

# The Adiabatic Scanning Calorimetry Booklet

## Summary

Adiabatic scanning calorimetry is a high-resolution calorimetric technique for solid and liquid samples. It has specific advantages for the study of phase transitions.

- The sample remains in thermodynamic equilibrium.
- The sample evolves freely through a phase transition.
- The enthalpy is measured directly.
- Sub-millikelvin temperature resolution.
- Absolute values within 2 %.
- One-time calibration.
- True shape of heat capacity curves: no instrument influences.
- Sample quantities from 10 µg in solutions to large gram-sized samples.
- DSC crucibles can be used.
- Rates from  $\text{mK h}^{-1}$  to  $20 \text{ K h}^{-1}$ .
- Current implementations cover  $-30 \text{ }^\circ\text{C}$  to  $120 \text{ }^\circ\text{C}$ .
- Constant power ASC mode, as well as DSC and heat-step modes.

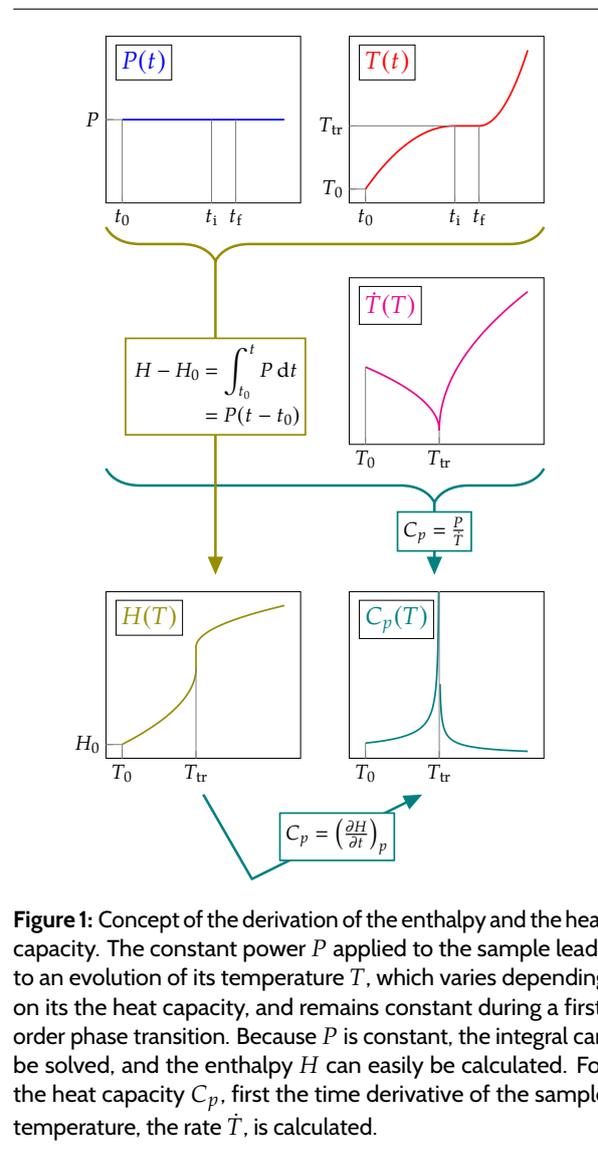
## Adiabatic scanning calorimetry

Calorimetric techniques aim to determine the energy content of matter. They generally implement one of the relations that define the heat capacity  $C_p$ :

$$C_p = \frac{dQ}{dT} \quad \text{and} \quad C_p = \frac{P}{\dot{T}}$$

For example, heat-step calorimetry uses the first equality, providing a finite amount of heat to the sample and measuring the corresponding temperature step. The common differential scanning calorimetry (DSC) is based on the second equality: continuously changing the temperature of the sample at a constant rate, while determining the power that is needed to achieve this.

But the second equality has also a second possible implementation: what would happen if, instead of a



**Figure 1:** Concept of the derivation of the enthalpy and the heat capacity. The constant power  $P$  applied to the sample leads to an evolution of its temperature  $T$ , which varies depending on its the heat capacity, and remains constant during a first-order phase transition. Because  $P$  is constant, the integral can be solved, and the enthalpy  $H$  can easily be calculated. For the heat capacity  $C_p$ , first the time derivative of the sample temperature, the rate  $\dot{T}$ , is calculated.

constant rate, a constant power would be provided to the sample? This question is answered by adiabatic scanning calorimetry (ASC): the result is a high-resolution technique that excels at the study of phase transitions. The core reason is that applying a constant power to the sample leaves it free: it can use the energy to do what it wants: changing its

temperature or changing its phase.

Figure 1 shows a simulation of an ASC run on a sample with a phase transition with a small latent heat. The constant power leads to a variable temperature evolution, in particular, near the phase transition, the temperature increases slower and even stays constant during the transition. This illustrates the core principle of ASC: *the sample controls the calorimeter*. As the prime consequences, the ASC provides the true data, without instrument influences, and offers excellent performance near phase transitions.

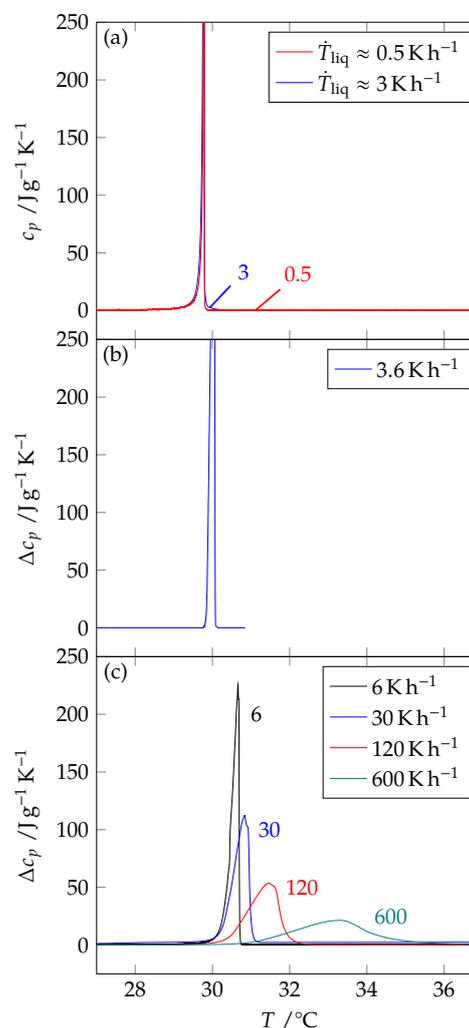
In the next sections, some concrete examples will be discussed, with results on melting transitions with large latent heats, on delicate transitions and on transitions of small quantities of materials in solutions. For the large melting transitions, a comparison with DSC will be made.

### Melting transitions

At melting transitions, a substance goes from a fully ordered, crystalline solid phase to a completely disordered liquid phase. The disruption of this order requires a large amount of heat: the latent heat that is needed to achieve melting. Providing this latent heat will melt the sample at a single temperature, unless there are impurities present.

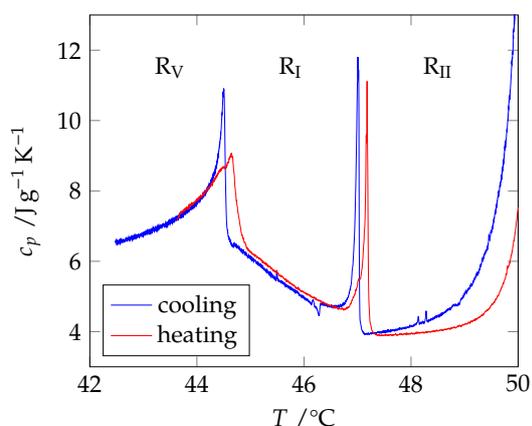
This is illustrated in figure 2, displaying results for the metal gallium, whose melting transition is a reference point for the temperature scale [1, 2]. The data are taken from reference [3]. According to ASC runs, displayed in the top panel, the heat capacity exhibits a very sharp peak just below 30 °C, with a small impurity-related pretransitional region on the low-temperature side. The middle panel shows the result of a custom-built high-performance DSC [4]: the heat capacity peak is markedly broader, and the transition region only starts where the transition ends in the ASC results. The bottom panel, showing results obtained with a commercial DSC (Mettler-Toledo 1 with FRS8 sensor) displays this effect even more clearly.

The broadening that is observed in the DSC runs, is a fundamental consequence of the DSC principle and is unavoidable, even for the best possible DSC. The underlying problem is the constant-rate approach used for DSC: all latent heat needs to be supplied to the sample immediately, and that is just



**Figure 2:** Comparison of the specific heat capacity of the smallest gallium samples. (a) ASC runs on sample C of 2.4 mg. (b) DSC run, literature data for 2.01 mg [4]. (c) DSC runs, obtained with a commercial DSC instrument, on sample D of 2.09 mg. The figures show that ASC leads to rate-independent heat capacity data and display sharper peaks than the DSC data, even if a custom-built high-resolution DSC is used.

physically impossible. ASC avoids this forced behaviour, by offering the sample energy and leaving it free to use this energy. As such, the sample undergoes the transition in thermal and thermodynamic equilibrium, and not in non-equilibrium dynamic circumstances like in DSC.

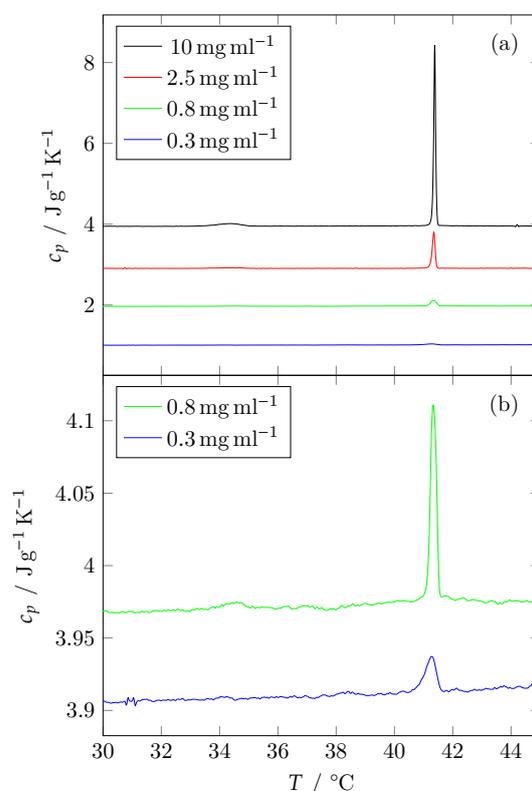


**Figure 3:** Cooling and subsequent heating run in the supercooled region of the rotator phases of the alkane tetracosane, showing the temperature resolution of ASC and the hysteresis of the transitions.

### Delicate transitions

Many substances do not only show the large melting transitions from solid to liquid, but also a whole number of more subtle transitions, involving much smaller amounts of heat. Examples of these include solid-solid transitions between different crystal forms, and the transitions between liquid-crystalline mesophases that are used in displays. The examples here are transitions of the rotator phases, a special kind of intermediate crystal phase in which the molecules can rotate. This occurs, among others, in elongated flexible molecules, of which alkane waxes are the prototypical examples.

In this example, we look into the case of tetracosane, the linear alkane with 24 carbon atoms (C<sub>24</sub>). This alkane shows three rotator phases, of which the two lower-temperature ones can only be accessed in cooling runs. For historical reasons, these are called R<sub>V</sub>, R<sub>I</sub> and R<sub>II</sub> with increasing temperature. Figure 3 shows data from reference [5], in a very specific case were first a cooling run was made so the lower rotator phases were formed, and a heating run was started before the sample could crystallise. These data provide a unique view on the properties of these rotator transitions, with high-resolution data present in both temperature direc-



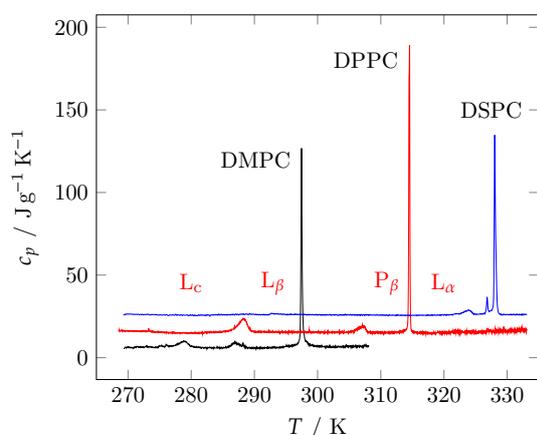
**Figure 4:** Heat capacity profiles of DPPC vesicles in aqueous solutions. The concentration of a stock solution was gradually reduced from 10 mg ml<sup>-1</sup> to 0.03 mg ml<sup>-1</sup>, decreasing the effective amount of lipid from 632 μg to 20 μg.

tions. This allows clearly to assess the hysteresis of these transitions, with a clear reproducibility for the higher-temperature R<sub>I</sub>–R<sub>II</sub> transition and a slightly different nature for the lower-temperature R<sub>V</sub>–R<sub>I</sub>. This data quality cannot be achieved with any other calorimetric technique.

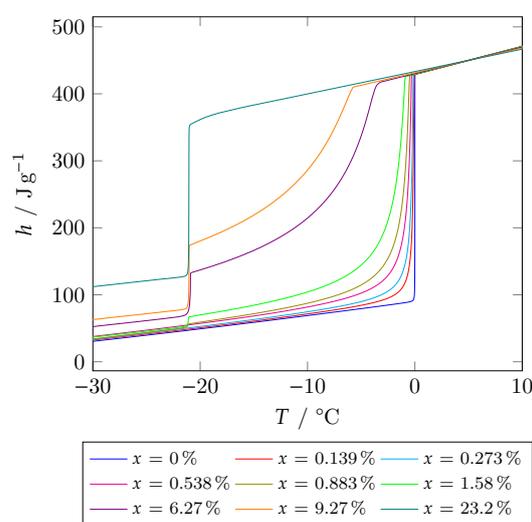
### Solutions

Many biological products are studied in aqueous environment, and such solutions are often very dilute. A common example of these are suspensions of lipid vesicles. The lipid bilayers that constitute the vesicles undergo several phase transitions with increasing temperature.

Figure 4 shows the ASC heat capacity results for suspensions of the prototypical lipid DPPC. The



**Figure 5:** Comparison of the heat capacity data of three lipids suspensions. They are chemically identical, with the exception of the double alkyl tails. In order of increasing length, they are DMPC ( $n = 14$ ), DPPC ( $n = 16$ ) and DSPC ( $n = 18$ ). The red labels indicate the four phases in which DPPC is observed in this temperature range, they are the sub-gel phase  $L_c$ , the gel phase  $L_\beta$ , the ripple phase  $P_\beta$ , and the liquid-disordered phase  $L_\alpha$ . The phase sequence of the other lipids is analogous, with the exception of the additional small transition in DSPC just before the main transition.



**Figure 6:** Enthalpy curves for different solutions of NaCl in water. The concentrations are expressed in mass%; the enthalpies are normalised at  $450 \text{ J g}^{-1}$  at  $5^\circ\text{C}$ . The data show the increase of the eutectic phase transition at  $-21.2^\circ\text{C}$ , the increasing curvature and the decreasing melting point with increasing salt concentration; also, the decreasing total heat needed to heat from  $-30^\circ\text{C}$  to the melting point can be asserted.

broad gel to ripple transition is observed around  $33^\circ\text{C}$ , and the main transition peak at  $41^\circ\text{C}$ . Starting from a solution of  $10 \text{ mg ml}^{-1}$ , three further dilutions were prepared, decreasing the effective amount of lipid in the samples from  $632 \mu\text{g}$  to  $20 \mu\text{g}$ . The gradual dilution shows that even for an absolute amount of  $20 \mu\text{g}$  DPPC in the sample, the main transition peak (ripple to liquid-disordered phase) remains visible in the four samples. The gel to ripple phase transition, on the other hand, becomes virtually invisible, a consequence of the much smaller amount of heat involved, and its more diffuse character. Focussing on the main transition peak, one clearly observes that although the height of the peak decreases, the onset and end temperature of the peak do not change, indicating that the peak does not diminish due to decreasing sensitivity of the pASC instrument, but only due to the decreasing amount of sample, and thus decreasing amount of transition heat. In fact, when a quantitative analysis of the specific transition enthalpy is made, the results extracted from each of the four runs coincide

with each other and are in line with literature data.

In figure 5, the results are shown for suspensions of three pure lipids, differing only in the length of their double alkyl tails, but identical otherwise. In order of increasing length, they are DMPC ( $n = 14$ ), DPPC ( $n = 16$ ) and DSPC ( $n = 18$ ), and the respective phase transitions are observed at higher temperatures with increasing chain length. For these three lipids, the phase transitions that are known from literature are detected without problem, and for DSPC the small transition just below the main transition, which is only rarely mentioned in literature, is detected with ease.

### Using enthalpy

One of the advantages of ASC is the possibility to measure a continuous enthalpy curve, simultaneously with the heat capacity data. While the heat capacity is generally used to study the results of an experiment, there are numerous cases in which certain information can be gained equally well or

even better from the enthalpy data. This is in particular the case when the energy content of phase transitions needs to be asserted.

As an example, the enthalpies of solutions of NaCl in water are presented in figure 6. When NaCl is dissolved in water, it decreases the melting point of the solution, until the so-called eutectic concentration of 23.2 mass% is reached. Due to the presence of the salt, the solutions have two transitions: a low-temperature (eutectic) melting at  $-21.2\text{ }^{\circ}\text{C}$  and the normal ice to water melting. A number of solutions covering this range were measured. The enthalpy curves are displayed such that they have a common value of  $450\text{ J g}^{-1}$  at  $5\text{ }^{\circ}\text{C}$ . This stresses the differences in the lower-temperature region.

The blue curve for pure water has a quasi-linear increase until at  $0\text{ }^{\circ}\text{C}$  the melting point is reached. The transition enthalpy is visible as the clear step in the enthalpy, immediately quantifying the latent heat, and the steepness shows that the material under study is very pure water. When the concentration of dissolved salt increases, the melting point decreases. Similarly, the enthalpy curves between  $-20\text{ }^{\circ}\text{C}$  and the melting point show increasing curvatures, for the concentrations above 6.27% even covering the whole range: this is the effect of the salt acting as impurity. At low temperature, the increasing contribution of the eutectic transition (at the expense of the normal melting) is easily observed; at the eutectic concentration of 23.2%, this transition is the only one present. Finally, the presence of the salt decreases the total amount of heat needed to heat the solutions from  $-30\text{ }^{\circ}\text{C}$  to the melting point.

## Conclusion

Adiabatic scanning calorimetry as currently offered by ASC-TC is an innovative re-implementation of the classical calorimetric technique that has proven its worth since the late 1970s in the field of high-resolution studies of phase transitions in soft matter [6–8]. In its modern pASC form, it offers the same capabilities, but in user-friendly setups and for smaller samples than before [3, 9, 10].

The ASC calorimeters provide marked improvements for the study of phase transitions as compared to other calorimetric techniques.

## References

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## Colofon

ASC-TC is the name under which the LRD division Acoustics and Thermal Physics of the University of Leuven brands its activities in the field of calorimetry and thermal analysis.

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