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Thermal conductivity as an indicator of fat content in milk

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Abstract

This paper presents recent developments of the transient plane source techniques, and a discussion about their ability to monitor structural changes. The application demonstrated here is the monitoring of milk fat by measurement of the thermal conductivity. A discussion on various issues such as probe design, probe size and thermal contacting area on the influence on measurement sensitivity and accuracy, are covered, as well as the connection between the thermal depth of probing and measurement time. The present results indicate that it is possible to design a thermal conductivity probe, capable of recording the fat content in milk with a sensitivity of better than 0.1%, within a total measurement time of 1 s. In these measurements, the thermal depth of probing was 0.8 mm with a sensor radius of 2 mm, corresponding to an active sample volume of 40 mm^3. If used as an online quality control indicator, these measurements can be repeated continually every 20 s with a single probe.

Keywords: Thermal conductivity; Hot disk; Quality control; Milk; Fat

1. Introduction

Thermal conductivity is a thermophysical property, very sensitive to the structural constitution of the material. Recent developments of transient measurement techniques make it possible to develop instrument probes which can monitor very small changes in the thermal conductivity in a reproducible manner. It is here demonstrated that the fat content of milk may be accurately determined by a 1 s measurement of the thermal conductivity, only requiring a small amount of sample volume which is heated typically less than 1 K. Such a technique may be a viable alternative in comparison with the common techniques used today in the milk industry for recording and controlling fat content.

A brief summary of the hitherto developed theory, empirical relations and numerical methods today available for estimating thermal conductivity and its dependency on structure is presented. Secondly, the class of transient methods referred to as the transient plane source- [1–7], transient hot strip- [8–11] or the pulse transient hot strip- [12–15] techniques which cover a wide range of materials, sample geometries and sample length scales, are presented. The final section presents tests with the Hot Disk technique [1–7,16] on milk having a various fat content.

2. Thermal transport properties

Thermal conductivity, the mechanisms of heat transfer at the atom level, and relations between these in solids, as well as extensions to empirical models for microscopic- or macroscopic observable structures, have been covered in the literature to a great extent. Grimvall [17] provides an excellent source for an overview of the hitherto known theory of thermal transport, focusing on results down to the atom level derived from solid state theory.

The general thermal conductivity equation for solids (excluding thermal expansion), $\rho c_p \partial T/\partial t - \vec{\nabla} \cdot (\lambda \vec{\nabla} T) = \overline{f}$, incorporates the thermal conductivity λ and the volumetric specific heat capacity ρc_p, cf., e.g. [18]. Temperature is represented by T and the local heating per unit volume by $\overline{f}$. The thermal diffusivity is defined as $\kappa = \lambda/\rho c_p$, and is a tensor property (i.e. direction dependent or potentially anisotropic), as is the thermal conductivity. The thermal effusivity, defined as $E = \lambda/\sqrt{\kappa}$, is also a tensor property. The apparent specific heat may attain high or low values at or near change-of-phase points, or when a chemical reaction occurs. The specific heat is generally defined as $c_p = (\partial h/\partial T)|_p$, where h is the enthalpy.

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One interesting result obtained from the solid state theory, also applicable for most solids and liquids, is that the specific heat per unit volume, ρc_p, varies little with temperature or the structural constitution, cf. [17]. It also turns out not to be too different when comparing different materials. For solids assuming $T > \Theta_D$, where Θ_D represents the Debye temperature, one may derive the approximate relation:

$$\frac{\lambda}{\kappa} = \rho c_p \approx \left(\frac{M}{\Omega_a}\right)\left(\frac{3k_B}{M}\right) = \frac{3k_B}{\Omega_a} \quad (1)$$

where c_p is assumed to be approximately $3k_B$ for each atom. In Eq. (1), M represents the (averaged) mass of an atom, k_B is the Boltzmann constant, $\Omega_a = V/N$ represents the volume for each atom, and N is the total number of atoms residing in a total volume V of the material. As Ω_a is approximately the same for different materials, the variation in the specific heat capacity for different materials will be relatively limited.

The thermal conductivity—and consequently the thermal diffusivity—will however vary a great deal when comparing different materials and structures.

Several theoretical studies have been made on thermal transport properties. Unfortunately, to this date, one has obtained limited success in analytically predicting thermal transport properties of a given structure.

Since the 90's, a number of numerical investigations have been made for the study of effective thermal conductivity of multiphase structures, where the discontinuous structure may be allowed to have a rather complicated geometry. Although additional insight on the dependency of local geometry on the global thermal conductivity property is obtained, it is difficult to derive quantitative models on thermal conductivity and its dependency on the structural constitution.

When a chemical reaction occurs in, for instance, a bioreactor, many things may change in the global structure, such as:

- change in orientation of cells;
- volume expansion/compression of cells;
- change in chemical composition of subsystem(s);
- split/merging of cells.

which are all expected to somehow influence the global thermal conductivity and thermal diffusivity property. It should be noted, however, that for bio systems water may often comprise a great volume fraction of the total composition. Eq. (1) indicates that the global specific heat of the bio system will often be fairly close to that of pure water.

3. Measurement of thermal transport properties

The transient plane source- (TPS), the transient hot strip- (THS) and the pulse transient hot strip- (PTHS) techniques have been developed for measurements of thermal conductivity, thermal diffusivity, thermal effusivity and specific heat capacity, covering a wide range of materials and sample geometries possible to study.

These techniques are based on a common approach, where a step-wise heating of a sensor embedded in a sample, or deposited onto a sample surface, results in a local heating of the sample neighborhood. The sensor—a resistance element with a well-defined or well-known temperature coefficient of resistivity—is designed to deliver heat and simultaneously measure the average temperature response of the heating element which results from this local heating process. This temperature response is recorded from the moment the experiment is initiated until the experiment is ended. From the data analysis of the transient temperature response, the thermal transport properties can be estimated.

The operating principle appears to in many ways resemble that of the traditional transient hot wire (THW) method, but there are a couple of key differences:

(A) The sensor geometry defines—in contrast to the THW technique—a comparatively large heating area, which together with the sample geometry and interfacial geometry between sample and sensor governs the heating of the sample and the resulting temperature response. The authors believe a large contacting area provide advantages in terms of a higher sensitivity in the temperature recording and improved model fittings, making it possible to measure thermal transport properties with high sensitivity, cf. [6,7].

(B) A number of sensor configurations are possible [2,5–7,19], which however must be chosen with care to ensure geometrical agreement with the physical model used in the analysis of data. The fundamental relation between sensor size, sample size and measurement time is chosen with respect to the so-called characteristic time $\theta = l^2/a$ of the measurement, where l is a characteristic length (e.g. strip width or sensor radius) and a is the thermal diffusivity of the sample. The time regions where the sensitivity coefficients indicate maximum sensitivity in the estimation of the different thermophysical properties can be stated in terms of the dimensionless time t/θ, where t is the measurement time, cf. [20,21].

Relating to issues (A) and (B), of great importance is partly the surface roughness of solids, influencing the thermal contact resistance between sensor and sample, as well as the structural inhomogeneity of the sample itself. For a fibrous structure, common in bio structures, or a layered structure, common in engineering, having an effective global-scale homogeneity, experience have shown that the thermal penetration depth, $d_p = 2\sqrt{a \times t_{max}}$, governed by the measurement time t_{max}, should exceed at least 10 local inhomogeneities or layers in order to estimate the anisotropic effective thermal conductivities and thermal diffusivities with reasonable reproducibility, cf. [7]. Selecting $\theta = t_{max}$ gives $l \propto d_p^2/a$, meaning that the characteristic probe size should be selected at least some 10 times the size of the characteristic length of the structural inhomogeneity. Successful thermal conductivity measurements of rough stone grains (in air) about 10 times smaller than the probe characteristic length have been made, for instance—experiments which also indicates limits on the maximum surface roughness possible to accommodate.

When performing a measurement with a TPS, THS, PTHS or a similar transient method, the temperature response ΔT is

a sum of two components, one component which is essentially constant [22], A, and a transient component, $Bf(\tau)$:

$$\Delta T = A + B\left(\frac{P_0}{\lambda_B \times l}\right) f(\tau) \quad (2)$$

cf., e.g. Fig. 1 and [1,6,7,19]. In Eq. (2), constant B incorporates the bulk thermal conductivity λ_B of the sample, the heating power P_0 and a characteristic length dimension l of the probe. The dimensionless time function f is expressed in terms of the dimensionless time $\tau = \sqrt{(t - t_c)/\theta}$, where t_c is a time correction. It should be noted that thermal contact influences are grouped into term A, clearly separated from the thermal transport properties of the bulk sample which are grouped in term $Bf(\tau)$.

Transient methods can be designed to estimate and separate these two components from each other rather well. A large contacting area, an improved thermal contact and a thinner sensor will reduce the influence of component A, with several advantages as indicated earlier. It should also be noted that the component A may be varying somewhat due to imperfect electronics as well as the specific heat capacity of the sensor itself [22]. A reformulation of Eq. (2) into a form with a strictly constant A can be made, as demonstrated in [22] and in Fig. 1.

There is no principal difficulty in applying the relation $\theta = l^2/a$ for smaller-scale samples. For practical reasons, the present TPS- and THS techniques may be used for measurements with a measurement time not lower than typically 0.5 s.

The same measurement principles and a similar theory can be applied for micro-sized probes, if using a different experimental setup. Instead of a single step-wise heating and recording of a single transient response, a pulsed approach can be realized with the PTHS technique [12–15]. A pulse generator introduces square heating pulses of lengths of the order 50 ms down to 50 ns, with sufficiently long cooling intervals between the heat periods. This results eventually in a voltage signal in an ac-coupled circuit, which has a time-averaged stationary voltage

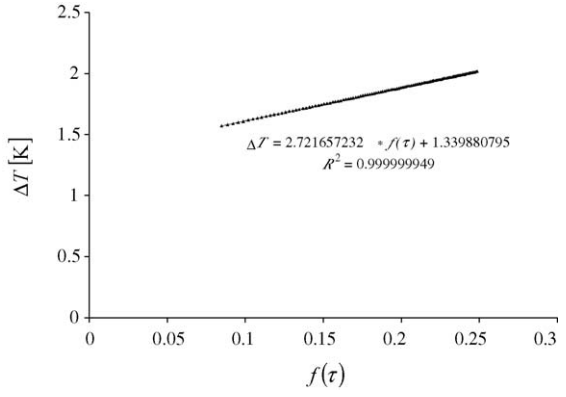

Fig. 1. Measurement of stainless steel with the Hot Disk technique (a TPS technique); with the graph depicting the optimal fit of data points to the model in Eq. (2). Sensor radius is 14.61 mm (including a 25 μm thick Kapton insulation on both sides of the sensor heating spiral), heating power is 3 W and measurement time is 6.05 s. A reformulation of Eq. (2) was made to obtain a strictly constant A. Optimal fitting was found in the time interval 0.65–6.05 s, for a measured temperature response of more than 2 K, resulting in a mean deviation in of 2.8×10^{-5} K and an R^2-value as indicated in the graph.

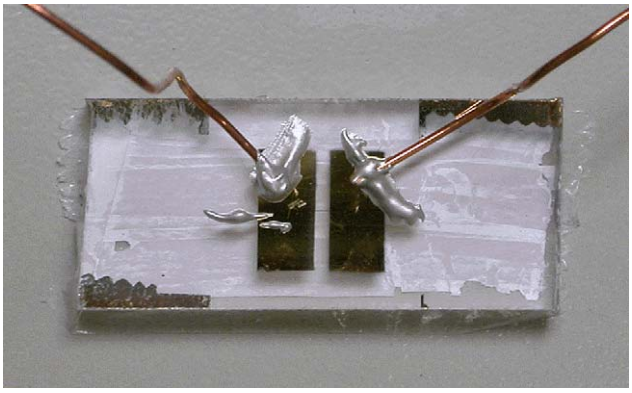

Fig. 2. Strip probe (gold) sputtered onto a PMMA substrate with known thermophysical properties. Dimensions: strip width 41.88 μm × strip length 1.269 mm. The liquid sample, a single drop, is placed onto the strip, completely covering the heating zone.

value recorded by a nano voltmeter. Varying the frequency, a model principally similar to Eq. (2) can be derived, relating the time-averaged temperature response with the pulse frequency. This method was originally developed to study thin insulating layers, and was recently developed to accommodate single-sided measurements of liquids, for probe sizes ranging from the micrometer- to the millimeter scale.

Unique for this technique, when considering measurements of liquids or bio liquids, is that the sample size can be reduced several orders of magnitude in comparison with the THW technique—probably the most common technique for measurements of liquids at present. For instance, it was demonstrated in [13] that the thermal effusivity of a single drop of water at room temperature conditions can be measured at around 1% accuracy, with a thermal probing depth not exceeding 17 μm. The measurement configuration for such a measurement is discussed in [13] and the strip probe is depicted in Fig. 2. The maximum amount of water that is heated by a single pulse in this PTHS experiment has a weight less than 1.7 μg, cf. [13], which is the theoretical minimum amount of liquid sample necessary for this experiment.

It should be pointed out that the sensitivity for small and very small probes have not yet been developed to comparable levels as can be routinely observed when using larger sensors, in particular for sensor dimensions $l \geq 10$ mm measured with the TPS- or THS techniques. However, small probes do have one important advantage; that of the ability of reducing the influence from potential convection [13]. It can be analytically shown that the relative influence from convection, assuming a steady convective flow, is downscaled in proportion with the experimental length scale, l, cf. [13]. This result has the perhaps interesting theoretical consequence that measurements of a liquids thermophysical properties is always possible, even if the liquid is in convective motion, provided the probe size is designed small enough.

4. Thermal conductivity versus fat content in milk

The Hot Disk probe (a TPS technique) has a bifilar spiral strip design, which has been etched out of a thin metal foil,

Fig. 3. Hot Disk sensor. The sensor insulation is Kapton of 25 μm thickness on each side. The sensing and heating pattern is made of 12 μm thick Ni.

and sandwiched between thin electrically insulating sheets, cf. Fig. 3. This probe has been specifically designed to maximize the heating area and length scale l for a given sample size, maintaining close agreement between the physical model and real experimental geometry. Measurements of this technique, which provides generally good model fittings, cf., e.g. Fig. 1, result in stable results of the estimated thermophysical properties, as is indicated in Fig. 4.

The sensitivity of this technique makes the technique sensitive to the structure of the sample. For instance, global inhomogeneities, gradients, local inhomogeneities such as significant cracks or dislocations or other phenomena such as onset of convection during the experiment will most often result in difficulty

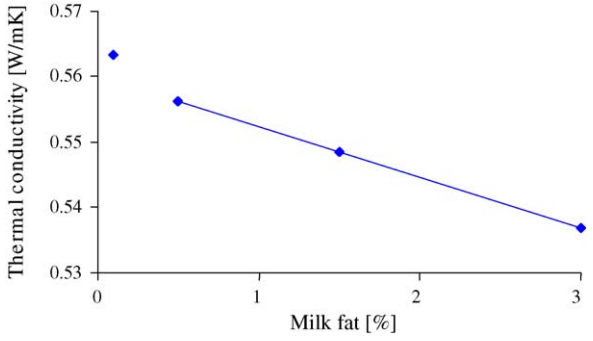

Fig. 4. Thermal conductivity of commercially available milk (Arla Inc. Sweden), with a stated fat content of 0.1% (maximum), 0.5%, 1.5% and 3%. Hot Disk sensor radius is 2 mm, measurement time 0.96 s and heating power 0.15 W. Temperature increase of sensor is 1.7 K. Probing depth less than 0.8 mm. Reproducibility is better than $\pm 0.0008\,\mathrm{W\,m^{-1}\,K^{-1}}$, indicating that fat content in milk can be estimated with a precision better than 0.09%.

of numerical fitting of experimental data to the model in Eq. (2). The Hot Disk technique may be utilized as a quality control (QC) indicator, with model deviation of experimental data to a reference experiment as a qualitative indicator of the structure or zero-flow stability. Quantitative information on the sample may on the other hand be obtained, if evenly distributed concentration differences exist. To maintain high sensitivity in comparative experiments, the experiment should be repeated with the same equipment and using the same probe, output of power, measuring time and time window for the analysis. The statistical scatter in the thermal conductivity is often a fraction of a percent if the initial temperature is stable and the temperature inside the sample is uniform when the experiment is initiated.

To demonstrate the sensitivity, a series of measurements were performed on milk with different fat concentrations: The milk was purchased on the open market and the concentrations given were: (a) less than 0.1%, (b) 0.5%, (c) 1.5% and (d) 3.0%. In order to make sure that the measurements were performed at the same temperature, a cylinder made of Aluminum (diameter 80 mm and height 60 mm) was used, in which 4 holes (diameter 20 mm and depth 50 mm) were drilled. These holes were then filled with the different qualities of milk. A Kapton insulated probe (design 7577 from Hot Disk Inc., Sweden) was successively dipped into the different milk samples. The diameter of the sensing spiral in the probe was about 4 mm and the Kapton insulation on both sides of the spiral had a thickness of 13 μm and the thermal conductivity of this insulation was $0.12\,\mathrm{Wm^{-1}\,K^{-1}}$.

In order to avoid convection and optimize model fittings, experiments were performed in a time period of 0.96 s. The analysis was performed assuming the specific heat capacity of milk equaling that of water, $4.17\,\mathrm{MJm^{-3}\,K^{-1}}$, an assumption that reduces the number of model-fitted variables from four (A, λ_B, θ and t_c) to three (A, θ and t_c) in the data reduction process, and significantly improves sensitivity in the estimation of the thermal conductivity property, cf. [23]. Within this measurement time, no sign of natural convection could be seen. The total output of power during the transient was 0.15 W resulting in a temperature increase totaling around 1.7 K. The probing depth was 0.8 mm.

Two measurements were made on each milk sample and the probe was moved from one hole to another between the measurements. First the four samples were measured with only a few minutes between each measurement. Later a similar second series of measurements were made after about 1 h.

The three last concentrations indicate an almost linear dependence of the thermal conductivity on the fat concentration. Comparing the change in thermal conductivity (with a reproducibility of better than $0.0008\,\mathrm{Wm^{-1}\,K^{-1}}$) with the change in fat concentration, indications are that it may be possible to determine the fat concentration with a sensitivity of about 0.09%.

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