Lecture 7: 10.03.05 Thermal Properties of Materials; Fundamental Equations

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Reading: Engel and Reid 3.1, 3.5

Supplementary Reading: -

ANNOUNCEMENTS
Last time

- We discussed the heat stored and released at first-order phase transitions. This applies to many transformations in materials. ...even complex materials like proteins:

**Solid (folded) –liquid (unfolded) phase transition in lysozyme**

Figure by MIT OCW.

![Graph of Enthalpy vs Temperature](#)

Figure by MIT OCW.
Thermal Expansion/contraction and mechanical expansion/compression

Two classes of solid materials with different thermal behavior

- Crystalline
  - E.g., most metals, ceramics, ionic solids, semi-crystalline polymers
  - Translational periodicity
  - Long-range order

- Amorphous
  - Glass
  - Disordered
  - Can also include metals, polymers, ceramics
  - Short-range order

Thermal expansion

- Materials tend to expand in volume as temperature is increased—generally, increasing temperature causes a loosening of intramolecular bonds. Why does volume expansion accompany a temperature increase?

ADD HEAT

ASSYMMETRIC POTENTIAL

INTERATOMIC DISTANCE

THermal Properties/fundamental equations

10/3/05
To quantify such changes, the thermal expansion coefficient ($\alpha$) is defined as:

\[
\alpha = \frac{1}{V} \left( \frac{\delta V}{\delta T} \right)
\]

- It is the fractional change in volume with temperature at constant pressure. (Note that in some texts, the symbol $\beta$ is used instead of $\alpha$ for the thermal volumetric expansion coefficient - but it has the same definition). $\alpha$ is proportional to the slope of a plot of volume vs. temperature for a material.²

**Figure by MIT OCW.**

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The specific volume $v$ (cm$^3$ g$^{-1}$) of polyethylene versus temperature $T$. The thermal expansion coefficient $\alpha$ is proportional to the slope $dV/dT$. At low temperature, polyethylene is a hard crystalline plastic material. On melting at around 130 °C, the specific volume $v$ increases sharply and $\alpha$ is large.

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As shown above, both volume and $\alpha$ typically depend on the phase of the material: solids have lower volume and $\alpha$ than liquids. At a first-order phase transition, there is a discontinuity in the volume of the material.
What will happen if we have a disordered (amorphous or glassy) material that becomes liquid? In contrast to the melting of crystalline solids, there is no volume discontinuity on heating an amorphous solid. There is however, a break in the slope of the volume vs. temperature:

The two general cooling paths by which an assembly of atoms can condense into the solid state. Route 1 is the path to the crystalline state; Route 2 is the rapid-quench path to the amorphous solid state.

Volume-versus-temperature cooling curves for an organic material in the neighborhood of the glass transition. \( V(T) \) is shown for two greatly different cooling rates, as is the coefficient of thermal expansion \( \alpha(T) \) is shown for the fast-cooling curve (0.02 hr). The break in \( V(T) \), and the corresponding step in \( \alpha(T) \), signal the occurrence of the liquid-glass transition.
Kinetic effects in the glass transition

- Importantly, the characteristics of first-order thermodynamic phase transitions like melting hold for systems in equilibrium and thus, questions of the rate of changes do not come into discussion. However, the glass transition is famous for exhibiting significant kinetic effects:

  - The possibility of ultraslow cooling giving rise to a glass with lower entropy than the crystalline form of a material is known as the Kauzmann paradox, after the researcher who's work raised many questions about kinetic effects in the glass transition. One solution to the Kauzmann paradox would be a true underlying thermodynamic glass transition temperature $T_{g0}$, which occurs to prevent the entropy of glasses from falling below that of crystals.

Compressibility

- Increasing temperature usually leads to expansion of materials, but increasing pressure tends to compress materials. The isothermal compressibility ($\kappa$), is used to quantify the response of materials to compressive pressures:

  \[
  \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T
  \]

- The compressibility is thus the fractional decrease in volume that occurs with pressure at constant temperature. $\kappa$ can be extracted from measurements of the volume as a function of pressure.

Figure by MIT OCW.

Thermal expansion coefficients $\alpha$ measured at atmospheric pressure of water (---), benzene (--), n-pentane (- - - - - -), and diethylether (--.--).

Compressibilities $\kappa$ measured at atmospheric pressure for water (---), benzene (---), n-pentane (- - - - - -), and diethylether (--.--).
Calculations using thermal expansion and compressibility: Example of calculating the pressure of a confined sample

Recall ideal gas: \( P = \frac{nRT}{V} \)

If \( n \) is fixed: \( P = P(T,V) \)

\[ dP(T,V) = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \]

State function.

Cyclic rule:

\[ \frac{\partial P}{\partial T} \left( \frac{\partial V}{\partial V} \right)_P \left( \frac{\partial V}{\partial T} \right)_P = -1 \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = -\frac{1}{kV} \]

\[ \left( \frac{\partial P}{\partial V} \right)_T = \frac{k}{V} \]

\[ \frac{1}{kV} = -kV \]

\[ dP = \frac{\alpha}{k} dT - \frac{1}{kV} dV \]

\[ \Delta P = \int_{T_i}^{T_f} \frac{\alpha}{k} dT - \int_{V_i}^{V_f} \frac{1}{kV} dV \]
Heat capacity and thermal expansion

- Why should \( dq/dT \) at constant pressure differ from \( dq/dT \) at constant volume? When materials are heated at constant pressure, thermal expansion changes the response of the material to added heat.

Temperature variation of \( \text{Cp} \) and \( \text{Cv} \) of \( \frac{1}{2} \text{ mol of NaCl} \).

- \( \text{Cp} \) contains the effect of thermal expansion:

\[
\text{Cv} = \text{Cp} - T \alpha \frac{\partial^2 V}{\partial T^2}
\]

- \( V_{\text{sp}} \) is the specific volume (cm\(^3\)/g) of the material. Thus, from 3 measurable quantities- \( \text{Cp}, \alpha, \) and \( \kappa \), we can indirectly arrive at the constant volume heat capacity. The difference \( \text{Cp} - \text{Cv} \) is zero at zero K, but increases as \( T \) goes up. Knowledge of \( \text{Cv} \) as a function of temperature is useful for the calculation of internal energy changes in a system. However, thermal expansion makes the practical measurement of \( \text{Cv} \) extremely challenging- enormous pressures are required to prevent a material from expanding over even small temperature increases. Thus, in practice, one usually determines \( \text{Cp} \) and uses the connection between \( \text{Cp} \) and \( \text{Cv} \) to calculate \( \text{Cv} \) indirectly.
A Graphical Summary of Thermal Behavior

- Let’s summarize everything we’ve learned so far about the variation of thermodynamic properties with temperature:

- We will see later in the term that the ‘upward trend’ of entropies with increasing temperature is an easily-proven thermodynamic requirement for stability in a system.
Thermodynamic driving forces: Writing a fundamental equation

What goes into internal energy?

- When we introduced the concept of work, we stated that every form of work can be thought of as a generalized thermodynamic force acting to create some generalized 'displacement' in the system. In a similar way, we said that temperature can be thought of as a thermodynamic force that causes a 'thermal displacement' which is the change in entropy of the system:

- The internal energy, which sums the contributions from these two terms, can be written as a perfect differential depending on $S$ and $V$:

The 'natural' variables of state functions

- Why do we write $U = U(S, V)$? Why not $U = U(T, V)$? The answer will unfortunately not be clear until we introduce the second law. The second law dictates that certain thermodynamic functions will reach extrema (maxima or minima) when the system is at equilibrium—e.g., the entropy will be maximized at equilibrium. When $U$ and $S$ are written as a function of $S, V$ and $U, V$ respectively, they are said to be written in terms of their natural variables. State functions of natural variables have extremum principles at equilibrium (they will be maximized or minimized at equilibrium). In other words, the reason we write $U$ as a function of $S$ and $V$ is that it is the most useful form to write internal energy equations for most problems—we can use this equation for internal energy to calculate equilibrium properties.

Generalized expression for the internal energy: internal energy of open systems

- The first law expression above only applies to very simple thermodynamic systems—which have can undergo only hydrostatic work and have no transport or chemical transformation of components. Extending our first law expression is straightforward for any thermodynamic case where other forms of work are important. It is useful to think of the differential as a sum of different forms of internal energy:
• Let’s first look at the case of describing an open system:

• To understand what goes into $U$, we can write an expression for the differential $dU$:

• We have already mentioned that we are generally most interested in changes in $U$ for making thermodynamic calculations—thus we will find the above differential equation very useful. In fact, this is often referred to as the **fundamental equation for a simple isolated system.**
References