11 Diffusion Measurements by Ultrasonics

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11.1 Introduction

The velocity of acoustic waves depends on the elastic properties and the density of the transport medium. The variation of these properties can therefore be observed with ultrasonic waves. The velocity of sound can sensitively be detected by observation of the phases of transit signals. Resolutions of 1 part in 10^8 with respect to changes of the velocity of ultrasound can be achieved for ultrasonic waves in the frequency regime of typically 10 to 100 MHz. Spatial resolution can be obtained with narrow beams of plane waves or with focused ultrasonic waves.

Ultrasonic beams generated and detected by planar transducers are routinely used to observe the temperature dependence of the velocity of sound in liquid or solid materials. Variations of the temperature lead to changes of the elastic properties as well as to thermal expansion. The temperature dependence of the velocity of acoustic waves is often used to observe phase transitions or to gain information on other thermodynamic properties of the samples. The observation of the velocity of sound can also be used as an extremely sensitive thermometer, capable to resolve temperature changes even below 1 mK. It is therefore almost surprising that only little effort has been paid so far to observe thermal diffusion processes or other transport processes by diffusion with ultrasonic detection schemes. An exception are somewhat related photoacoustic excitation schemes including the so-called thermal wave methods which have even been applied with microscopic resolution.

To demonstrate the feasibility of ultrasonic detection schemes with phase resolution, applications are presented for the observation of the diffusion of hydrogen in single-crystalline tantalum and the diffusion of heavy water in gels and living cells. Acoustic interferometric detection schemes and acoustic imaging techniques have so far only been used in these applications. They are demonstrated here to inform about these novel developments and to supply the information needed to decide if such methods can be used advantageously for measurements which cannot easily be performed by established techniques.

11.2 Diffusion of Hydrogen in Single-Crystalline Tantalum

The transport properties of hydrogen in metals have an obvious technical relevance for hydrogen storage devices where metals are employed, capable to store large amounts of hydrogen dissolved in the metal matrix. Single-crystalline samples are normally used to study the basic physical properties under idealized conditions.

A two-beam interferometric setup has been employed (Fig. 11.1) to observe the temperature dependence of the transport properties of hydrogen in metals [1]. The ultrasonic interferometric device is comparable to an optical Mach-Zehnder interferometer. Acoustic waves travel along two paths at different positions in the sample, monitoring integrally the hydrogen concentration along the paths. Piezoelectric transducers (quartz) mounted on the sample convert electric signals into acoustic signals and vice versa. Different to the optical equivalent the remaining part of the interferometer involves only electrical signals. This is possible since ultrasonic transducers are linear devices converting the amplitudes and not simply the power of the respective electric or acoustic signals.

The dependence of the velocity of transverse polarized ultrasonic waves v_t on the hydrogen content c with respect to a small variation of this content Δc is given by [2]:

$$v_\mathrm{t} = \sqrt{\frac{c_{44}^0 + (\Delta c_{44}/\Delta c)c}{\rho + (\Delta\rho/\Delta c)c}}, \tag{11.1}$$

where ρ is the density and c_{ii} the element i, i of the tensor of the elastic stiffness constants of tantalum. The relative change of c_{44} per variation of the hydrogen content of one atomic percent is $1.4 \cdot 10^{-3}$ [2]. The respective value for c_{11} is only $8.9 \cdot 10^{-5}$ [2]. Therefore transverse polarized acoustic waves, travelling along the [100] direction of the tantalum crystal, are employed for

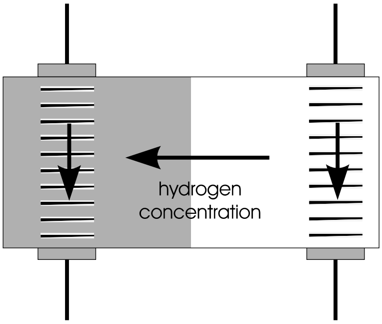


Fig. 11.1. Tantalum sample with gradient in the hydrogen distribution and four transducers for generation and detection of ultrasonic waves travelling along two separated paths.

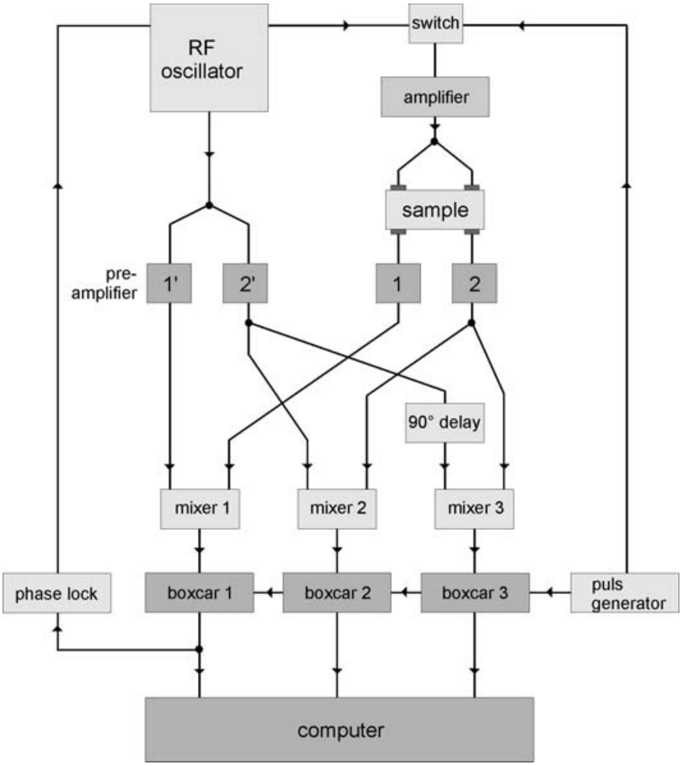


Fig. 11.2. Schematic of the ultrasonic two-path interferometer with vector phase detection. Channel 1 is used for phase-locking of the oscillator. Channels 2 and 3 detect relative changes of the phase of the ultrasonic signal with respect to channel 1. Changes in the velocity in path 1 can be determined from the frequency variation of the locked RF-oscillator.

optimum sensitivity to the hydrogen content which is about 16 times higher than for longitudinal waves.

In the experimental setup phase detection is achieved by multiplicative mixing techniques (Fig. 11.2). The frequency used for excitation is varied in such a way, that the phase observed in one of the paths with respect to an electronic reference derived from the oscillator used for excitation remains at a constant value. The amplitude is stabilized to achieve optimum resolution. The phase observed for the other path is monitored with respect to the same electronic reference by vector detection schemes. Pulses are used to discriminate echoes in the acoustic paths. Some of these features are introduced to achieve optimum sensitivity and long-term stability. This is necessary since rather slow changes have to be observed. Equilibration times for samples of typical sizes of 1 cm can reach several days or even months, depending on the temperature of the sample.

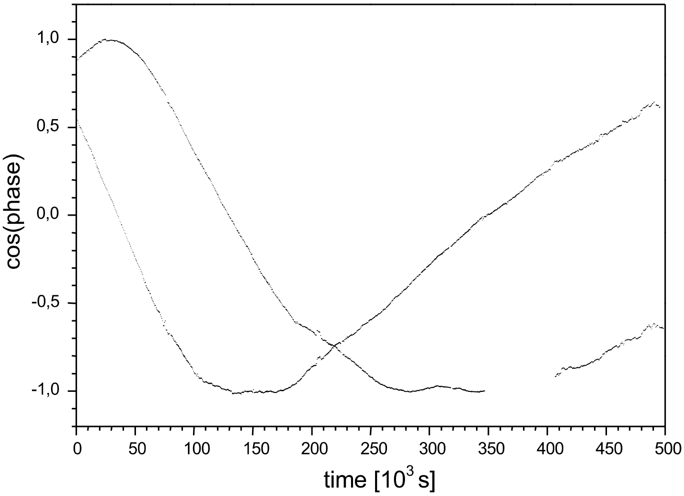


Fig. 11.3. Time dependence of the phase signals (channels 2 and 3 in Fig. 11.2) referenced with a shift of 0° and 90° with respect to the oscillator signal during the equilibration of the graded hydrogen distribution in tantalum by diffusion at a temperature of 273 K (frequency of the ultrasound: 10.6 MHz).

The data are collected and stored with a computer, controlling also the temperature of the sample.

The hydrogen distribution in the tantalum sample is varied by applying unidirectional electric currents at temperatures of about 400 K. This creates a gradient in the hydrogen content across the sample. Subsequently the crystals are cooled to the temperature where the transport processes are studied. The equilibration of the hydrogen distribution is observed with one path of the acoustic interferometer in the region of elevated hydrogen content and the other path in the region where the content has been reduced.

The data collected over time spans up to several days (Fig. 11.3) may be used to determine the diffusion coefficient D taking into account that the relaxation of the hydrogen distribution is determined by a quasi-one dimensional diffusion process following Fick's second law (see, e.g., (1.8) in Chap. 1):

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \ . \tag{11.2}$$

The diffusivities obtained for different temperatures are presented in Fig. 11.4. The temperature dependence of the diffusion coefficient is found to follow an Arrhenius relation

$$D = D_0 \mathrm{e}^{-\frac{E_\mathrm{a}}{k_\mathrm{B} \cdot T}} \tag{11.3}$$

with $E_\mathrm{a} = 0.14$ eV, where D_0 is the diffusivity at temperature $T \to \infty$.

Results presented in the literature [3] which have been obtained by conventional methods show errors of up to almost 100%, even for data from the

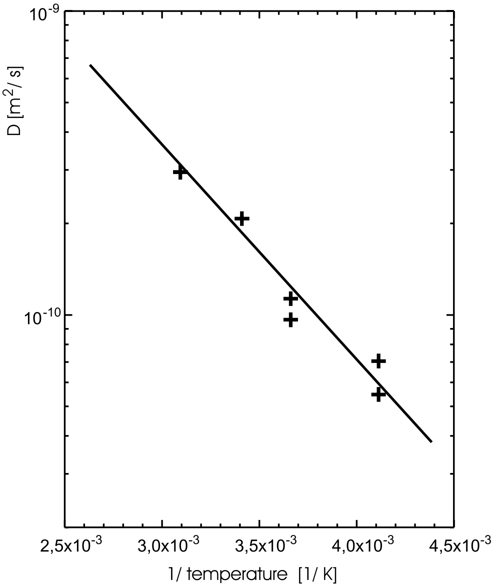


Fig. 11.4. Arrhenius plot of the diffusion coefficient D derived from measurements as represented in Fig. 11.3 (crosses) at different temperatures and line fitted to the data.

same author. The results obtained here show deviations of only up to 23% from the expected linear behaviour. The extrapolation to the value of the diffusion coefficient for $T \rightarrow \infty$ leads to $D_0 = 4.5 \cdot 10^{-8}$ m^2/s, which compares well with the value of $D_0 = 4.4 \cdot 10^{-8}$ m^2/s obtained by Völkl and Alefeld [3].

The ultrasonic detection scheme has the advantage, that surface effects play a negligible role, since the hydrogen content is monitored along a path in the volume of the sample. Even extremely slow processes can be studied. As unwillingly demonstrated in the data (Fig. 11.3), the measurement can be continued in the case of temporal failure of the electronics, caused here by a failure of the current supply. Such events are otherwise disastrous for long-time observations. Furthermore the rather low power level of the acoustic signals does not influence the observed hydrogen distribution in the sample.

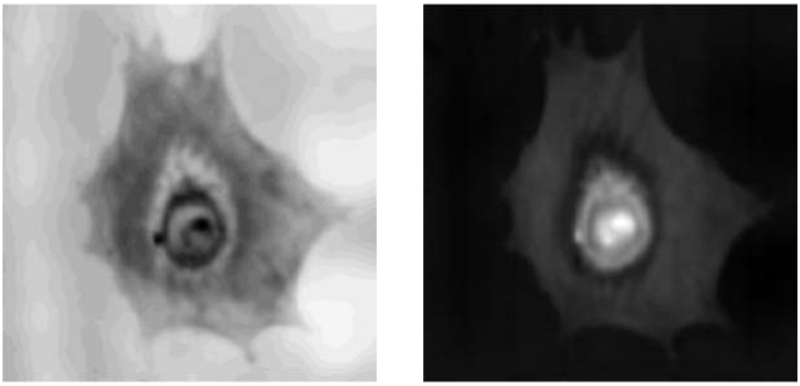
The method presented here can be used for any sample with two plane parallel surfaces. Due to the integrated detection along the paths of the ultrasonic waves, transport properties can be studied for a direction normal to these surfaces. Lateral resolution is restricted by the fact that planar acoustic waves are employed. Resolutions down to typically 2 mm are feasible with available transducers. Temporal resolution is determined by the repetition rate at which the ultrasonic pulses are generated. The maximum repetition rate depends on the absorption in the sample, since ultrasonic echoes must reach a negligible level prior to the following excitation. Repetition rates of at least 1 kHz can usually be obtained, leading to a temporal resolution of at least 1 ms. More than two paths can be used with the aid of electronic switches.

11.3 Observation of Diffusion of Heavy Water in Gels and Living Cells by Scanning Acoustic Microscopy with Phase Contrast

Scanning acoustic microscopy (SAM) [4] in the reflection mode is a confocal version of microscopy similar to confocal laser microscopy but based on acoustic waves. In commercially available equipments frequencies up to 2 GHz are used. With water as a coupling fluid a lateral resolution down to 0.6 μm can be achieved.

Recently, high resolution phase contrast has been developed for this version of scanning microscopy [5]. For demonstration of a typical image obtainable by scanning acoustic microscopy with phase contrast (PSAM), Fig. 11.5 shows an image of a cell.

The phase contrast can be employed to detect local changes of the transport properties of ultrasound induced by diffusion processes [6]. To establish this method droplets of gel deposited on a glass substrate have been used. The gel is manufactured from household gelatin dissolved in ordinary water. Heavy water (D_2O) is used in exchange for ordinary water as a coupling fluid. This leads to time-dependent changes in the phase images. A set of images



Amplitude contrast Phase contrast

Fig. 11.5. Images of an XTH2-cell on glass. The grey scale in the image in phase contrast is proportional to the phase of the reflected ultrasonic waves. The width of the images is about 100 μm. The images were obtained at a frequency of 1 GHz with water as a coupling fluid. The maximum thickness of the cell somewhat below the center of the images is about 2 μm.

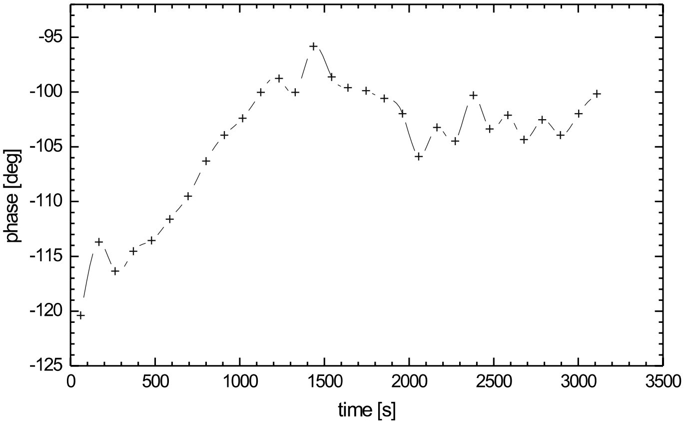


Fig. 11.6. Time dependence of the phase of the reflected ultrasonic waves (1.2 GHz) observed with an ultrasonic microscope for a position on a sample of gelatin deposited on glass. The coupling fluid has been changed from normal water to heavy water at time equal zero.

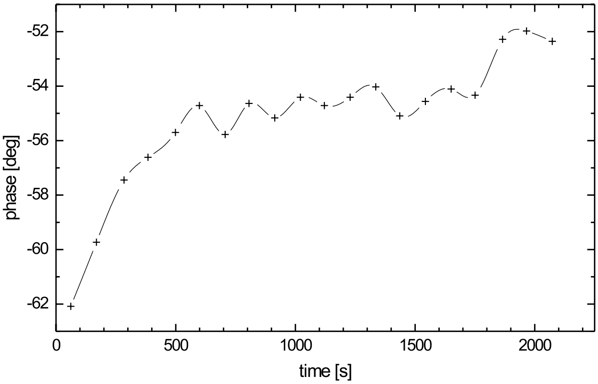


Fig. 11.7. Time dependence of the phase of the reflected ultrasonic waves (1.2 GHz) observed with an ultrasonic microscope for a fixed position on a living cell on glass. The coupling fluid has been changed from normal water to heavy water at time equal zero.

was taken at constant time intervals. A reference area close to the deposited droplet is used as a reference to detect changes of the phases in the image of the droplet. Figure 11.6 shows the result for a fixed position in the image of a droplet. The area at this position is only limited by the lateral resolution of the acoustic microscope of about 1 μm. The temporal dependence of the phase signal exhibits a distinct change following the contact to heavy water over a time span of about 100 s. This change is attributed to the exchange of normal water by heavy water in the gel by diffusion. Variations at later times are in part caused by solution processes of the deposited material.

Fig. 11.7 shows the response of a living cell under similar conditions. A relaxation time of about 200 s can be derived from the early part of the response. The distinct change at time 1800 s represents the exitus of the cell due to an overdose of heavy water.

These observations represent only a first step to demonstrate the possibility to observe transport processes including diffusion with acoustic microscopy. We restrain therefore from a quantitative analysis of the data. The transport properties in the cell are expected to be dominated by diffusion through the cell membrane. The observation is at least sufficient to determine the typical time scales for transport processes even in living objects.

For determining quantitatively the diffusivities, the thickness of the objects is needed. The technique is therefore especially suitable for coatings of constant thickness. For irregularly shaped objects of limited size on planar substrates (as employed here), the thickness can be monitored by atomic force microscopy (AFM), available in the developed microscope [5]. Homogeneous materials can also be characterized by phase sensitive scanning acoustic microscopy (PSAM) and model calculations fitted to the data [7].

In addition to the techniques demonstrated here microscopic holographic detection schemes have been developed [5, 8], which can be employed for the spatially resolved detection of the variation of the elastic properties in extended objects.

11.4 Conclusion

The novel detection schemes based on ultrasonic interferometers can be used to determine the diffusion coefficient following a non-equilibrium distribution of the diffusing species – in the demonstrated application the diffusing hydrogen. The rather high sensitivity allows the observation of slow processes, respectively small deviations from equilibrated distributions. Scanning acoustic microscopy with phase contrast representing also an interferometric method can be used in a similar way to observe relaxation processes with spatial resolution down to about 1 μm (lateral). Due to the rather short interaction length in the observed objects which is typically in the range of the lateral resolution or below, the sensitivity is significantly reduced with respect to interferometric detection schemes employed in macroscopic objects.

Notation

c	hydrogen concentration in atomic percent
c_{11} , c_{44}	stiffness constants
D	diffusion coefficient

D_0	diffusion coefficient at $T \rightarrow \infty$
E_a	activation energy
k_B	Boltzmann constant
t	time
T	temperature
v_t	velocity of transverse ultrasonic waves
x	position
ρ	density

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