND THERMOPHYSICS*

J. W. Shaner
Los Alamos National Laboratory
Los Alamos, New Mexico, USA 87545

I. INTRODUCTION

The primary motivations for trying to measure thermophysical properties of materials on subsecond timescales are to extend measurements to higher temperatures than can be conveniently maintained continuously, or to make measurements on systems out of thermodynamic equilibrium. Since these measurements are difficult, one must keep in mind the needs for the data. These include the ability to use materials cleverly in new high-pressure/high-temperature applications, as well as the development of calibrated models for the response of materials to rapid energy deposition, by laser pulses for example.

For experiments in the 1-ms to 1-s range, techniques are well developed to make thermophysical property measurements up to the melting point of the sample.[1] Good temperature standards have been established. These time scales are too long if the temperatures exceed 10^4 K or the samples melt. For the range from 1 μs to 1 ms, measurements of reasonable accuracy (<5%) can be made, even on samples that melt during pulsed heating.[2] On this time scale, however, accurate temperature standards have been limited to below the sample melting points. On the time scale of 1 ps to 1 μs, required for very high temperatures, there are no temperature standards, the systems are typically out of equilibrium, and many of the measurements are post mortem, and, therefore, inferential. But it is just in this range that the small total energies can give high-power fluxes to seriously modify very small samples. The interest by industry in using pulsed heating on this time scale, for surface modification of materials for example, make this activity particularly important.

Several key areas have been identified in which effort is needed for substantial progress in subsecond measurements, and which have unusual promise for useful new scientific results. These areas include the problems of high-temperature standards, equilibration during rapid heating, measurements at higher temperatures combined with higher pressures, measurements on specific interesting materials, and measurement of microstructural properties at high temperature and their relation to macroscopic response. Each of these areas will be touched upon here.

II. TEMPERATURE STANDARDS

Temperature standards can be defined to high accuracy up to the melting points of the most refractory materials.[1] So long as the material remains solid, a good approximation to a black body cavity can be made. The effective emissivity of a small hole in the cavity wall is close to one, and the hole dimensions are stable. Since the speed of light is so high, thermodynamic equilibrium can be established in the cavity, even on submicrosecond time scales. If, however, the cavity material begins to melt, surface tension and gravity will

* This work was supported by the US Department of Energy.

distort the cavity opening, making the radiance temperature determination much less accurate.

In the temperature range above 4000 K, where most materials are molten except at extreme pressures, a new way of establishing temperature standards must be developed. Since liquid metals can be held in a stable form in the 4000 to 10,000-K range for several microseconds,[2] a characterization of the temperature and wavelength dependence of the emissivity, $\epsilon(T, \lambda)$, may be possible. Since this function tends to be relatively smooth, it may be possible to fit it for some metal with relatively few, simple polynomials. This program would require a large number of intensity data points and a detailed sensitivity analysis to determine potential accuracy.

A particularly interesting aspect of a program to determine $\epsilon(T, \lambda)$ is that any deviations from a relatively smooth surface will indicate structure in the joint density of electronic states. Although the loss of long range order in the fluid metals eliminates many of the critical points in the electronic density of states, there will still be structure which may be observed in reflectivity, or equivalently, in emissivity. The use of this "emissivity spectroscopy" may provide useful new data on the electronic structure of fluid metals for which reflectivity measurements are not possible.

III. EQUILIBRATION PROBLEMS

In dynamic experiments two kinds of deviation from equilibrium can occur. Systems can be inhomogeneous, although in local thermodynamic equilibrium (LTE), and systems can be homogeneous, although out of LTE. Examples of the former are rapidly pulse-heated metals where the skin effect causes inhomogenous energy deposition, or where radiation cooling of a surface creates a temperature gradient. An example of the latter is a molecular system in which a vibrational degree of freedom has been excited, by stimulated Raman scattering, for example, to a temperature much higher than the translational degrees of freedom.

The problem of temperature gradients resulting from the skin effect in pulsed heating experiments has been dealt with in detail.[2] Careful attention is required in 1 to 10-μs heating to assure reasonably homogeneous samples. The radiation cooling effect can be treated qualitatively. Since the thermal radiation flux from a surface is $\epsilon\sigma T^4$, where ϵ is the emissivity, σ is the Stefan-Boltzmann constant, and T is the temperature, an equal energy flux must be transported down a thermal gradient near the surface. Assuming a very rapid establishment of a high temperature, in a time δt this gradient propagates $\delta x \sim (\kappa\, \delta t/c)^{1/2}$ in from the surface, where κ is the thermal conductivity and c is the heat capacity. Combining these expressions, the difference between surface and bulk temperatures is

$$\frac{\delta T}{T} \sim \epsilon\sigma T^3 \left(\frac{\delta t}{\kappa c}\right)^{1/2} .$$

For experiments lasting 10^{-4} s in typical metals, $\delta T/T \sim 1.5\%$ for $T \sim 10^4$ K. The radiative cooling is a problem primarily for longer term experiments. If the hot sample is in contact with a good thermal conductor, as in a diamond-anvil cell for example, with a long heating pulse, or in steady state, the gradients can cause a significant temperature heterogeneity.[3]

Another significant problem associated with pulsed systems at high temperature is the question of how long a crystal takes to melt, and what is the degree of superheat possible in a solid. Recent shock wave measurements indicate that on a nanosecond time scale, solids may be superheated by as much as 500 K.[4] The general problem of the dynamics of melting both in bulk and on surfaces needs quantitative investigation.

A final example of equilibration problems is the dynamics of vapor-bubble nucleation and growth in complex systems, like metals. The long range interaction in metals complicates the usual nucleation and growth models. For both theoretical and practical reasons, associated, for example, with problems of hypervelocity impact, a quantitative knowledge of vapor-bubble dynamics is required.

IV. HIGHER TEMPERATURE AND PRESSURE

Combining extreme conditions of temperature and pressure simultaneously presents an experimental challenge. The diamond-anvil cell has allowed some progress and more can be expected. By using special materials, diamond cells can be operated at over 200 kbar and 1500 K, and much higher temperatures have been achieved if large thermal gradients are acceptable.

Shock pressures up to several megabars are possible with laboratory impact facilities. Associated shock temperatures of up to 10,000 K allow us to make a wide range of thermophysical measurements of reasonable accuracy. Higher pressures and temperatures require more energetic driving systems, like nuclear explosions, or smaller experiments, like those used for laser pulse driven shock waves. Both of these options will be limited into the indefinite future.

One recently developed technique to achieve a wider range of temperatures and pressures in a shock wave experiment involves pulsed preheating and then shocking a sample.[5] These techniques are difficult to control and add inaccuracy to the measurements. The overall usefulness remains to be seen.

One technical area where pulsed heating should be very interesting is in the production of dense non-ideal plasmas. These systems, from 0.1 times the critical density to the critical density, have all the complexity of fluids with strong ion correlations, electronic transitions, cluster formation, and plasma phase transitions. Very little is known about the thermophysical details of these dense plasmas.

V. SPECIFIC MATERIALS AND MEASUREMENTS

Carbon remains one of the most poorly characterized elements in terms of its basic thermophysical properties. For example, the solid-liquid-vapor triple point of graphite still is uncertain to roughly a factor of two in pressure and several hundred degrees in temperature. Another uncertainty is the slope of the diamond-liquid phase boundary, although recent measurements seem to show it must have a positive dP/dT.[6] The slope of this particular phase boundary tells whether the liquid is more or less dense than the diamond phase, so it is a very basic thermophysical property. Finally, there remains uncertainty about whether fluid carbon is metallic ($\rho \sim 100$ $\mu\Omega$-cm), like Si and Ge, or

whether there may even be two fluid phases. All of these problems are associated with the extreme temperatures required to hold fluid carbon, and, therefore, the carbon problems represent fundamental challenges to subsecond thermophysical measurements.

With the exception of mercury and the heavier alkali metals, the thermophysical properties of fluid metals within a factor of two of the critical density ($0.5\ \rho_c < \rho < 2\rho_c$) are poorly measured. We typically have to rely on equation-of-state models calibrated well away from the critical point to establish even this basic thermodynamic point. Critical phenomena in metals may well be qualitatively different from those in simple fluids, since in metals the potential changes from long to short range around the critical density. Also, the relationship between the critical fluctuations and transport properties is still far from clear. A great deal of work will be necessary to make measurements, necessarily pulsed, at the high pressures and temperatures of metal critical points. However, the physics of these strongly correlated systems should make the effort worthwhile.

Metals can be heated electrically in a carefully controlled manner. Non-metals, like minerals and ceramics, present a different set of problems, both technical and scientific. The primary scientific problem is understanding the relationship between chemical reactions and critical fluctuations. The technical challenge is to find a way to pulse heat insulators to high temperature. Volume heating by relativistic electron beams has been tried, but complete thermophysical measurements have been difficult, and inaccurate as a result of inhomogeneous energy deposition and electrical noise. Preliminary attempts to use pulsed neutron heating of uranium impurities show another possible approach. By controlling the impurity concentration, one can achieve a reasonably uniform heating. However, pulsed neutron sources of sufficient intensity are rare.

VI. MICROSTRUCTURAL DATA

The thermodynamic properties of condensed matter are determined by the interparticle potential and the structure of the atoms or molecules. When systems are pulsed heated, through melting for example, the microstructure obviously changes. More subtle changes associated with the way atoms of type A cluster around particles of type B in binary systems will affect the thermodynamic properties. Also, the dynamics of formation of equilibrium microstructures may be of interest. These problems may be approached by combining pulsed heating with pulsed x-ray or neutron scattering, although very little data of this type is presently available.

REFERENCES

1. See, for example, A. Cezairliyan, J. Res. NBS 75C, 7 (1981).

2. See, for example, G. R. Gathers, J. W. Shaner, and R. L. Brier, Rev. Sci. Inst. 47, 471 (1976).

3. J. M. Brown, private communication.

4. C. A. Swenson, J. W. Shaner, and J. M. Brown, Phys. Rev. 34, 7924 (1986).

5. R. N. Keeler, A. C. Mitchell, and J. W. Shaner in High Pressure Geosciences and Material Synthesis, H. Vollstädt, Ed.

6. J. W. Shaner, J. M. Brown, C. A. Swenson, and R. G. McQueen, J. de Physique C8;235 (1984).