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A PERSONAL PERSPECTIVE ON THE RISE OF MTDSC

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For me the story of Modulated-Temperature DSC began many years before it was introduced as a commercial product in 1992. It started when I was trying to determine why the signal I was getting from my DSC was so noisy. The noise appeared random but seemed too low in frequency to be electrical in origin. Also it disappeared when I carried out a baseline experiment with empty pans. I discovered it got worse as I increased the sample mass so it occurred to me that the noise might arise from irregularities in the heating rate. At normal resolutions the temperature trace appeared perfectly linear but I decided to take a close look at it. I obtained a high resolution temperature derivative and compare it to the 'noise' in the heat flow signal. There was a perfect match. My colleagues immediately set about the task of eliminating the fluctuations. It seemed clear to me then that the way to go was to ensure that they were deliberately incorporated in a controlled and regular way.

I started carrying out experiments using the saw tooth modulations achievable by combining short 'linear' ramps (although the response time of the calorimeter meant the results quickly started to resemble a sine wave). It soon became apparent that certain transitions, like glass transitions, gave rise to increases in the amplitude of the response to the modulations (as I began to call the deviations from the underlying ramp rate) while other transitions, such a cold crystallizations, shifted the response away from the baseline without changing the amplitude. The nature of reversing and non-reversing processes became clear and the basis of the deconvolution methodology began to evolve. Then came the day when I saw a glass transition in the amplitude of the response to the modulation in a sample where this transition was imperceptible during a conventional DSC experiment. I confirmed that the transition did indeed exist using DMA. I began to think that there might be real potential in the idea, that it might be more than an interesting curiosity.

All of this work was in the nature of a diversion that was difficult to fit in between the normal business of earning a living. I had changed jobs and joined a large multinational where pursuing a career was time consuming, especially when the moment for management responsibility arrived. I began to look for a collaborator in academia who might be interested in developing the idea as this seemed the only way progress might be made. It was around this time that TA Instruments launched their 'Hi-Res$^{\text{TM}}$' TGA product. This technique incorporated

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ideas that I was very familiar with because I had spent most of my PhD working on the related technique of Controlled Rate Thermal Analysis. Someone in TA Instruments must have heard of this because I received a phone call from them asking whether I was interested in meeting someone from TAI to talk about their latest product? I replied yes. During the meeting that followed I was asked whether I had any ideas for how this 'Hi-Res$^{\text{TM}}$' or controlled rate approaches might be applied to DSC. I had been thinking about how separating heat capacity from other processes might provide a route to just this type of temperature control. Yes I said, but I would need the agreement of my employer before I could talk about it.

The bureaucracy took a while but it wasn't too long before I found myself explaining the principles of MTDSC to the management team at TAI. I sensed disbelief in the air but everyone was very polite. Interesting, they said. They might be in touch.

I may never know all of what passed at TAI in the hours and days that followed, I do know that powerful voices expressed grave doubts about the wisdom of pursuing this idea. It was a close run thing but soon I had a phone call. They were interested and wanted to buy the rights.

My employers at that time, a large chemical company, were very clear that they were not in the instrument business so they were only too happy to sign away the rights. I wrote a report in which I described the theory of MTDSC and gave examples of the results I had obtained. I handed it over to a software engineer from TA Instruments called Ben Crow. Within few months I had a working MTDSC system in my lab. The control over the amplitude of the modulation was not as good as it is now and some of the results seemed strange, but we were in business. All that remained was for another TAI employee, Brian Hahn, to suggest using a Fourier Transform method instead of the curve fitting approach we were using. The FT algorithm proved faster while giving the same results and the basis of the first commercial product was complete.

Once we had deconvoluted the cyclic response from the total heat flow and also obtained its phase lag, it was clear that we could use this information to obtain the in-phase and out-of-phase components in a manner similar to DMA and DETA, thus providing a further deconvolution step. In DMA and DETA the out-of-phase response is usually called the loss signal because, in these techniques, it represents the conversion and 'loss' of the energy expended in the modulation (mechanical or electrical) in the form of heat. In MTDSC the signal being measured was heat and it was clearly was not being lost. At this point it is appropriate to say a few words about our theoretical analysis of MTDSC.

Our starting point was very simple. If the sample is effectively at (or very close) to equilibrium at every instant during the modulation then, by definition, it is responding instantaneously (or nearly instantaneously) to the modulation. Because there is no slow (kinetically hindered) response there cannot be any out-of-phase and non-reversing signal. There is another case when this applies, when the sample is in quasi-equilibrium. In other words, it is not at equilibrium but is moving toward equilibrium immeasurably slowly. This is the case below the glass transition for example. The sample is not at equilibrium but is stable over long periods of time because the relevant molecular motions are frozen. As soon as the sample is not in equilibrium and is moving toward equilibrium at a measurable rate, then there will be an out-of-phase signal and, usually, a non-reversing signal. This is then a manifestation that there is some process, such as a chemical reaction, that is not occurring instantaneously. It will be described by some function of time and temperature, thus it is kinetically hindered (the function of time and temperature being the kinetics of the transition). The out-of-phase component is, therefore, not an sign of 'loss' but simply a manifestation of the sample not responding instantaneously, of there being some kinetics associate with its response.

The out-of-phase response to the modulation has, therefore, a clear physical meaning that was expressed as the quantity C in our early papers [1–7]. It is a measure of the kinetics of the response of the sample to the modulation. The use of the phase lag to calculate it would seem straightforward. However, there was a problem. In principle, by this argument, the phase lag should be zero except when a transition is occurring whereas, experimentally, this was never the case. It seemed clear that it was never zero because the calorimeter was not an ideal instrument and had its own 'kinetics' i.e.. had its own non-zero response times and imperfect heat paths. The question then arose as to how we were to correct for this non-ideal behaviour. From this then followed a practical problem. Calibrating calorimeters is a well established business. The average or underlying signal in MTDSC is equivalent to conventional DSC and can, therefore be calibrated and checked in the normal way. The in-phase reversing signal is ordinary heat capacity when no transition is occurring thus can be calibrated and checked using the usual inert heat capacity standards (usually sapphire). Let us say that we have devised a scheme for correcting for the non-ideal behaviour of the calorimeter so that we can calculate values for the out-of-phase components, what standard do we use to confirm that our methodology is correct?

Very early on we proposed a simple correction procedure where we interpolated a baseline under any peak in the phase lag between regions where there was no transition [2]. The peak height was then taken as the true phase lag. There then followed a very lengthy debate between myself and several colleagues as to whether this or some other procedure was the best approach. Meanwhile TA Instruments were seeing real benefits from MTDSC without using the phase lag. While the exact magnitude of the out-of-phase signal was not known with certainty, is was clear that is was very small, in fact negligible in polymer transitions except melting. At that time, with or without the phase lag, it was not possible to interpret quantitatively the magnitude of the reversing response in the melt region, consequently the value of the phase lag correction was open to question even in this case. TA Instruments, therefore, launched the first commercial system without the phase lag correction. To avoid the suggestion that I might have overlooked this aspect of the technique, I published my proposed method of exploiting the phase lag [2] while continuing my research into this area. I again mentioned the desirability of using the phase lag and the problems associated with so doing in a subsequent publications [4, 5]. I began a collaboration with Prof. Andrew Lacey on a mathematical model of the calorimeter and sample behaviour under modulated temperature conditions in order to construct a rigorous theoretical basis for determining a suitable correction procedure for the phase lag signal. This eventually took the form of a PhD project with Christos Nickolopolus as the student.

In the meantime an article appeared severely criticising my approach to MTDSC on the basis that I forgotten the phase lag (this despite citing one of the articles in which I had specifically discussed how to use it) and claiming a 'new' approach based on calculating the in and out-of-phase components of the cyclic response [8]. The figure illustrating our use of the phase lag to calculated the in and out-of-phase components taken from our 1992 article [2] is reproduced in Fig. 1, the critical article [8] was published in 1995. While the charge that we were ignorant of the importance of the phase lag was entirely spurious and this 'new' approach was easily shown to be simply a duplication of our earlier work, there was something original in this paper. A new theoretical approach was advanced based on irreversible thermodynamics that suggested that the out-of-phase response (misleadingly called the 'loss' component) was a measure of entropy changes in the sample. The article also claimed that our theoretical approach could not deal with the glass transition and, furthermore, that the non-reversing component was 'illogical'! While these claims were also incorrect [9–11], the new theoretical approach seemed interesting and remains today a potentially important contribution to this field.

It is, perhaps, worth mentioning a few points that have led to some confusion in some people's minds. We originally expressed all of our signals in terms of heat flow [1, 2], thus there was the total heat flow, reversing heat flow, out-of-phase heat flow etc. Other workers have preferred to express these quantities as heat capacities [4–8]. There is no fundamental difference whatever between these two approaches. The signals are the same except they have been divided or multiplied by the average heating rate and, in the case of heat capacities, the usual baseline correction should be applied. Probably best practice is to use heat capacities as this quantity is a materials property while heat flow varies with experimental conditions. However, it should be borne in mind that the non-reversing and out-of-phase heat capacities are not heat capacities in the normal use of this word but best thought of as apparent heat capacities. Another point is the prevalent use of complex notation where the in-phase response is called the real

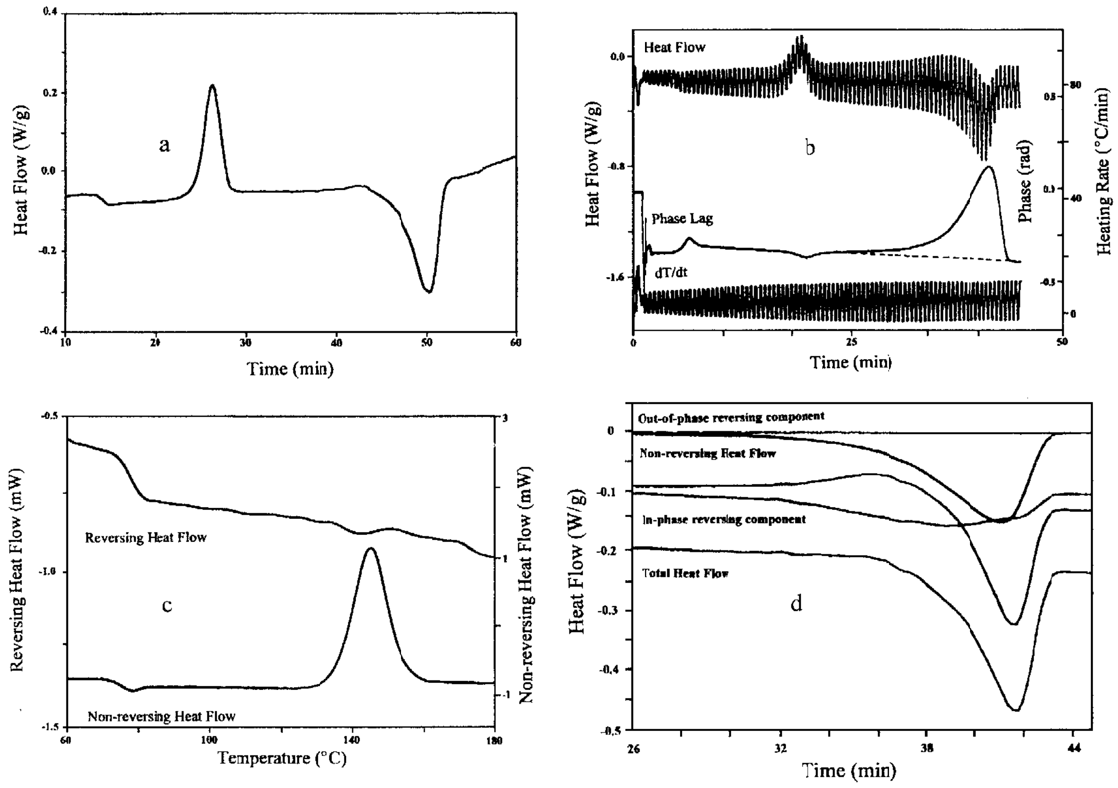

Fig. 1 Reproduction of the figure from the NATAS 1992 article [2] showing a) the result from conventional DSC for quenched PET, b) the raw data from a MTDSC experiment including the dashed line which is the interpolated base-line for the phase lag, c) the simple deconvolution procedure, where the phase lag is not used, for the glass transition and cold crystallization of PET while also illustrating d) the complete deconvolution procedure using the phase lag and the base-line subtraction method to determine the in and out-of-phase reversing components (legends retyped for clarity)

part and the out-of-phase response the imaginary part [6, 8]. This formalism is popular in DMA and DETA and does represent a convenient way of expressing these quantities. However, the use of complex notation is by no means necessary and we did not use it in our early papers. It has now become a popular way of referring to the in- and out-of-phase components and we also use it, but this does not represent a new or changed theory. Our theoretical approach has not changed, merely our nomenclature and notation.

Our mathematical modelling work bore fruit, providing a rigorous model of the behaviour of a heat flux DSC under MTDSC conditions. It confirmed the validity of the baseline subtraction technique we had originally proposed for the phase lag [2, 10]. While there will certainly be improvements in methodology, we were able to show that this simple approach represents a reasonable starting point and we devised a means of confirming this experimentally. In addition, we have described the basis of interpreting MTDSC results for chemical reactions, crystallization, polymer melting (without reorganisation) and the glass transition [10, 11]. This brings us close to the present day. We have an experimental procedure that consists of adding a perturbation to the normal liner or isothermal temperature programme. Currently this perturbation is either a sine wave or a square wave. A mathematical procedure, presently a Fourier transform is the most popular, is then applied to deconvolute the underlying from the cyclic response. The cyclic response can then be deconvoluted into an in and out-of-phase response (although in many cases this step can be neglected as the out-of-phase response is small and has not yet been shown to be of much value). The in-phase signal (or the cyclic response without any phase lag correction) is then subtracted from the total signal to produce the non-reversing signal. One very satisfying aspect of the development of MTDSC has been its use, further development and application by so many scientists other than myself and my co-workers. I shall not mention them all here for fear of offending by forgetting someone, also this would make the list of references too long. However, a glance at the rapidly rising MTDSC literature is sufficient to see who they are. I am very grateful to them. There is one name I would like to mention, Bernard Wunderlich. His early interest, guidance, encouragement and example of scientific rigour have been a consistent source of support.

Another pleasing aspect of the development of MTDSC has been to see these principles applied to other thermal methods. We have seen the introduction of modulated temperature TGA [12] and TMA [13]. In calorimetry we have seen the introduction of more sophisticated methods of analysing the samples response such as parsing where the heat, cool and reheat parts of the modulation cycle are looked at separately [6]. The use of more than one frequency simultaneously has also been demonstrated [6]. There will certainly be more refinements of the basic method in future, including the use of a Fourier transforms to obtain the complete frequency response for both to sine and square wave perturbations. We have not yet seen the use of MTDSC with higher resolution or constrained rate temperature programming, which was the original reason for TA Instruments interest in the idea. I anticipate that one day we will.

No account of MTDSC would be complete without some mention of the controversy it aroused. Some have maintained that AC calorimetry, because it is sometimes differential [14] and sometimes includes determining the in and out-of-phase components [15], is the same technique as MTDSC. This proposition ignores the fact that AC calorimeters by design and certainly in application have not provided the total signal that enables latent heats, heats of reaction to be determined. This then precludes the principle deconvolution step of determining the reversing and non-reversing signals. The fact that MTDSC does provide the ability to measure all thermal processes is one of the reasons for its usefulness and, therefore, popularity. The commercial tensions that the invention of MTDSC has occasioned has led to this and even stranger misrepresentations. However, this is, hopefully, now all in the past.

As for the future; for myself, the most important aspect of the development of MTDSC has been the fact that it led me to a hybrid of Atomic Force Microscopy with MTDSC to produce Calorimetric Analysis with Scanning Microscopy (CASM also called micro-MTDSC) [16, 17] and from there to develop micro-thermal analysis which combines thermal imaging with local calorimetric and mechanical analysis [18]. I believe this new family of techniques to be far more important than MTDSC. I only hope that, when we look back in a few years time, my collaborators and I will be thought to have made the world of thermal methods a little bit more interesting.

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