TEMPERATURE-MODULATED DIFFERENTIAL SCANNING CALORIMETRY THROUGH HEAT DIFFUSION ANALYSIS

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Abstract

In the present study, a complete model of thermal diffusion in a 1 MDSC specimen is presented. The governing equation takes into account thermal conductivity and does not neglect temperature gradients. This model is solved analytically for a specimen of cylindrical geometry with two surfaces following the block temperature and considering the third surface insulated. The full analytical solution consists of a transient and an asymptotic expression. The asymptotic expression is divided into an underlying and a cyclic part to allow comparison with existing models. The present model finds that the phase angle between the temperatures of sample and block are dependent upon the sample material, which has not been predicted by existing models. Moreover, the present model does not require the use of an experimentally determined constant as long as the cell is ideal. It was found that the phase lag between sample and block temperatures could be described by two effective thermal diffusivities, $\Lambda'$ and $\Lambda''$, instead of complex heat capacities $c'_p$ and $c''_p$. These heat capacity parameters were viewed as mathematical artifacts arising from the use of an over-simplified governing equation that does not take into account thermal conductivity and thermal gradients within the specimen.

Keywords: complex heat capacity, heat transfer, phase lag, TMDSC

Introduction

Temperature Modulated Differential Scanning Calorimetry, or TMDSC, MTDSC, is a rather new technique that was conceived in the early 90's by Reading and co-workers and commercialized by TA Instruments [1–3]. The advantage of TMDSC compared to conventional DSC is that the temperature signal can be modulated as a sinusoidal wave, and be superimposed over the traditional heating rate. This technique offers the possibility of deconvoluting the signal into an in-phase and an out-of-phase response, which can be used to calculate heat flows or heat capacities [1, 2, 4].

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In 1985, Birge and Nagel performed an experiment with a sinusoidal heat flux applied to a sample [5]. This technique is also known as AC calorimetry [6]. Birge and Nagel reported that the product of \( c_p k \) was measured, where \( c_p \) is the specific heat capacity of the sample and \( k \) is its thermal conductivity. This product was found to have a real and an imaginary component. However, the authors estimated the contribution of \( k \) to be very small and therefore considered only that of \( c_p \) and deconvoluted the product of \( c_p \) and \( k \) into \( c''_p k \) and \( c'''k \). Reading et al. applied an oscillatory condition to a traditional heat flux DSC and through a discrete Fourier transformation the resulting signal was separated into total, reversing, and non-reversing heat flows [3]. This method was commercialized as TMDSC and reinforced the idea of a complex heat capacity. Many authors followed on this concept, including Gill and Schawe [7–9]. Furthermore, Schawe proposed a frequency dependent \( c_p \), which has been observed under certain conditions by Birge and Nagel [5].

The existence of a complex heat capacity has troubled many scientists over the past years. Heat capacity is a scalar that is thermodynamically defined as the derivative of enthalpy with respect to temperature at either constant pressure or volume. Some authors have tried to justify the existence of a complex heat capacity from a thermodynamical viewpoint based on entropy, while others suggest \( c''_p \) to be linked to dissipative phenomena [5, 8–11]. However, no entropic origin can be attributed to \( c''_p \) using reversible thermodynamics as the derivative of entropy with respect to temperature at constant pressure is equal to heat capacity over temperature, \( (\partial S/\partial T)_p = C_p/T \) [12]. Therefore if entropy does change dependent upon \( c_p \), it does not contribute to a loss heat capacity within the limit of application of reversible thermodynamics. Other authors proposed to use irreversible thermodynamics to explain the origin of \( c''_p \) [13]. However, as noted by Höhne, irreversible thermodynamics is a rather complicated theory which is not yet fully developed [11]. Basically, there is no well-founded physical or thermodynamical interpretation of \( c''_p \). Moreover, heat capacity is a bulk property of the material and is therefore isotropic, very much like density \( \rho \). Heat capacity gradients, as well as density gradients, can exist in heterogeneous materials, but not in homogeneous matter \( c_p \) and \( \rho \) are not tensors, unlike the thermal conductivity \( k \). The thermal conductivity \( k \) can be anisotropic, and is found to be in many materials like carbon fibers. \( k \) can be expressed as a tensor, and its anisotropic properties make it a very likely candidate for a complex expression: \( k'' = k' + i\kappa'' \) [14, 15]. The thermal diffusivity \( \kappa \), which is defined as \( k/\rho c_p \), should therefore have a complex part as well, but the \( c''_p \) utilized by many authors might very well be an artifact due to a simplistic mathematical model of the TMDSC.

Numerous mathematical models for the computation of the heat capacity have been published since the commercialization of the TMDSC in the early 1990’s. Most of these models consider the sample temperature to be uniform throughout the sample at any time, and begin by equating the heat accumulation