ELSEVIER

Thermochimica Acta 355 (2000) 43–57

thermochimica
acta

www.elsevier.com/locate/tca

Temperature-modulated calorimetry in the 21st century[☆]

Bernhard Wunderlich[*]

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197, USA

Received 3 June 1999; received in revised form 6 August 1999; accepted 16 August 1999

Abstract

It is attempted to extrapolate to future developments in the field of thermal analysis, and, specifically, temperature-modulated calorimetry (TMC), the latter being a subject that developed to prominence in the last 10 years. The predictions are made on the basis of the present techniques and on the need for the characterization of materials. Key issues are the advancement of the practice of TMC to quantitative calorimetry. Special topics mentioned are the analysis of nonequilibrium states and the characterization of nanophases. In instrumentation, the extensions of modulation to higher frequencies and the introduction of new techniques for smaller sample masses are discussed. One of the biggest needs is, however, to increase the teaching effort in this field, since many of the quantitative methods already available are not applied to the fullest because of a lack of qualified thermal analysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Temperature-modulated calorimetry; Microcalorimetry; Irreversible processes; Nanophases; Teaching of thermal analysis

1. Introduction

In this last year of the 20th century and second millennium, it seems to be of great interest to speculate on the development in various fields of science and engineering that one may expect to see in the beginning of the 21st century. Such activities are certainly generated by the special human fascination with particular numbers, since the development of science is not cognizant of the periodic arrangements of our calendar. If the speculation is kept to the very beginning of the new millennium, the chances may be good to predict certain developments by judicious extrapolation of the present newest developments. Predictions of longer-range developments are most likely as hopeless as it was to make these at the end of prior centuries and millennia.

In the year 1800, it was certainly humanly impossible to predict that the speculative caloric, "the indestructible fluid that occupies spaces between the molecules of matter as the substance of heat," will be replaced by the fact that the cause of heat is not a substance, but the molecular motion of atoms and molecules. And it was impossible to predict in the year 1900 that, in the 20th century, a few micrograms of a material are enough to do differential scanning calorimetry, and that supercomputers can simulate the thermal behavior of thousands of interacting molecules for

---

[☆] The submitted manuscript has been authored by a contractor of the U.S. Government under the contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish, or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

[*] Present address: Department of Chemistry, The University of Tennessee, Knoxville, TN 37996-1600, USA;
Tel.: +1-423-974-0652; fax: +1-423-974-3419.
E-mail address: athas@utk.edu (B. Wunderlich)

PII: S0040-6031(00)00436-6

times approaching microseconds. On the other hand, it was also quite unlikely that one could predict in 1800 that 200 years later a large fraction of the world's population still measures temperature in units of the Fahrenheit scale, invented in 1714, outdated since the development of Celsius scale in 1742, and the even more useful Kelvin scale of 1854. Similarly, in 1900, one would have predicted the quick demise of the calorie as the unit of heat since the absolute joule as the basic unit of energy could be measured with ever-increasing precision and reached that of the calorie by about 1925. Checking today's literature, however, one still finds a considerable fondness for the calorie, and the judgment of the energy content of foodstuffs in the United States could not be thought of in anything else but calories (kilocalories, thermochemical=4.184 kJ). And how about forecasting in 1900 that the newly defined second, the proper fraction of the ephemeris year 1900, would be replaced in 1967 by the period of the cesium-133 clock (defined by the separation of the two hyperfine electron spin states of the ^{133}Cs ground state of ca. 6.1×10^{-24} J)? This new clock has a precision of better than one part in 10^{11} and, furthermore, the time based on the 'atomic clock' in Boulder, CO, is available by automatic radio control in wrist watches since about 1990.

With these thoughts in mind, Section 2 of this paper will contain a discussion on the developments in the 20th century from modern calorimetry to temperature-modulated calorimetry (TMC) and, specifically, the temperature-modulated differential thermal analysis (TMDSC) and its applications [1]. This can naturally be accomplished with perfect hindsight. Section 3 will then be the task of extrapolation of these developments of the past into the future. Certainly, it will be much more fun to read this paper in the year 2100, at the end of the first century of the new millennium when all the wrong predictions and missed developments will be obvious.

2. Twentieth century calorimetry and the development of temperature modulation

The survey of the development of instrumentation in calorimetry and its understanding and theory displayed in the first two parts of this section is a story of great progress, culminating in the development of temperature modulation. A survey of the teaching of the subject, on the other hand, shows that the necessary base for progress in the 21st century does not parallel the exciting new developments in instrumentation and theory. The third part of this section is an effort to suggest a reason for this problem, so that it can possibly be overcome in the 21st century.

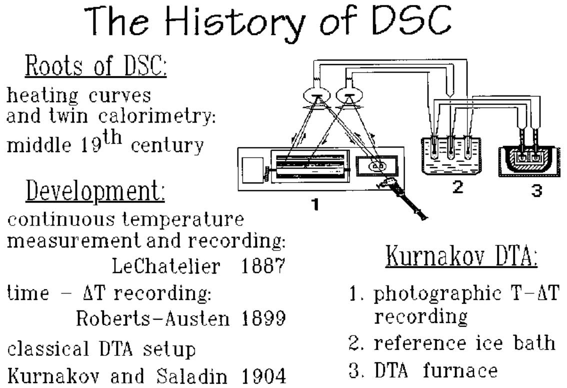

Fig. 1. The development of DSC had its beginning in the Kurnakov DTA [1].

2.1. Instrumentation

Two major developments in instrumentation for calorimetry took place early in the 20th century and would have hardly been considered related at that time. The first was the invention of differential thermal analysis, DTA. Fig. 1 shows one of the very first DTA set-ups by Kurnakov [2]. In the beginning, DTA could not be classified as calorimetry since no heat was measured quantitatively. Only the temperature was determined with the precision of the thermocouple. The most important applications were in the assessments of phase diagrams, transition temperatures, and chemical reactions, as well as the qualitative analysis (fingerprinting) of metals, oxides, salts, ceramics, glasses, minerals, soils, and foods.

The quantitative heat effects were always measured by calorimetry. Instrumentation for the determination of heat capacity was based on the classical adiabatic calorimeter design of Nernst [3], reached after more than 50 years of experimentation with increasingly more precise calorimeters [1]. Fig. 2 illustrates a more modern version of the Nernst-type calorimeter [4] with some of the first control circuitry that became

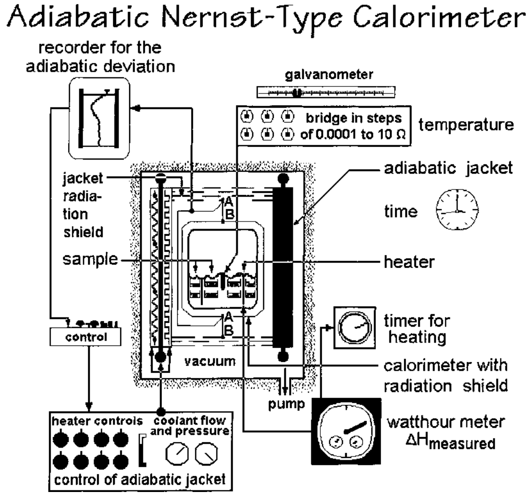

Fig. 2. Schematic of an adiabatic calorimeter based on the Nernst design [3,4].

possible at that time and has by now advanced to much higher degrees of perfection using computers for the control of the calorimeter and analysis of the data.

Even in the 1950s, it was an unlikely prediction that DTA and adiabatic calorimetry would join and produce a differential scanning calorimeter (DSC). The name DSC was first mentioned for a differential calorimeter that achieved a continuous, close-to-complete power-compensation between sample and reference [5]. This development came about because the key concern of calorimetry is the reduction of, and correction for, heat losses or gains due to inadvertent temperature fluctuations in the surroundings of the calorimeter. The heat to be measured can never be perfectly insulated. Even in adiabatic calorimeters, continued heat-loss corrections have to be made. In fact, in calorimeters, such as shown in Fig. 2, about 75% of the data calculations deal with the evaluation of heat losses. A constant rate of drift of the calorimeter due to a mismatch of the temperatures of the jacket and calorimeter shields during isothermal periods, while the calorimeter is at rest, can easily be extrapolated from the largely linear changes of the temperature of the sample. During the heating from T_1 to T_2 during a measurement of the change in enthalpy, ΔH, however, the changes across A–B due to the heating of the sample must be monitored continuously. The resulting adiabatic deviation must then be corrected for using extensive calibration experiments.

In classical calorimetry, as displayed in Fig. 2, one increases precision by measuring relatively large masses of samples (typically >100 g), so that the heat losses are reduced by decreasing the specific surface area (cm^2 g^{-1}). Attempts at twin calorimetry to cancel the heat losses between two symmetric calorimeters, one filled with the sample, the other identical, but empty or filled with a reference material, presented control problems that were difficult to handle [6]. In addition, the conduction of heat into the sample and its equilibration in classical calorimeters was, of necessity, slow, and extended the period of measurement up to 1 h for a single step of the measurement.

Efforts to shorten the time for adiabatic calorimetry by continuous scanning, and by increasing the quality of the calorimetric information that underlies the endotherms and exotherms of DTA were made some time ago. The need to determine the thermal behavior of polymers, which change their stability during the lengthy experimentation in the transition region, accelerated these developments [7,8]. The development of commercial DSCs making use of sample masses of as little as 10 mg and heating rates of 10–40 K min^{-1} closed the gap between the two measurement methods. Three major types of DSCs emerged that are classified as scanning, isoperibol twin-calorimeters [1,9]. One type makes use of an approximate power compensation between two separately heated calorimeters [5], and the other two rely on heat flux of two calorimeters placed symmetrically inside a single heater, but differing in the positions of the controlling thermometers. A typical example with temperature control close to the heater is shown in Fig. 3. Fig. 4 illustrates the other type of heat-flux DSC with a control close to the sample. In the chosen example, three differential measurements are carried out between as many calorimeters, an empty one, one filled with Al_2O_3 (sapphire) as a reference substance, and one filled with the unknown sample. Outside of an asymmetry adjustment, the measurement can be completed in a single run, as indicated in the figure [10].

The heat-loss problem was minimized in the DSCs by having shorter times for measurement. The differential measurements reduce the losses even further. Ultimately, it became possible for the analysis of polymers to have a similar precision for the DSC and the adiabatic calorimeter in the region of overlap in temperature (about 150–450 K). At lower tempera-

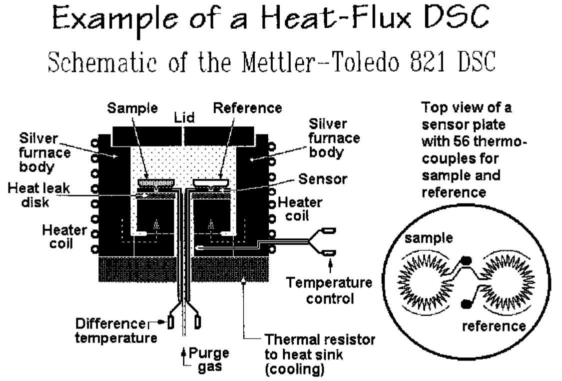

Fig. 3. Heat-flux DSC with a control close to the heater. The multiple thermocouples on the sensor plate average the calorimeter temperatures.

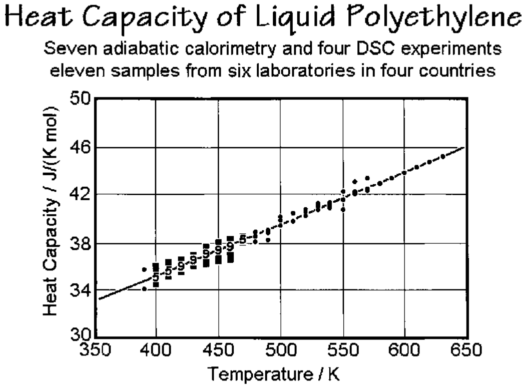

Fig. 5. All available data on the heat capacity of liquid polyethylene. Most of the data that reach to higher temperatures are by DSC.

tures, down to 10 K, the adiabatic calorimeter is the only available precision instrument, and at higher temperatures (up to 1000 K) the DSC may have the higher precision. Fig. 5 is a typical example from the ATHAS data bank of heat capacities of polymers [11–15]. Both types of calorimeters yield a similar precision for the data, making the faster and more convenient DSC the instrument of choice for their typical temperature range from 150 to 1000 K.

Another type of thermal measurement that had an early beginning, but initially did not see wide application, is the AC calorimetry (alternating current calorimetry) [16]. The advantage of this type of measurement lies in the application of a modulation to the sample temperature, T_s, followed by an analysis of the response. By eliminating any signal that does not correspond to the chosen operating frequency, many of the heat-loss effects can be eliminated. Furthermore, it may be possible to probe reversibility and potential frequency-dependence of changes of the studied sample. The heat capacity C_s of the sample can be determined from the ratio of the heat-flow response of the sample, represented by its amplitude A_{HF}, to the product of the amplitude of the sinusoidal sample-temperature modulation, A_{T_s} and the modulation frequency $\omega(=2\pi/p$, where p is the duration of the modulation period, usually given in seconds). The following equation gives an expression for the calculation of C_s from AC calorimetry:

$$C_s = \frac{A_{HF}}{A_{T_s}\omega} \tag{1}$$

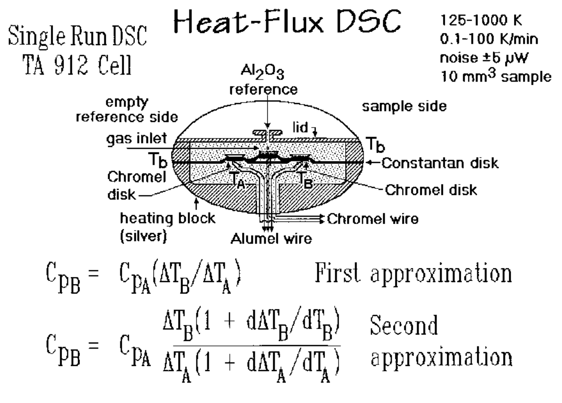

Fig. 4. Heat-flux triple scanning calorimeter.

The next advancement in calorimetry occurred in 1992 with the combination of DSC and temperature modulation to the temperature-modulated DSC (TMDSC) [17–20]. Fig. 6 shows a typical TMDSC of the heat-flux type. In the quasi-isothermal operation, T_s oscillates about T_0 as in an AC calorimeter. The phase lag, ε, is taken relative to a reference oscillation. The figure also illustrates the typical TMDSC run where an underlying heating rate $\langle q \rangle$ is applied in addition. By deconvolution of the two signals, an average signal, practically identical to the standard DSC output and a reversing signal, related to the AC calorimetry of Eq. (1) results. Additional factors need to be considered because of the twin calorimeter construction. The following equation was

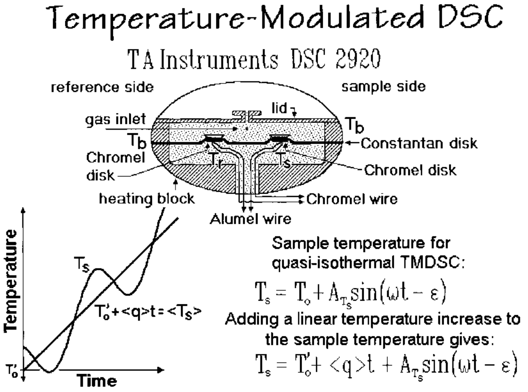

Fig. 6. Schematic of a TMDSC.

proposed for the reversing heat capacity from the TMDSC of Fig. 6 [21]:

$$(C_{\mathrm{s}} - C_{\mathrm{r}}) = \frac{KA_{\Delta}}{A_{T_{\mathrm{s}}}\omega}\sqrt{1 + \left(\frac{C_r}{K}\right)^2 \omega^2} \tag{2}$$

where C_{r}, K, and A_{Δ} are the heat capacity of the reference calorimeter (usually an empty aluminum pan), the Newton's law constant, assumed to describe the thermal conductance from the DSC heater to the sample and reference, and the amplitude of the temperature difference between the sample and reference temperatures $\Delta T(=T_{\mathrm{r}}-T_{\mathrm{s}})$, respectively. For the derivation of Eq. (2), one had to assume that (1) there is no thermal conductance between the sample and reference calorimeters, (2) zero temperature gradients from the temperature sensors to the sample and the reference pans, and, also, (3) zero temperature gradients within the contents of the pans. In other words, one assumes infinite thermal conductance between temperature sensors and the corresponding calorimeters.

Three directions of calorimetry were, thus, combined in the 20th century to dramatically change the capabilities of thermal analysis of materials [1]: The high precision of adiabatic calorimetry, the speed of operation and small sample size of DSC, and the possibility to measure frequency dependence of thermal behavior in AC calorimetry. All three types of calorimetry still have their unique applications, but can also be combined in the TMDSC. A modern thermal analysis laboratory should have all this instrumentation in addition to some of the directions of calorimetry not highlighted in this article, such as combustion calorimetry for the evaluation of chemical heats of reaction and the isothermal calorimetry, often used for following slow biological reactions.

2.2. Theory and understanding of thermal analysis

Parallel to the development of the ever more sophisticated calorimetry went the advancement of the theory and understanding of thermal analysis. The basic theory of thermal analysis, the thermodynamics, was well established at the turn of the century [22]. Its basic laws are based on general observations and do not need a detailed knowledge of the atomic structure. Equilibrium thermodynamics became a central part of physical chemistry and physics. In its classical form, thermodynamics describes the functions of state, such as enthalpy, *H*, entropy, *S*, and free enthalpy, *G*, in terms of the independent variables of state, such as temperature, *T*, pressure, *p*, and the amount of matter, *n,* [23]. While *H* is closely connected to the conservation law of energy (First Law of Thermodynamics), *S* and *G* are indicators of the equilibrium properties (Second Law of Thermodynamics, $\Delta S_{\mathrm{total}}=0$ for equilibrium processes and *G* assumes a minimum for stable states).

During the first half of the 20th century, it became customary to describe the nonequilibrium states and processes in a separate discipline, that of irreversible thermodynamics [24]. The key strategy of handling nonequilibrium systems is to divide the overall system into a series of subsystems that can be approximated by local equilibria and their changes with time are then characterized by flux across the boundaries and production within the subsystems. The main feature of the thermodynamics of irreversible processes consists in the evaluation of the rate of entropy flow, $\mathrm{d_e}S/\mathrm{d}t$, and the entropy production, $\mathrm{d_i}S/\mathrm{d}t$, during the approach to equilibrium.

Perhaps the biggest progress in the understanding of materials occurred through the advance of knowledge about the atomic and molecular structures. It accelerated through such events as the discovery of the nucleus and its electrons, the basic particles of the atom. This was followed quickly by the development of quantum mechanics for the description of atoms and molecules [25]. The discovery of X-ray diffraction allowed to establish the detailed structures of crystals by determining their electron-density distribution [26]. Also of importance was the final recognition of the existence of polymers, the flexible, linear macromolecules [27] which represented the last important class of molecules that needed to be discovered for a full description of all possible materials. Ultimately macromolecular science led to a major industrial progress through development of plastics, synthetic fibers, films and protective coatings and it also accelerated the understanding of biological materials.

At the same time, the link between the molecular nature of matter and thermodynamics was established by statistical thermodynamics [28]. Perhaps the most important connection was that the Third Law of Thermodynamics was now given a simple interpretation. In the words of Nernst, as quoted in [23]: "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite, positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in case of perfect crystalline substances." With the Boltzmann equation, $S=k \ln W$, with W representing the number of ways a system can be arranged microscopically, the Third Law is perhaps the easiest of the laws of thermodynamics to comprehend. Statistical thermodynamics also allowed a better understanding of the kinetics of chemical and physical processes, another of the disciplines of importance to thermal analysis [29].

The fields of thermodynamics, irreversible thermodynamics, statistical thermodynamics, and kinetics which make up the unique combination of theories that is needed to understand thermal analysis were, thus, well developed by about 1950. Taking, as an example, the knowledge of heat capacity, $(\partial H/\partial T)_{\mathrm{p,n}}$, the basic quantity of thermal analysis, and specifically the heat capacity of polymers, one finds that the first papers date back to 1928 [30], 1935 [31], 1937 [32] and 1938 [33]. The basis of the theory of heat capacity of simple solids in terms of statistical thermodynamics connecting vibrational frequencies to the macroscopically measured quantity was given by Einstein [34] and Debye [35], and an extension to polymers was suggested by Tarasov [36]. A more detailed analysis of the vibrational characteristics of a polymer was first made by Stockmayer and Hecht [37]. The full description of the frequency spectrum of polymers in terms of an approximate skeletal and precise group vibrations was developed as the basis of the ATHAS system [38]. Fig. 7 illustrates the interpretation of the measured heat capacity of crystalline polyethylene in terms of its frequency spectrum. Not only does this figure help the understanding of the heat capacity, it also allows the extrapolation to temperatures beyond the range of measurement and shows up any changes in the state of motion from the vibrations known to be the sole contributor to heat capacity at low temperatures. From Fig. 7, one can see, for example, that above 300 K there is an additional contribution to the experimental heat capacity, which ultimately could be linked to conformational mobility, the basis of motion responsible for plastic deformation, making the connection of thermal properties to mechanical properties [39].

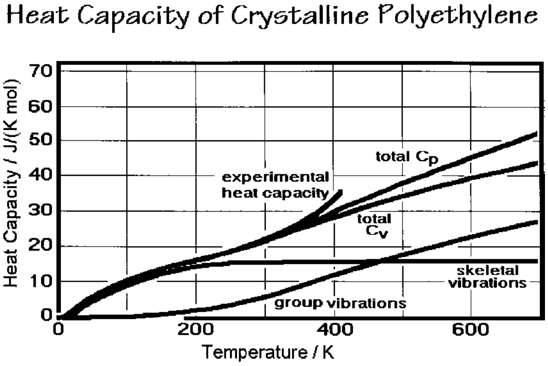

Fig. 7. Vibrational contributions to heat capacity.

The additional knowledge that is needed for the understanding of temperature modulation also had its roots in the early 20th century. As one goes from the descriptions by equilibrium thermodynamics to time-dependent processes, one may need to consider the delay of heat absorption when applying an oscillating temperature. This problem was solved by introducing a complex heat capacity $C_{\mathrm{p}}(\omega)^*$ when describing the effect of thermal conductivity of gases with slowly responding internal degrees of freedom for the understanding of dispersion and absorption of high-frequency sound waves [40,41]. To divide the frequency-dependent complex specific heat capacity $c_{\mathrm{p}}(\omega)^*$ into a real part c'_{p} and an imaginary part ic''_{p}, one uses the following equation:

$$c_{\mathrm{p}}(\omega)^* = c'_{\mathrm{p}}(\omega) - ic''_{\mathrm{p}}(\omega) \tag{3}$$

The real quantities in Eq. (3), according to [42], can be expressed as:

$$c'_{\mathrm{p}} = c^{\mathrm{e}}_{\mathrm{p}} - \frac{\omega^2 (\tau^{\mathrm{e}}_{\mathrm{T,p}})^2 \Delta^{\mathrm{e}} c_{\mathrm{p}}}{1 + \omega^2 (\tau^{\mathrm{e}}_{\mathrm{T,p}})^2} \tag{4}$$

and

$$c''_{\mathrm{p}}(\omega) = \frac{\omega^2 \tau^{\mathrm{e}}_{\mathrm{T,p}} \Delta^{\mathrm{e}} c_{\mathrm{p}}}{1 + \omega^2 (\tau^{\mathrm{e}}_{\mathrm{T},p})^2} \tag{5}$$

where $c^{\mathrm{e}}_{\mathrm{p}}$ is the equilibrium heat capacity, $\Delta^{\mathrm{e}} c_{\mathrm{p}}$ represents the equilibrium change of specific heat capacity due to the process, such as the increase in c_{p} at the glass transition, and $\tau^{\mathrm{e}}_{\mathrm{T},p}$ the relaxation time of the process. The use of complex heat capacity, in analogy to the description of the modulus in isothermal dynamic mechanical analysis (DMA) is, however, more complicated because of the change of the enthalpy and entropy with *T*. Furthermore, over wide ranges of temperature, outside the transition ranges, c''_{p} approaches zero, making $c_{\mathrm{p}}(\omega)^* = c'_{\mathrm{p}}(\omega)$. The major application attempted to be described by complex heat capacity has been the glass transition. In this case, however, the relaxation caused by the glass transition is governed by a nonlinear differential equation [42]. The $|C_{\mathrm{p}}(\omega)^*|$ gained from Eq. (2) can, in this case, not be used for the evaluation of the kinetics of the glass transition, since it represents only the first harmonic oscillation of the response.

Other problems of TMDSC that are not fully resolved involve the separation of time effects due to the calorimeter from the sample effects. Fig. 8 shows a plot of the heat flow vs. temperature of the isotropization of a liquid crystal. From small-amplitude, quasi-isothermal TMDSC, it was possible to fix the onsets of the transition to ±0.05 K, and the breadths of the transition to ±0.1 K [43]. Fig. 8, in contrast, suggests a breadth of close to 1.5 K. Most of this broadening is instrument-caused and special caution must be applied when trying to extract kinetic data from TMDSC of first-order transitions [44].

A final point to be mentioned about TMDSC is the fact that Eq. (2) holds only for the calorimeter of Fig. 6, and even there only to a limited degree. More generally, Eq. (2) should be written as [45]:

$$(C_{\mathrm{s}} - C_{\mathrm{r}}) = \frac{K A_{\Delta}}{A_{T_{\mathrm{s}}} \omega} \sqrt{1 + [\tau(m)^2] \omega^2} \tag{6}$$

with $\tau(m)$ representing a relaxation time that depends on mass and sample. Fig. 9 illustrates the use of measurements of heat capacity with different frequencies fitted to Eq. (6). By using multiple frequencies for modulation, the indicated correction can be made in a single run [46,47].

2.3. Teaching of thermal analysis

In Sections 2.1 and 2.2 of this paper, the impressive progression of instrumentation and knowledge to temperature-modulated calorimetry was described. One would assume that teaching this subject, as outlined in Ref. [1], would be the prime objective in creating a discipline of thermal analysis. Unfortunately, such a development of a well-integrated field

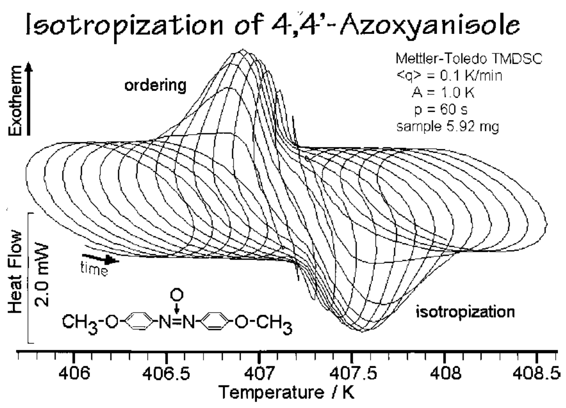

Fig. 8. Lissajous figure of the isotropization of a liquid crystal.

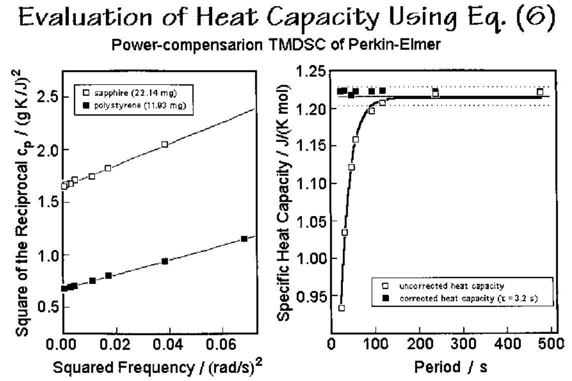

Fig. 9. Frequency dependence of heat capacity when using TMDSC.

of thermal analysis including instrumentation, theory, and teaching did not take place. In fact, the teaching of the sub-disciplines of equilibrium, nonequilibrium, and statistical thermodynamics, as well as kinetics, became rather special topics distributed among physics, chemistry, and engineering. Rarely could one expect a student to gain a cross section of all areas needed for gathering expertise in thermal analysis. As a result, the teaching of the subdisciplines themselves declined toward the end of the 20th century, most likely because of their separation from their practical applications in the thermal analysis of materials [48].

A survey of the International Confederation for Thermal Analysis and Calorimetry, ICTAC, in 1990/1991 of 443 university and college professors involved in teaching of thermal analysis or thermodynamics in the United States revealed that too little is done in teaching of thermal analysis. Some startling results from this survey were that only 3.6% of the surveyed departments of chemistry, polymer science and engineering, and materials and chemical engineering have a specific course in thermal analysis, 20% did not even offer a course in thermodynamics. Taking as a base the 10,400 students that were instructed in thermodynamics by the professors surveyed, only 6% of the students took a course in thermal analysis and only 21% heard about thermal analysis in courses like analytical instrumentation, polymers, physical chemistry, or materials. This is clearly not a good foundation for the future of thermal analysis, and is particularly perplexing since 51% of these same departments polled had one or more pieces of modern thermal analysis instrumentation and more than 1000 students and their faculty were involved with this equipment in their research.

As so often in the historical development of teaching of scientific and engineering topics, the universities are overwhelmed by newly developing fields, and the volume of knowledge increases at such a rate that it is difficult to generate a constantly updated store of knowledge. Perhaps, it is not the greatest difficulty to introduce the new material to be taught, but rather to make the decision as to what of the well-established, classical material must be omitted to keep the overall volume of knowledge manageable. The field of thermal analysis has particular problems because its base is interdisciplinary. It has its roots in physics, chemistry, and materials science. Using only specific topics of each of these fields makes it difficult to generate a curriculum of thermal analysis, especially since some of the needed topics are often considered to be advanced material in their own discipline.

The situation worsened with the widespread introduction of temperature-modulated calorimetry. Without a well-established curriculum in thermal analysis, no fast expansion to include the new knowledge in the education of students could be made. Unfortunately, the level of the existing thermal analysts is often also not sufficient in the more theoretical and mathematical tools to accommodate the new technique. Efforts to create short courses are often limited to instruct in the very basic techniques and analysis methods. A subject taught in several college semesters is not easily assimilated in day- or week-long short courses. As a result, much of the TMDSC and DSC capacity is presently underutilized. Besides the knowledge in thermal analysis, it is self-understood that there has to be a high level of expertise in the field of materials science of interest. A simple observation is that from a laboratory staffed with operators of limited education in thermal analysis and the appropriate materials science, only poor DSC and even poorer TMDSC is forthcoming.

3. Extrapolated TMDSC in the 21st century

Turning now to the difficult job of extrapolating to the next century, one finds it easiest to see the next developments by looking at signs of experimentation that could satisfy needs for the characterization of materials and are already obvious from theoretical considerations presently available. Similarly, advances in knowledge and theory can, to some degree, be guessed at from developments during the last years. Advances in teaching, on the other hand, are almost impossible to predict. In this area, however, lies the chance of future advancement in the field.

3.1. Instrumentation

Temperature-modulated calorimetry, having acquired prominence in the form of TMDSC only in the last decade of the 20th century, can easily be predicted to continue to develop. The first result is expected to be an optimization of the instrumentation. At present, it is not certain if one of the two types of measurement, compensation or heat flux, or one of the four types of control, either control of the temperature at the sample, reference, or heater positions, or control of the temperature difference (heat flow), will prove better suited for some or all applications. Certainly, the basic design of the present calorimeters, which have all seen only minor improvements since the 1960s, is expected to be optimized due to the higher demands when measuring with temperature modulation. Some of the methods to achieve this goal are improvements in assessing a given design by finite-element modeling and measurement of actual temperature gradients by contact-free, fast, and high-resolution IR thermometry. The main goals and expectation are better precision in calorimetric information, a wider range of modulation modes and frequencies, and an extension of the temperature of operation to the cryogenic range, i.e., towards 10 K, and to the high-temperature range above 1000 K. Present characteristics are not fully established, and often depend not only on instrumentation, but also on the nature of the sample (see Fig. 9), but one expects today an absolute precision in heat capacity approaching 1–3%, a time constant t for correction of the frequency dependence in Eq. (6) of 3–5 s, and a low-temperature limit of 150 K and hopes for improvements of all by a factor 0.1, as well as an extension of the high-temperature limit to 2000 K.

Along with the optimization of instrumentation, it is easy to predict improvements of the software for data acquisition and analysis. At present, most commercial software is available through the instrument makers only. Being proprietary, most software is not very transparent or user-friendly toward custom changes and improvements. In the future, it will be necessary to allow the user a greater flexibility in programming of the modulation (sinusoidal, sawtooth, step-function, quasi-isothermal, multi-frequency, and custom design), but all without an undue complication of the default applications that have been proven useful for common measurements. The standard DSC is a simple measuring method which can be extended by TMDSC to make many additional measurements, such as to check on reversibility, to separate reversing and nonreversing processes, and to determine frequency dependence. Many of the traditional determinations will remain work for the standard DSC, such as measuring melting temperatures, heats of fusion, purity determination, and chemical stability. And a large number of applications can be analyzed by both techniques, such as the study of heat capacities, glass transitions, isothermal kinetics of transitions and chemical reactions. Overall, one looks for a calorimeter that can switch easily from a standard DSC to a TMDSC, and back, as the need arises.

Naturally, the same applies to an even greater degree to the data analysis. Data compression and smoothing, the fitting of functions, Fourier transformations, calibration routines, etc. are presently not sufficiently detailed to the user to satisfy such basic questions as: How was this calculated? What is the statistical significance? What about error propagation? How many data points were used, and if not the maximum number, how were they averaged? Which are the fitted variables and which were assumed precise? How were the corrections made for temperature calibration, thermal lags, and other systematic experimental errors? How do I make changes for my special application? These problems with dedicated software generated by the supplier of the hardware were foreseen during the emergence of computers in calorimetry. In 1985, it was suggested during a workshop on the use of computers at the 8th ICTA in Bratislava [49]: "For the future development, especially in light of increasing development of networks of computers in and between larger institutions, it is important to produce hardware which can be combined with any type of software" (E. I. Gmelin, MPI Stuttgart). Today, it is still a hoped-for future development that the commercial calorimeter comes with a basic operating system that can easily be extended with software developed by others and is compatible with many of the available mathematics software packages and programs to tailor-make the operation, and analysis software for the special needs for any given thermal analysis laboratory. These are the easy predictions and suggestions for TMDSC instrumentation in the 21st century. Next are some larger developments that may be discerned from small beginnings.

In the same easy extrapolation of present technology one expects a better combination of TMDSC techniques with temperature-dependent structure analysis, such as X-ray and neutron diffraction and, possibly, also solid state NMR. Some of these combined techniques were already in use for the standard

DSC, but certainly TMDSC would broaden the analysis capabilities, particularly when needing to analyze metastable and unstable systems, as illustrated in Fig. 8.

Just as the roots of adiabatic calorimetry, DSC, and TMDSC extended many years back, one should look for earlier experimental developments that may revolutionize calorimetry in the future. Increasingly, industrial applications deal with unstable samples and systems of nanophase structures that are only metastable. This is particularly true in the polymer field and in the study of biological systems, pharmaceutical compounds, and food stuffs. To assess metastable and unstable compounds, attempts were made some time ago to measure phase transitions at high heating rates [50]. The metastable substances become unstable on heating and reorganize during slower heating. For example, a growth spiral of 10-nm thin lamellar crystals of polyethylene, as shown on the left in Fig. 10, changes its melting temperature on slow heating by as much as 10 K due to crystal perfection, so that any slow DSC can say little about the original sample. The melting data as a function of heating rate are shown in the lower right of Fig. 10. The instrumentation is illustrated by the schematic. Only heating rates above 100 K min^{-1} can safely outrun the reorganization during heating. Such studies of melting as a function of the heating rate cannot only identify the original sample, but also characterize its reorganization properties. Similarly, to duplicate industrial production processes that involve fast heating and quenching, as seen for the crystallization and annealing of spun fibers on drawing or texturing, one has to employ much faster analysis-methods than are found on a standard DSC. Another fast calorimeter is the foil calorimeter [51]. With this calorimeter, heating rates from 1000 to 30,000 K min^{-1} were possible and melting could be studied avoiding irreversible reorganizations, i.e. achieving zero entropy production. More modern versions of such fast-reacting calorimeters could be based on silicon-chip technology for measuring heat flow using large numbers of thermocouple junctions integrated in the chip as well as resistors for the calibration of heat flow, measurement of the sample temperature via its resistance, and for modulation of the sample temperature. The presently available calorimeters [52] have not reached the miniaturization needed to attain the rates of measurement indicated, but have the potential to surpass them with simultaneous capability of more quantitative measurement.

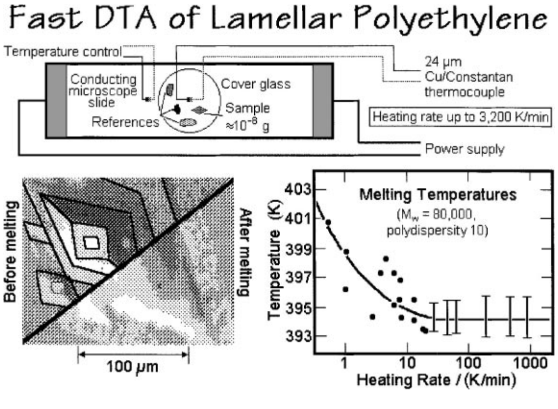

Fig. 10. Fast-melting DTA mounted on an optical microscope [50].

Other possibilities to advance calorimetry to higher heating rates and faster temperature modulation are to change from the just described small-sample analysis using a relatively big device to a small device analyzing only a small volume of a much bigger sample. The two techniques that have been developed to a certain degree are the so-called third-harmonic detection method (3ω-method) of fast calorimetry [53] and the microcalorimetry (µTA$^{\mathrm{TM}}$ of TA Instruments) [54]. The 3ω-method was discovered long ago [55], but can only now be coupled with sufficiently advanced electronics to yield more quantitative data. The µTA$^{\mathrm{TM}}$, in contrast, is based on the method of detection of the topography by the scanning tunneling microscope (STM) and the atomic force microscopy (AFM), known since the 1980s [56,57].

In the 3ω-method, a heater of known geometry is placed in contact with a surface of a practically infinite substrate. The diffusion of the oscillating heat into the semi-infinite medium can then be evaluated as a function of the thermal conductivity and heat capacity [53]. The resulting modulated temperature can be measured by determination of the resistance $R(t)$ of the same heater, since the resistance changes with temperature [$\alpha=(1/R)\mathrm{d}R/\mathrm{d}T\approx 0.004\ \mathrm{K}^{-1}$] and is proportional to Joule heating, which, in turn, is proportional to the square of the electric current $I(t)$ ($=I_0 \cos \omega t$):

$$R(t) = R_0[1 + \alpha A_{T_\mathrm{h}} \cos(2\omega t + \phi)] \tag{7}$$

where R_0 is the base temperature, A_{T_h} is the amplitude of the oscillation, and ϕ the phase-shift relative to the current. The voltage across the heater, $V(t)$, is given by the product $I(t)R(t)$ as:

$$V(t) = I_0 \cos \omega t\, R_0 [1 + \alpha A_{T_\mathrm{h}} \cos (2\omega t + \phi)] \tag{8}$$

which can be written as:

$$V(t) = I_0 R_0 \left[\cos \omega t + \tfrac{1}{2} \alpha A_{T_\mathrm{h}} \cos (\omega t + \phi) + \tfrac{1}{2} \alpha A_{T_\mathrm{h}} \cos (3\omega t + \phi)\right] \tag{9}$$

The thermal analysis information is contained in the last two terms of Eq. (9). Because α is small and A_{T_h} is usually $\ll$1 K, these terms are rather insignificant relative to the first term. By measuring the last term, the third harmonic, with a lock-in amplifier it is possible, however, to obtain the amplitude and phase of the small signal in the presence of the much larger, unwanted signal of different frequency. Thus, by measuring the power and temperature of the heater, it is possible to carry out thermal analysis for a given geometry and a reproducible contact. Typical frequencies that have been employed for the 3ω method are 0.1–1000 Hz at amplitudes of A_{T_h} of about 20 mK [53]. This type of measurement extends the frequency of temperature-modulated calorimetry substantially.

Fig. 11 illustrates the principle of microcalorimetry using the µTA$^{\mathrm{TM}}$ of TA Instruments. The tip of an AFM is replaced by a Pt-wire that can be heated and modulated. Typical present day resolution is about 1.0 µm with heating rates up to 1000 K min^{-1}, a temperature precision of about 3 K and a modulation frequency up to 100 kHz. Fig. 12 shows a typical application [54]. A polyethylene sample similar to the one in Fig. 10 is analyzed, but note that the sample diameter is only 1/10 of that of the growth spiral in Fig. 10. Fig. 12 shows, in the bottom figure, the melting of the apex of the upper right growth spiral with the tip of the microcalorimeter after establishing its location by the scan at the top. The thermal information was gained by the power input, the topographical change of height with temperature (thermomechanical analysis or TMA), and the topography.

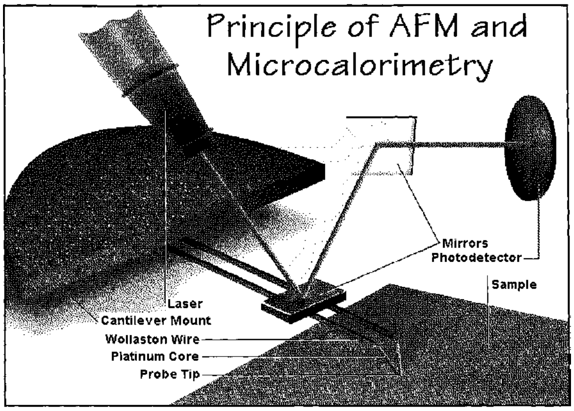

Fig. 11. Analyses by atomic force microscopy (AFM).

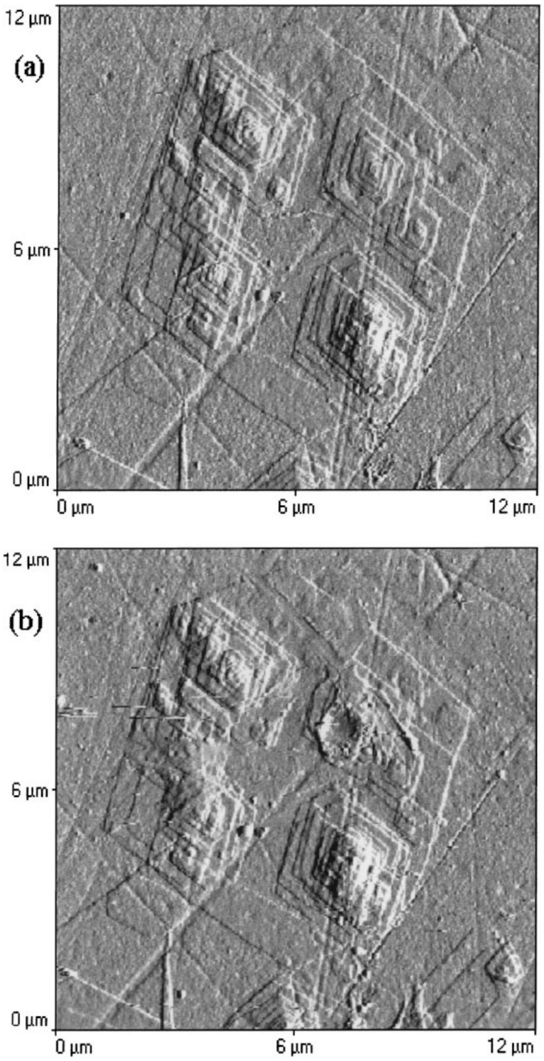

Fig. 12. Observation of the local melting behavior with a microcalorimeter.

Very little of the large amount of information potentially available by these methods of super-fast calorimetry (SFC), integrated circuit calorimetry (ICC), 3ω-calorimetry, and microcalorimetry (MC) has been quantified to date, but one can speculate that just as TMDSC grew out of elements of DSC and AC calorimetry in the 20th century, in the 21st century one will combine these new, already tried methods into an SFICMC with 3ω-capability. Of particular interest would be a compact and robust calorimeter of high precision which, let us say, can have heating rates of up to 100 K s^{-1}, can be modulated with frequencies up to 100 kHz, and can still yield calorimetric information of the presently common precision, and reaches a resolution in its topology analysis of about 10 nm. Such an instrument could, for example, be based on the principle displayed in Fig. 11 with an SFICMC tip as sketched in Fig. 13. The main advantage of such a calorimeter would be to explore the nanophase structure of polymers [58] and other materials which is known to govern the overall properties of macroscopic products. Only with such nanotechnology will it be possible to understand the structure–property–processing triangle that is at the heart of materials science.

3.2. Theory and understanding of thermal analysis

The theory of the basic, vibrational heat capacity is well understood, as outlined in Section 2.2. What is expected in the 21st century is an easier data interpretation by detailed computational programs with sufficiently quantitative force-constants for the bonded and nonbonded interactions between all atoms, so that the heat capacity of any solid can be computed based on the chemical and physical structure information alone. Further advances in the computational aspects of DSC and TMDSC involve computation programs for data evaluation and interpretation, coupled to the complete experimental information gathered in critically evaluated data banks containing heat capacities, transition parameters, vibrational frequencies, and the other thermodynamic parameters, such as specific volume, expansivity, compressibility, and thermal diffusivity. Similarly, a collection of kinetic parameters that can link equilibrium to metastable and unstable states is hoped for.

Next, on a macroscopic level, progress is expected in the description of irreversible processes ranging from glass transitions to first-order phase transitions and chemical reactions. While equilibrium thermodynamics has given a frame for the interpretation of the data of thermal analysis, it has proven insufficient to lead to details in the description. In fact, in the field of polymers, it has led to many erroneous "theories of melting and phase relationships." For example, in Fig. 14, a schematic of the possible phases of a one-component system is given which applies to systems which are able to exhibit the three equilibrium phases ① to ③ [59]. The other 12 phase areas are only metastable and clearly, all multiphase areas violate by their existence the phase rule

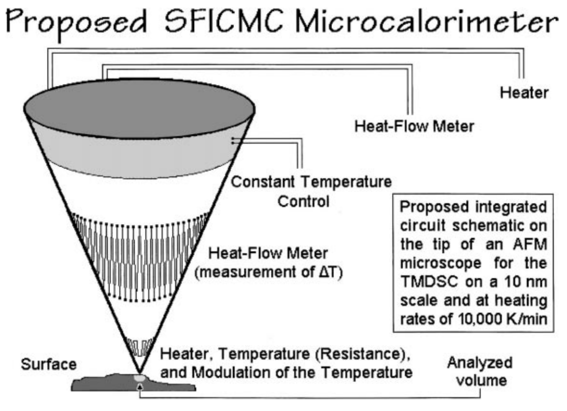

Fig. 13. Proposal of a microcalorimeter as shown in Fig. 11, based in integrated circuit technology.

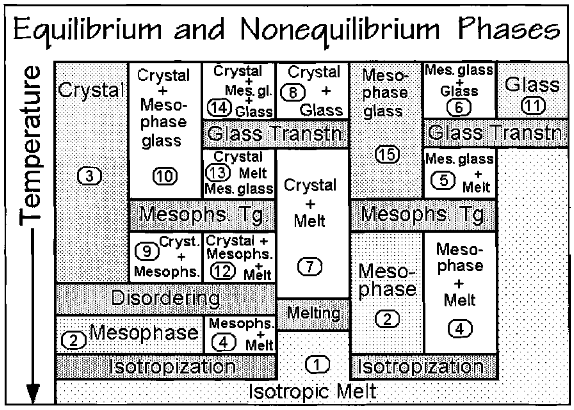

Fig. 14. Possible equilibrium and nonequilibrium phases for a one-component system. The areas further from the left are increasingly metastable phase structures [59].

which allows the existence of two phases in equilibrium for a one-component system at constant pressure only at the transition temperature. All semicrystalline polymers are, thus, not in equilibrium. Examples for all 15 phase areas of Fig. 14 have been presented [59], but their detailed description is still incomplete and presents one of the challenges of the 21st century.

A combination of the macroscopic nonequilibrium description with detailed microscopic molecular dynamics simulations is foreseen to be possible in the near future. The important nanophase structures contain sufficiently few atoms ($\approx$1000) to be handled with present computers for macroscopic time scales. As outlined above, the nanophase structure is at the center of the structure-property correlation (see Section 3.1). Such combinations of macroscopic and microscopic theoretical tools are expected to bring major progress in the early 21st century and strengthen the connection between theory and practice that leads to an understanding of materials. The description of nanophases will only be possible by exploring macroscopic thermodynamics and microscopic structure analysis. As shown in Section 3.1, the expected developments of the instrumentation will yield the experimental data for such progress. Full computational thermal analysis that could be run parallel to the experiment has been demonstrated a few years ago and awaits increased computer power to be refined, speeded up, and extended to at least nanophase structures [60]. A final computational technique that gained application is the neural network prediction of connections between data sets for the purpose of prediction of materials properties [61]. Advanced TMDSC installations are expected to incorporate many of these theoretical and computational concepts in the form of integrated computer software so that many questions can be answered by detailed analysis of the experimental results as they are generated. Typical examples are answers to the questions: Is this material fully rigid (is the heat capacity caused by vibrations only)? Is this increase in the baseline a glass transition (is the Δc_{p} of the proper magnitude and what are the kinetics and how does it correlate to the mechanical properties as determined by DMA)? Which are the possible large-amplitude motions that cause a specific, broad transition region (is there a mobile interface, are there multinanophases possible, etc.)? What is the state of cross-linking of the epoxy or prepolymer, and what further processing is needed to reach given specifications [62,63]?

3.3. Teaching of thermal analysis

The 21st century brings the hope of a rather wide-ranging change in the teaching of thermal analysis. In the past, the teaching, particularly in universities, has been developing conservatively. As pointed out in Section 2.3, the historical development of teaching has neglected the inclusion of newer topics needed for the progress of thermal analysis and also in polymeric materials at an early level in the education of the students to awaken their interest for this important field of analysis and development of new materials. Naturally, if this problem that developed in the 20th century does not get resolved, the optimistic predictions in the last two sections may take longer to come true. Only if highly talented students select to train in this field can one hope to progress in instrumentation, theory, and understanding of DSC, TMDSC and any new instrumentation.

The experimentation with new teaching methods [1,48] has shown that by now one can design personal learning programs with many tools, and computer networks can interlink the material world-wide. While in the 15th century, with the invention of easy reproduction of books in the Western world, one might have predicted the decline of teaching by lecturing, the opposite was true. The book has proven to be a valuable teaching tool, but few students learn entirely from books alone. The presentation of all material by professors in lectures seems to be the goal of higher education in the United States, a goal that is increasingly difficult to attain. It certainly is one of the main reasons of the prohibitive cost of instruction since class sizes become increasingly smaller as the topics get more specific and the teacher has to have a higher level of expertise. By making computer-based instruction readily available and including it as part of a network of information over the internet, this problem of high cost for small audiences can be removed. Specialization becomes easier, and interaction with the teacher is still possible via modern communication, such as e-mail. Additional personal contact through short periods of laboratory instruction, summary lectures, workshop discussions, consulting arrangements, etc. can then round out the instructional experience. Such rearrangement of teaching must be coupled closely with a reassessment of the basic learning which has to cover all exciting and important fields of science and engineering, so that an intelligent choice for specialization can be made by the student. It is necessary, for example that if one finds that over 50% of scientists and engineers are employed in the polymer and textile industry, a similar number of students must get interested in this field early in their studies. Present choices suggest that only <5% of the students choose this field. The discrepancy for the field of thermal analysis was documented in Section 2.3 and is similarly unfavorable.

One must hope, thus, for a major change of the education of thermal analysts in the 21st century. An advantageous development would be, for instance, the replacement of education in thermodynamics with the special combination of equilibrium, irreversible, and statistical thermodynamics, as well as and kinetics, which is taught in thermal analysis [1]. In the treatment of molecules, similarly, one should divide the field equally into three major classes: Those of small molecules (inorganic and organic molecules of <1000 atoms), large and flexible molecules (polymers, textiles, adhesives, biomaterials, etc.), and large rigid molecules (metals, ceramics, salts, etc.) [64]. The hope is that a basic education will evolve which does not rely on re-education of the new graduates as soon as they enter employment using teaching methods developed outside the university curriculum. Similarly, it may be more efficient (and beneficial to the university) that the branching into new specialization, and updating of knowledge and certification through degrees remains under university control.

4. Conclusions

Based on the developments in the past it is possible to make a number of optimistic predictions about the development of instrumentation, theory, and understanding of temperature-modulated calorimetry as a special field of thermal analysis. All of these predictions hinge, however, on new developments in the teaching of the subject. If no qualified scientists and engineers are available in the field, the already developed instrumentation will not be used to its fullest and the data analysis will not challenge the theory to advance to the next level of understanding. Since, in the past, the universities have not managed to show aggressive leadership in the field of thermal analysis and not even the development of modern teaching methods, one must hope that the regional professional organizations collected under the leadership of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) will take over this effort.

Acknowledgements

This work was supported by the Division of Materials Research, National Science Foundation, Polymers Program, Grant # DMR-9703692 and the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy, under contract number DE-AC05-96OR22464.

References

[1] Note that more detail is available in the computer course Thermal Analysis of Materials, which contains about 3000 computer screens of text, figures, and hypertext and is available without cost from the internet URL: http://web.utk.edu/~athas/courses/tham99.html
[2] N.S. Kurnakov, Z. Anorg. Chemie 42 (1904) 184.
[3] W. Nernst, Ann. Phys. 36 (1911) 395.
[4] A.E. Worthington, P.C. Marx, M. Dole, Rev. Sci. Instr. 26 (1955) 698.
[5] M.J. O'Neill, Anal. Chem. 36 (1964) 1238.
[6] C. Sykes, Proc. Roy. Soc. (London) 148A (1935) 422.
[7] B. Wunderlich, M. Dole, J. Polymer Sci. 24 (1957) 201.
[8] B. Wunderlich, W.H. Kashdan, J. Polymer Sci. 50 (1961) 71.
[9] W. Hemminger, G. Höhne, Calorimetry, Verlag Chemie, Weinheim, Germany, 1984.
[10] Y. Jin, B. Wunderlich, Thermochim. Acta 226 (1993) 155.
[11] U. Gaur, H.-C. Shu, A. Mehta, S.-F. Lau, B.B. Wunderlich, M. Varma-Nair, B. Wunderlich, J. Phys. Chem. Ref. Data 10 (1981), 89; 119; 1001; 1051
[12] U. Gaur, H.-C. Shu, A. Mehta, S.-F. Lau, B.B. Wunderlich, M. Varma-Nair, B. Wunderlich, J. Phys. Chem. Ref. Data 11 (1982), 313; 1065.
[13] U. Gaur, H.-C. Shu, A. Mehta, S.-F. Lau, B.B. Wunderlich, M. Varma-Nair, B. Wunderlich, J. Phys. Chem. Ref. Data 12 (1983), 29; 65; 91.

[14] U. Gaur, H.-C. Shu, A. Mehta, S.-F. Lau, B.B. Wunderlich, M. Varma-Nair, B. Wunderlich, J. Phys. Chem. Ref. Data 20 (1990) 349.

[15] B. Wunderlich, Pure Applied Chem. 67 (1995) 1919; for data collection, see our website at the address: http://web.utk.edu/~athas

[16] P.F. Sullivan, G. Seidel, Phys. Rev. 173 (1968) 679.

[17] M. Reading, D. Elliot, V.L. Hill, J. Therm. Anal. 40 (1993) 949.

[18] P.S. Gill, S.R. Sauerbrunn, M. Reading, J. Therm. Anal. 40 (1993) 931.

[19] M. Reading, Trends Polym. Sci. 8 (1993) 248.

[20] M. Reading, B. Hahn, B.S. Crowe, US Patent 5,224,775 (July 6, 1993).

[21] B. Wunderlich, Y. Jin, A. Boller, Thermochim. Acta 238 (1994) 277.

[22] H.A. Bumstead, R. Gibbs Van Name, The Scientific Papers of J. Willard Gibbs, originally Longmans, Green and Co., London, 1906.

[23] G.N. Lewis, M. Randall, Thermodynamics, McGraw–Hill, New York, 1923.

[24] See, for example, I. Prigogine, Introduction to Thermodynamics of Irreversible Processes, Interscience, New York, 1955, and S.R. de Groot, Thermodynamics of Irreversible Processes, North Holland, Amsterdam, 1951.

[25] See, for example, L. Pauling, E.B. Wilson, Introduction to Quantum Mechanics, McGraw–Hill, New York, 1935.

[26] The Proceedings of the Annual Conference on Application of X-Ray Analysis; for example, Advances in X-Ray Analysis, vol. 39, Plenum, New York, 1997.

[27] H. Staudinger, Helv. Chim. Acta 5 (1922) 788.

[28] R.H. Fowler, E.A. Guggenheim, Statistical Thermodynanics, Cambridge University Press, New York, 1939.

[29] C.H. Bamford, C.F. Tipper, Comprehensive Chemical Kinetics, vols. 1–26, Elsevier, Amsterdam, 1969–1986.

[30] M. LeBlanc, M. Kröger, Z. Elektrochem. 34 (1928) 242.

[31] N. Bekkedahl, H. Matheson, J. Res. Natl. Bur. Stand. 15 (1935) 503.

[32] C.T. Anderson, J. Am. Chem. Soc. 59 (1937) 1036.

[33] F.T. Gucker Jr., W.L. Ford, J. Am. Chem. Soc. 60 (1938) 2563.

[34] A. Einstein, Ann. Physik 22 (1907) 180; 800.

[35] P. Debye, Ann. Physik 39 (1912) 789.

[36] V.V. Tarasov, Zh. Fiz. Khim. 24 (1950) 111.

[37] W.H. Stockmayer, C.E. Hecht, J. Chem. Phys. 21 (1953) 1954.

[38] B. Wunderlich, H. Baur, Adv. Polym. Sci. 7 (1970) 151.

[39] B.G. Sumpter, D.W. Noid, G.L. Liang, B. Wunderlich, Adv. Polym. Sci. 116 (1994) 27.

[40] F.O. Rice, Phys. Rev. 31 (1928) 691.

[41] J.O. Hirschfelder, C.F. Curtis, R.B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1954.

[42] H. Baur, B. Wunderlich, J. Therm. Anal. 54 (1998) 437.

[43] W. Chen, M. Dadmun, G. Zhang, A. Boller, B. Wunderlich, Thermochim. Acta. 324 (1998) 87.

[44] B. Wunderlich, A. Boller, I. Okazaki, K. Ishikiriyama, W. Chen, M. Pyda, J. Pak, I. Moon, R. Androsch, Thermochim. Acta 330 (1999) 210.

[45] R. Androsch, I. Moon, S. Kreitmeier, B. Wunderlich, Thermochim. Acta in press (2000).

[46] M. Pyda, B. Wunderlich, Heat Capacities by Multi-Frequencies Saw-Tooth Modulation Using Standard DSC, Proc. 27th NATAS Conf. in Savannah, GA, 19–22 September, 1999 (submitted for publication Thermochim. Acta.).

[47] B. Wunderlich, M. Pyda, J. Pak, R. Androsch, Y.K. Kwon, Heat Capacities by Multi-Frequencies Saw-Tooth Modulation, Thermochim. Acta, in press 2000.

[48] B. Wunderlich, J. Therm. Anal. Cal. (accepted, 2000).

[49] B. Wunderlich, P. Fellner, Report on the Workshop at the 8th ICTA, The Use of Computers and Data Storage in Everyday Thermoanalytic Practice. Thermochim. Acta 110 (1987) 67.

[50] E. Hellmuth, B. Wunderlich, J. Appl. Phys. 36 (1965) 3039.

[51] E. Hager, Rev. Sci. Instr. 43 (1972) 1116.

[52] C. Mathonat, G. Bourdin, C. Parazza, J.L. Daudon, P. Le Parlouër, in: K. R. Williams (Ed.), Proc. 26th NATAS Conf. in Cleveland, OH, 13–15 September 1998, 26 (1998) 570.

[53] I.K. Moon, Y.H. Yeong, S.I. Kwun, Rev. Sci. Instr. 67 (1996) 29.

[54] See, for example: I.K. Moon, R. Androsch, W. Chen, B. Wunderlich, J. Therm. Anal. Cal. 59 (2000) 1870.

[55] O.M. Cobino, Phys. Z. 12 (1911) 292.

[56] G. Binning, H. Rohrer, C. Gerber, E. Weidel, Phys. Rev. Lett. 49 (1982) 57.

[57] G. Binning, C.F. Quate, C. Gerber, Phys. Rev. Lett. 56 (1986) 930.

[58] W. Chen, B. Wunderlich, Macromol. Chem. Phys. 200 (1999) 283.

[59] B. Wunderlich, Macromol. Symp. 113 (1997) 51.

[60] S.N. Kreitmeier, G.L. Liang, D.W. Noid, B.G. Sumpter, J. Therm. Anal. 46 (1996) 853.

[61] B.G. Sumpter, D.W. Noid, J. Therm. Anal. 46 (1996) 833.

[62] G. Van Assche, A. Van Hemelrijck, H. Rahier, B. Van Mele, Thermochim. Acta 268 (1995) 121.

[63] G. Van Assche, A. Van Hemelrijck, H. Rahier, B. Van Mele, Thermochim. Acta 286 (1996) 209.

[64] B. Wunderlich, A Classification of Molecules and Transitions, as Recognized by Thermal Analysis, Thermochim. Acta 340/41 (1999) 370.