7. Thermal Properties

7.1 Definition and Methods
Gibbs free energy $G$ is a thermodynamic potential that measures the "useful" or process-initiating work obtainable from an isothermal, isobaric thermodynamic system.

$$G(p, T) = U + pV - TS$$

entropy $S = -\left(\frac{\partial G}{\partial T}\right)_p$

volume $V = \left(\frac{\partial G}{\partial p}\right)_T$

enthalpy $H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_p$

heat capacity at constant pressure $C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$

cubic coefficient of thermal expansion $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

isothermal cubic compressibility $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

**DSC (Differential Scanning Calorimetry)**
Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.

- sample and reference are maintained at nearly the same temperature throughout the experiment: $\Delta T = 0$
- sample holder temperature increases linearly as a function of time
- reference sample should have a well-defined heat capacity over the range of temperatures to be scanned
measuring the temperature dependence of the needed heat $\Delta Q$: less or more heat must flow to the sample depends on whether the process is exothermic or endothermic.

When the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature.

Example of generic DSC curve:

- solid-solid transition temperature $T_{ss}$
- glass transition temperature $T_g$
- liquid-liquid transition temperature $T_{ll}$
- crystallization temperature $T_{cryst}$
- melting temperature of crystallites $T_M$
- exothermic reaction temperature $T_{react}$
- decomposition temperature $T_{decomp}$

Example: Glass transition temperature measurement

Compatible polymer blend

Compatible polymer blend

Incompatible polymer blend

glass transition is relatively broad and extends over a temperature range of 60K between -110°C and -50°C

two glass transitions are present: glass transition of NR occurs at -58.8°C, while the glass transition of SBR occurs at -44.1°C
Example: Phase transition measurement
copolymer PVDF-TRFE (polyvinylidenfluoride-trifluorethylen) without and with addition of ceramic PZT (lead zirconate titanate)

TGA (Thermal Gravimetric Analysis) → measure sample composition
Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature.

• analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change
• As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted.
• derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

Example:
Weight percent and derivative of weight percent curves for the TGA of the as-received CoMoCAT SWNT-containing powder in oxygen.
Yehia et al. Journal of Nanobiotechnology 2007 5:8

TGA is commonly employed in research and testing to determine characteristics of materials, to determine degradation temperatures, absorbed moisture content
of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Example: determine thermal stability of coating
Resin wood

Simultaneous TGA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss (e.g. melting and crystallization) and those that involve a weight loss (e.g. degradation).

Example: ligand decomposition of WO$_{3-x}$ nanorods
The sample was heated at constant rate under N2 atmosphere up to 195 °C for removing moisture and then up to 700 °C for removing the oleylamine ligands

- From 0 – 10 min assigned to water evaporation.
- From 65 – 75 min assigned to OA evaporation.
- From 155 – 164 min assigned to WO$_{3-x}$ oxidation.
- From 168 – 175 min is also due to further oxidation of W$^{5+}$ atoms.
**DTA (Differential thermal analysis)**

Differential thermal analysis (or DTA) is a thermoanalytic technique, similar to differential scanning calorimetry. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. This differential temperature $\Delta T$ is then plotted against time, or against temperature.

- changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference
- DTA curve provides data on the transformations that have occurred: glass transitions, crystallization, melting and sublimation
- area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample

**Example: Cu–In compound in N2 atmosphere**
TMA (Thermo Mechanical Analysis)
Thermomechanical analysis (or TMA) is a thermoanalytic technique, which measures a change of a dimension or a mechanical property of the sample while it is subjected to a temperature. A special related technique is thermodilatometry (TD), the measurement of a change of a dimension of the sample with a negligible force acting on the sample while it is subjected to a temperature.

Example: characterize the properties of PTFE powder material

TMA Set-up:
sample sits on a support within the furnace

- measure changes in length by a sensitive position transducer, normally a Linear Variable Displacement Transducer (LVDT)
- probe and support are made from a material such as quartz glass (vitreous silica), which has a low, reproducible, and accurately known coefficient of thermal expansion, and also has low thermal conductivity, which helps to isolate the sensitive transducer from the changing temperatures in the furnace
• thermocouple near the sample indicates its temperature

Different configurations:

Summary Thermal analysis
The properties of materials are studied as they change with temperature. Several methods are commonly used - these are distinguished from one another by the property which is measured.

All measurements depend on the heating / cooling rate!
Typical value 10°C/min

In addition to controlling the temperature of the sample, it is also important to control its environment (e.g. atmosphere).

Atomic force microscopy (AFM) uses a fine stylus to map the topography and mechanical properties of surfaces to high spatial resolution. By controlling the temperature of the heated tip and/or the sample a form of spatially resolved thermal analysis can be carried out.
7.2 Heat Capacity

An object's heat capacity is defined as the ratio between the amount of heat energy transferred to the object and the resulting increase in temperature of the object,

\[ C = \frac{Q}{\Delta T} \]

- Heat capacity of spherical gas atoms \( C_{v,m} = 3R = 3 \times 8.318 \text{ J/K} \)
- Heat capacity of polymers is smaller because some degrees of freedom are frozen-in

**Specific heat capacity**, often simply called **specific heat**, which is the heat capacity per unit mass of a material.

Examples:
- quartz \( c_p = 0.72 \text{ J/K/g} \)
- polyvinylchloride \( c_p = 0.85 \text{ J/K/g} \)
- polystyrene \( c_p = 1.30 \text{ J/K/g} \)
- polyethylene \( c_p = 2.1 \text{ J/K/g} \)
- water \( c_p = 4.2 \text{ J/K/g} \)

Difference between amorphous (○) and semi-crystalline polymers (●)

\[ \begin{array}{c|c}
\text{T small: linear increase of } c_p \text{ because atoms vibrate stronger around their rest positions} \\
\text{T}_g: \text{ strong increase of } c_p \text{ because additional movement along polymer chain at covalent connections} \\
\text{T}_M: \text{ maximum of } c_p \text{ because heat is required to melt crystals} \\
\text{T}_{M,0}: \text{ in case of crystal domains of different sizes the biggest ones will melt latest} 
\end{array} \]
Low temperature behavior:
The Debye model correctly predicts the low temperature dependence of the heat capacity for crystalline material

\[
\frac{C_v}{Nk_B} \approx \frac{12\pi^4}{4} \left( \frac{T}{\Theta_D} \right)^3
\]

with the Debye temperature \( \Theta_D \).

Polymers show deviation from \( C_{V,P} \sim T^3 \) behavior


a disordered system of coupled classical harmonic oscillators with a continuous distribution of coupling parameters exhibits generally a low-frequency enhancement ("boson peak") of the density of states \( g(\omega) \), as compared with the Debye law


Reduced density of states \( g(\omega)/\omega^2 \) as calculated in SCBA for the disorder parameters (from top to bottom) \( \gamma_\mu = 0.1666, 0.1664, 0.166, 0.164, 0.16, 0.15 \).

7.3 Thermal Expansion

- Difference between cubic $\beta$ and linear thermal expansion coefficient $\alpha$
- In case of oriented polymers a negative thermal expansion coefficient is possible because of a chain contraction perpendicular to the fiber orientation
- In contrast to metal, polymers have very large thermal expansion coefficients

Examples:
- quartz $\alpha = 1 \times 10^{-6}$/K
- steel $\alpha = 10 \times 10^{-6}$/K
- polystyrene $\alpha = 60-80 \times 10^{-6}$/K
- PMMA $\alpha = 50-110 \times 10^{-6}$/K
- polyethylene $\alpha = 100-250 \times 10^{-6}$/K

→ this causes problems in applications which combine different materials (polymer and metal) and which are used in a large range of different temperatures, such as cars, airplanes, computer

7.4 Thermal Conductivity

- Polymers exhibit a bad electrical conductivity, because phonons have a small free path-length of 0.7 nm → thermal conductivity in polymers much smaller than in metals

Example:
- quartz $\lambda = 10.5$ W/m/K
- metal $\lambda = 100$ W/m/K
- polystyrene $\lambda = 0.16$ W/m/K
- polyethylene $\lambda = 0.35$ W/m/K

- Thermal conductivity in ordered, semi-crystalline polymers (●) is larger as compared with disordered, amorphous polymers (○)

- The conduction is via phonons, which means that the conductivity will be higher the higher the degree of crystallinity.
- Minor change of thermal conductivity at $T_g$ because the packing density of the segments is basically unchanged
• With increasing temperature the packing density of the segments is reduced and the thermal conductivity $\lambda$ decreases

**Low temperature behavior:**
Again deviations from the simple behavior of crystals

![Graph showing thermal conductivity variation](image)

Scaled thermal conductivity data of several glasses (from top to bottom): PB, PMMA, PET, B$_2$O$_3$, PS, SiO$_2$, with theory calculation


*theory of disordered solids based on the model assumption of randomly fluctuating transverse elastic constants:* The plateau in the temperature variation of the thermal conductivity $\kappa(T)$ and the behavior beyond the plateau is shown to arise from the enhanced scattering in the boson peak regime and to be essentially a harmonic phenomenon.

![Graph showing calculated thermal conductivity](image)

Calculated thermal conductivity $\kappa(T)$ using the same $D(\omega)$ as in the insert. The bottom curves correspond to $\gamma_\mu = 0.1664$

7.5 Thermodynamic Transitions and Relaxations

1. phase transition of first order:
   ------ melting of a crystal with defects
   - - - - melting of a perfect, infinite crystal

2. phase transition of second order:
   ------ transition dominated by intermolecular cooperative phenomena
   - - - - transition having only intermolecular cooperative phenomena

G. glass transition:
   ------ real experiment
   - - - - ideal, infinite slow experiment

7.6 Glass Transition
exists not only for polymers but also for low molecular weight glass formers

Glass transition is no thermodynamic equilibrium state, transition from an
ergodic to a non-ergodic state

An ergodic state of a system is an equilibrium state that the system has had
sufficient time to explore and represents a global minimum in energy.

State of the glass will depend strongly on the cooling rate: depend on the
local order and on density variations

polydisperse colloidal system
Kawasaki et al. PRL 99, 215701 (2007)
Experimentally probed glass transition temperatures depend on the cooling rate $dT/dt$.

Examples:
- Polybutadiene: $T_g = -109°C$
- Poly(n-buthylacrylate): $T_g = -43°C$
- Poly(n-buthylmethacrylate): $T_g = 35°C$
- Polystyrene: $T_g = 104°C$
- Polyamide-61: $T_g = 130°C$

The glass transition is characterized by the freezing of relaxations on mesoscopic time scales:
- If $T<T_g$, the system is quenched in a history-dependent non-equilibrium state, relaxations on the pico-second time scale, on longer time scales the system is rigid and non-ergodic.
- If $T=T_g$, relaxations are possible on long time scales with $t>>1$ sec, but on mesoscopic time scales $10^{-12} \rightarrow 1$ sec system is non-ergodic.
- If $T=T_c>T_g+30K$, no plateau, system is ergodic.

**Mode Coupling Theory (MCT) of the Glass Transition:**

Time dependence of a density correlator $\Phi(t)$ for different temperatures: how does the polymer react on an initial density fluctuation as a function of time.


One observable in particular, namely density fluctuations:

Specific time correlation function $C(t) = \langle A(t)A(0) \rangle$

Left: time evolution of the instantaneous fluctuations of the quantity $A$. The product of fluctuations separated by time $t'$, averaged over all $t_0s$, gives the correlation function $C(t')$, at equilibrium. Right: fluctuations of the density on length scale $L \sim 2\pi/k$; if $k$ is small, the area of density fluctuations is large.


Calculate density correlation function $F(k,t)$

$F(K,t=0)=S(k)$ the static structure factor of the liquid.
Left: radial distribution function $g(r)$ for a simple liquid of size $\sigma$. Right: the corresponding structure factor $S(k)$. A sample structure is also depicted where the solvation shells are indicated by the dotted lines. The exclusion radius can be seen in the absence of amplitude of $g(r)$ for $r<<\sigma$.


Left: Correlation function $F(k, t)$ exhibiting exponential $e^{-t/\tau}$ decay for a normal liquid. Right: supercooled liquids do not have such a simple decay but various temporal regimes. Notice the logarithmic scale.


Left: Density correlator $\Phi(t)$ decay in the ergodic (supercooled) case. The correlation vanishes on a finite timescale. Right: in the non-ergodic (glassy) case, that same function remains finite even for infinite times.

1) free movement \( t \rightarrow 0 \) ballistic
2) plateau: cage effect, atoms vibrate
3) \( \beta \)-relaxation: cages move as well for \( T < T_c \)
4) \( \alpha \)-relaxation: diffusion, hopping, \( T > T_c \)
5) long-range diffusion

**Applications of MCT:**

a) A colloid-polymer mixture is simulated in order to study gelation. The phase diagram of the system is studied and the gel transition is analysed using the formalism of Mode Coupling Theory (MCT). Gelation can be interpreted as a regular non-ergodic transition, similar to the glass transition in simple liquids or hard-spheres. The comparison with MCT yields qualitative agreement with the theoretical predictions.

b) Predicting the glass-transition temperature of polymers using lattice MC

The above graph shows the time evolution of the configuration at several temperatures — \( T \) decreases from left to right. In the four snapshots of the system (corresponding to the four squares of the graph) the black beads are part of an unrelaxed domain and the green beads did relax.