ABOUT COMPLEX HEAT CAPACITIES AND TEMPERATURE-MODULATED CALORIMETRY

H. Baur* and B. Wunderlich

Department of Chemistry, The University of Tennessee, Knoxville, TN 37996-1600, and the Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-0197, USA

Abstract

With increasing use of temperature-modulated calorimetry, TMC, it is has been proposed to use a complex heat capacity for the description of the response of samples to periodic temperature changes. In this article the ramifications of this approach are discussed on the basis of irreversible thermodynamics. Experimental results are summarized which describe heat capacities of liquids and solids, as well as TMC during transitions. It is concluded that the complex heat capacity is of limited value. Solids and liquids have no dissipative (imaginary) contributions. In the glass transition, the thermal response is nonlinear, so that a detailed kinetic model (in real notation) is more advantageous to describe the heat capacity. The crystallization is often so far from equilibrium that it is not modulated. During melting and chemical reactions the heat flow is frequently so large, that steady state is lost and complex heat capacity is of questionable value, even if modulation is accomplished.

Keywords: complex heat capacity, heat capacity, irreversible thermodynamics, temperature-modulated calorimetry

Introduction

In general, one can represent a complex number \( z = a + ib \), with \( i = \sqrt{-1} \), as:

\[
z = |z| e^{i\theta} = |z| (\cos \theta + i \sin \theta), \quad \text{with} \quad (1a)
\]

* Sonnenwendstr. 41, D-67098 Bad Dirkheim, Germany

Note that \( a \) and \( b \) are real numbers. The complex numbers \( z = (x, y) \) have the following addition and multiplications rules: \((a, b) + (c, d) = (a + c, b + d)\) and \((a, b) \times (c, d) = (ac - bd, ad + bc)\). The real numbers \( a \) and \( b \) are the real and imaginary parts of the complex number \((a, b)\). The terms real and imaginary are historical accidents since both \( a \) and \( b \) are real numbers, and complex numbers are often useful to describe real phenomena. It is easy to see from \((0,1) \times (0,1) \) that \( i^2 = -1 \).

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\[ |z| = \sqrt{a^2 + b^2}; \quad \cos \theta = \frac{a}{|z|} \quad \text{and} \quad \sin \theta = \frac{b}{|z|}. \]  

Any periodic process with an angular frequency of \( \omega = 2\pi v \), where \( v \) is the oscillation frequency in Hz (s\(^{-1}\)), can therefore be depicted by a uniform motion tracing a circle in the complex plane, mapping the complex numbers:

\[ A e^{i\omega t} = A (\cos \omega t + i \sin \omega t). \]

For the description of periodic changes or a Fourier analysis of complicated processes, the introduction of complex quantities is convenient and lucid. Naturally, it can bring new physical insight over the representation in real numbers.

The so-called linear response theory makes extensive use of the possibility of complex formulations in its treatment of dissipative systems [1]. The response functions appear as complex quantities \( \chi' + i \chi'' \) with the real component \( \chi' \) representing the reactive part, and the imaginary component \( \chi'' \), the dissipative part. Preconditions for linearity are fixed internal equilibrium states as reference, and sufficiently small deviations from these states. The question whether a complex representation is suitable for heat capacity is to be investigated in this paper.

The similarity of the description of temperature-modulated DSC (TMDSC) and dynamic mechanical analysis (DMA) and also dielectric thermal analysis (DETA) has brought up this question whether a complex heat capacity and the application of linear response theory would be of use in TMDSC [2]. Analysis of the instrumentation [3] has established that one must determine the phase lags relative to the reference frequency \( \omega \). First, the effect that represents the calorimeter response to the oscillating heater temperature. Second, the sample response. In case of a sample that has no slowly responding modes of motion, as in heat capacities of solids and liquids, there should be no lag due to the sample response. Typically, the response of molecular modes of motion to heat flow are in the picosecond range \( (10^{-12} \text{ s}) \) [4]. The lag measured [5] is then entirely due to the thermal conductivity of the calorimeter. Note, that one of the basic conditions of DSC is that there be a negligible temperature gradient within the sample so that the effect due to the thermal conductivity of the sample is negligible [6]. The apparent heat capacity in the glass transition region, in contrast, is time dependent [7] and there should be an additional phase lag of the heat flow relative to the amplitude of the sample temperature [8]. Only this latter phase lag is to be discussed in the present paper.

In TMDSC, the heat capacity is calculated from the modulation amplitude \( \psi \) phase lag of the heat flow responding to the sample-temperature modulation. The complex representation of this calculation for fast responding systems is well understood [9]. It is based entirely on the thermal conductivity of the path between heater and sample and reference calorimeters. Finally, it should be remarked that

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