

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

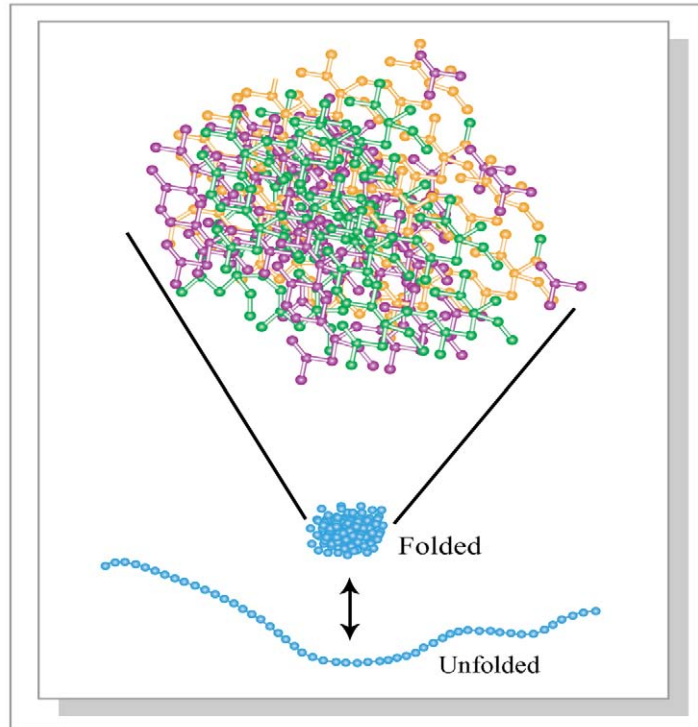


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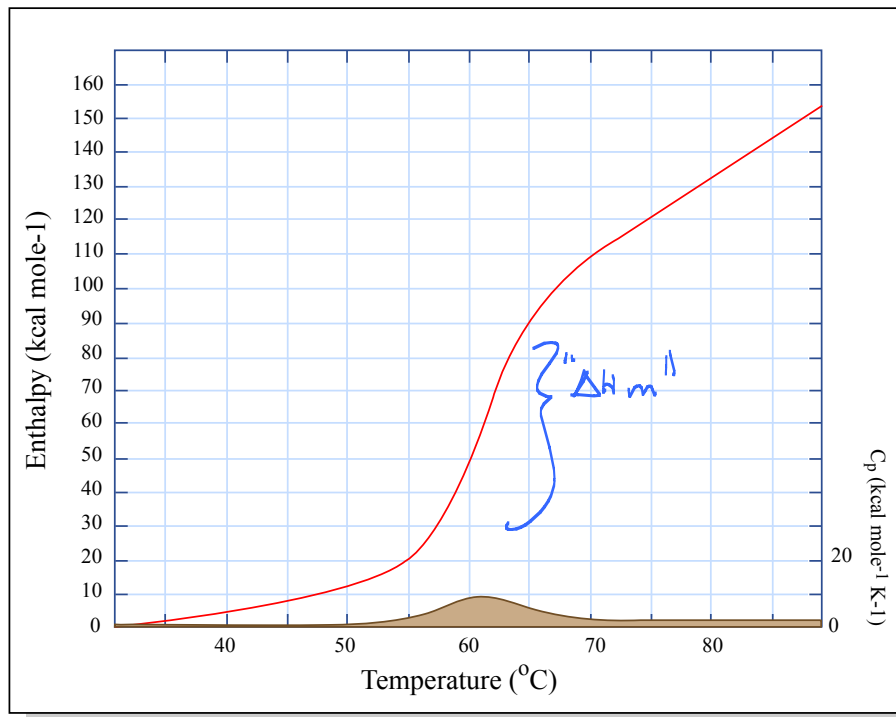
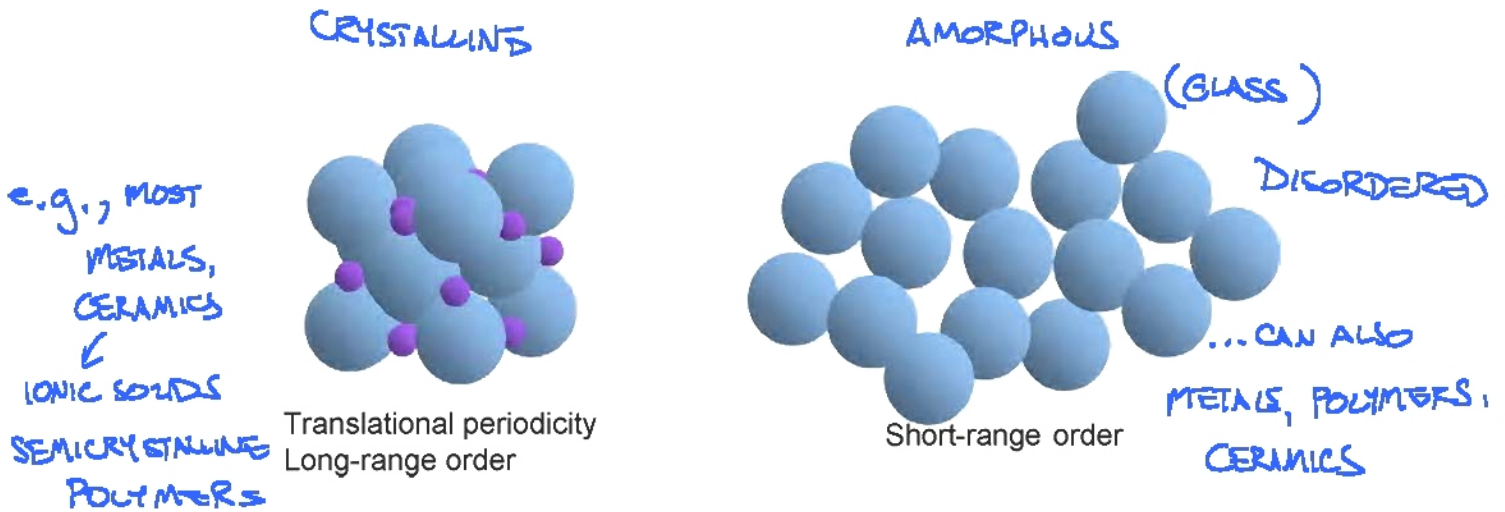


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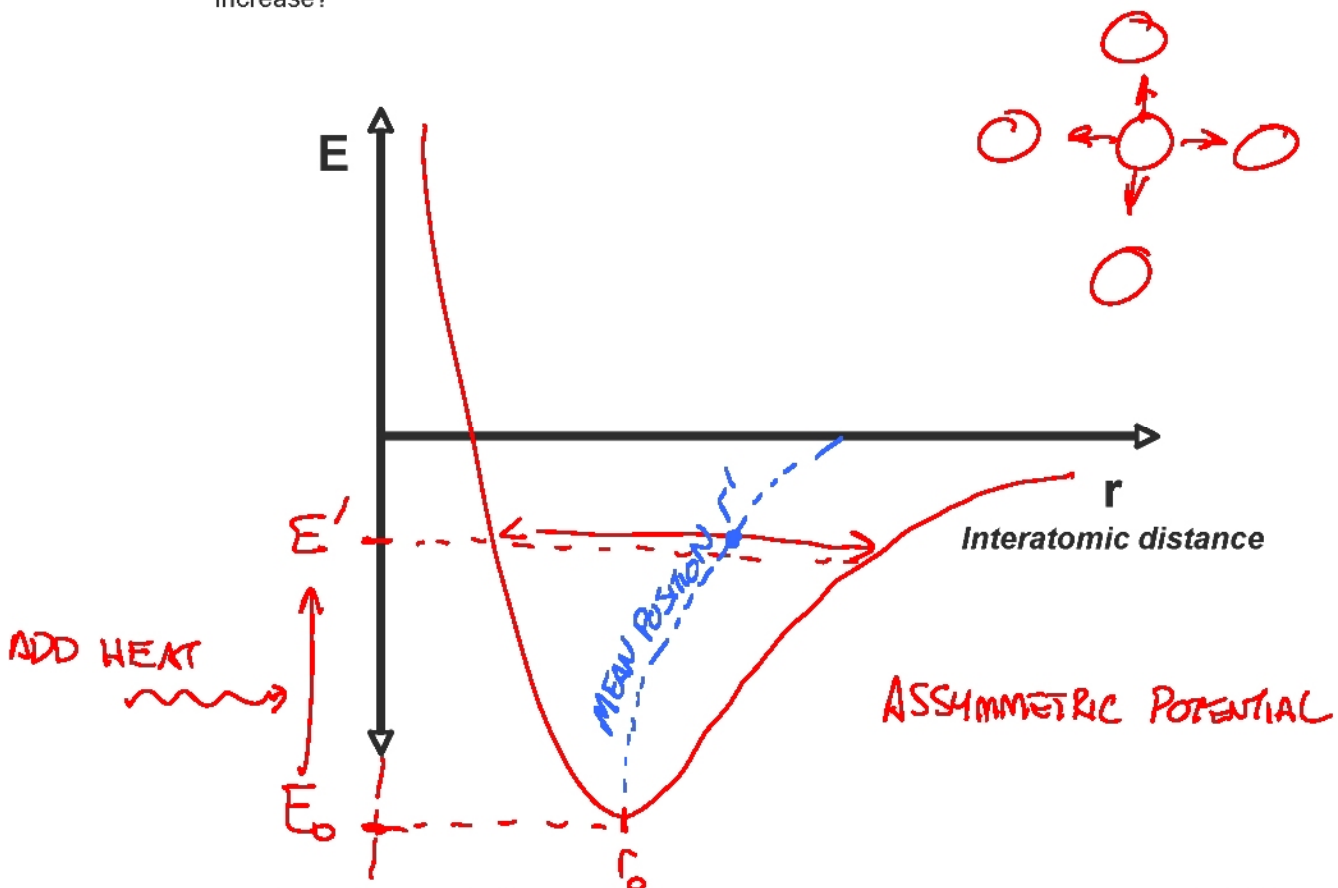
Thermal Expansion/contraction and mechanical expansion/compression

Two classes of solid materials with different thermal behavior



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?

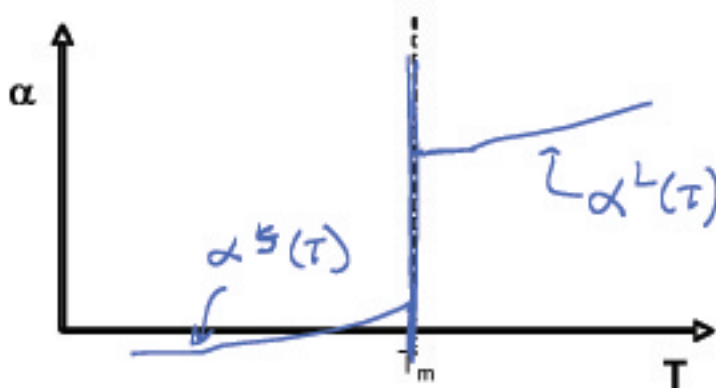
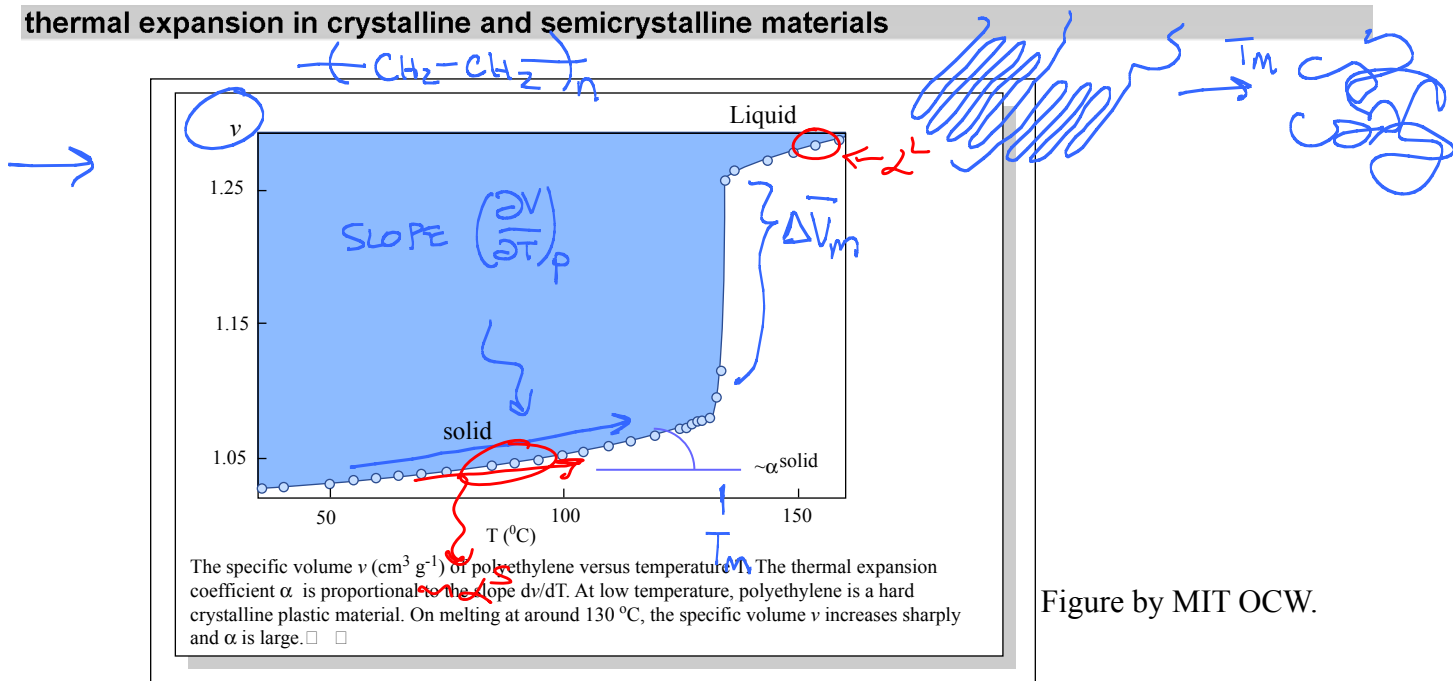


- To quantify such changes, the thermal expansion coefficient (α) is defined as:

VOLUMETRIC THERMAL EXPANSION COEFFICIENT $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

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

thermal expansion in crystalline and semicrystalline materials



- As shown above, both volume and α typically depend on the phase of the material: solids have lower volume and α than liquids. At a first-order phase transition, there is a discontinuity in the volume of the material.

Thermal expansion in noncrystalline (amorphous) materials: The glass transition³

- 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:

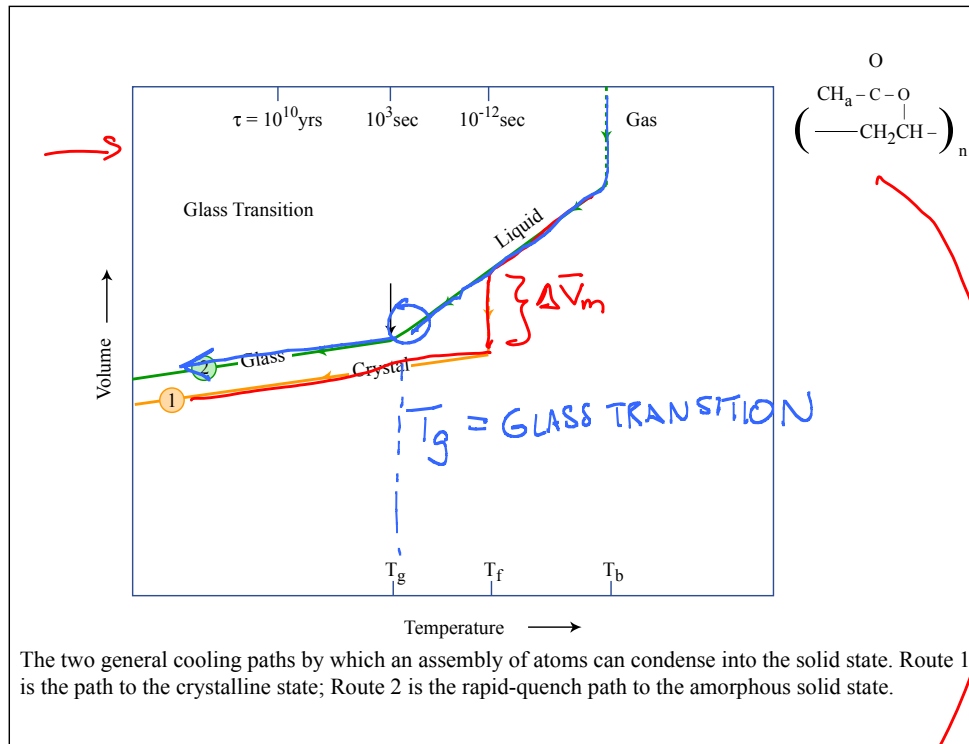


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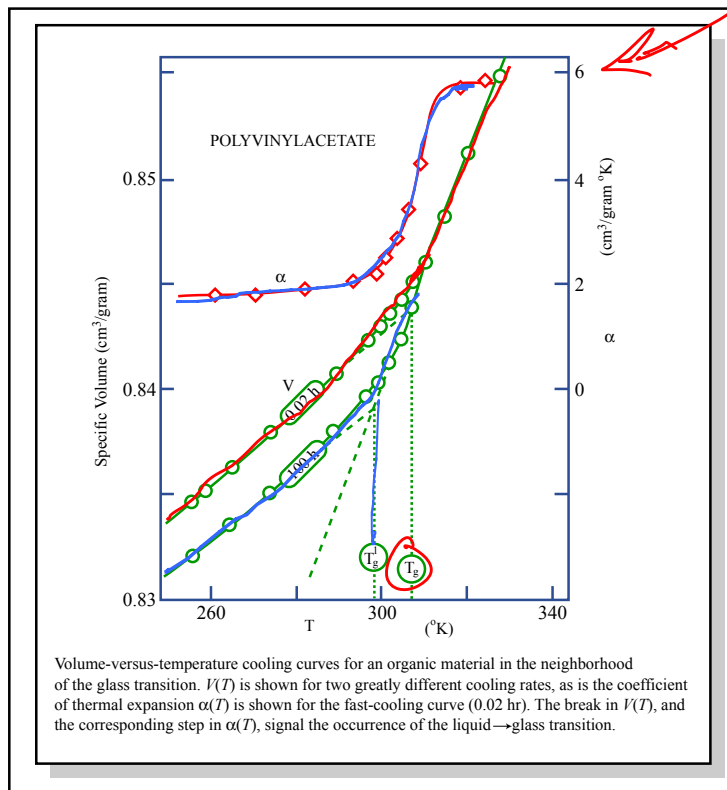
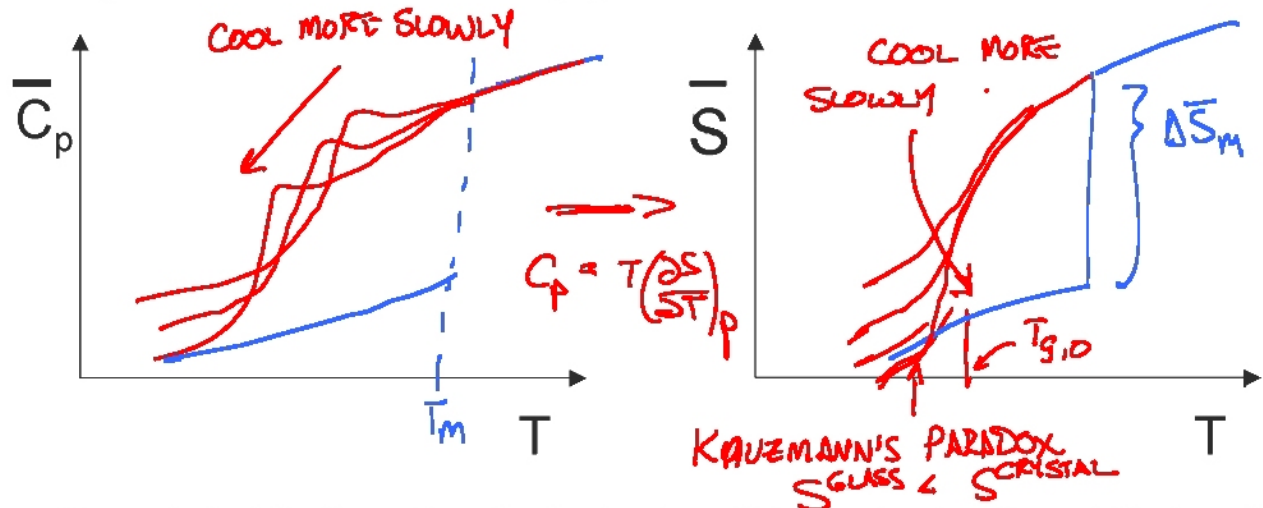


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Kinetic effects in the glass transition

- 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 $T_{g,0}$, which occurs to prevent the entropy of glasses from falling below that of crystals.

Compressibility

PRESSURE EFFECTS

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

ISOTHERMAL
COMPRESSIBILITY

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

- The compressibility is thus the fractional decrease in volume that occurs with pressure at constant temperature. κ can be extracted from measurements of the volume as a function of pressure:²

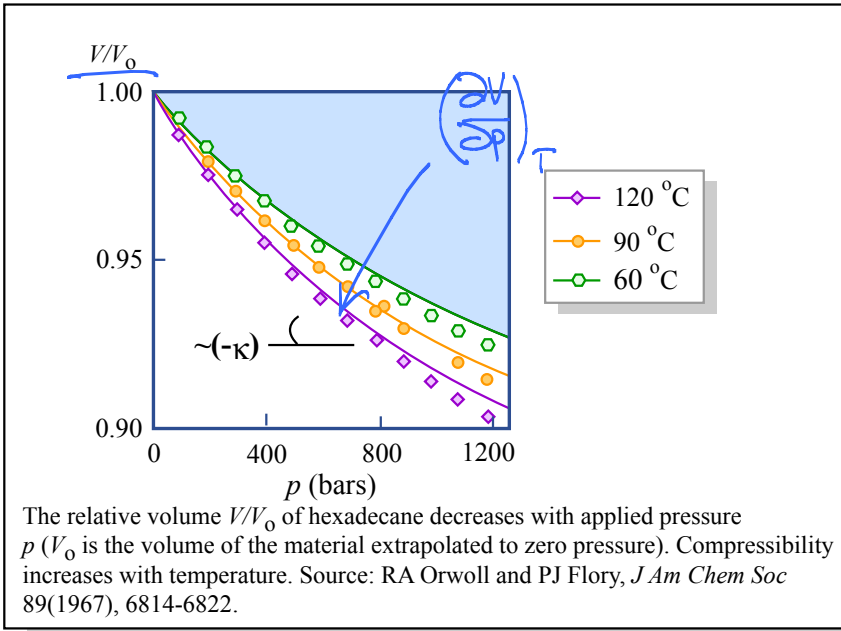


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WEAK, OMNIDIRECTIONAL
VAN DER WAALS
BONDING

n-pentane

water

RIGID, STRONG

DIRECTIONAL

H-BONDS

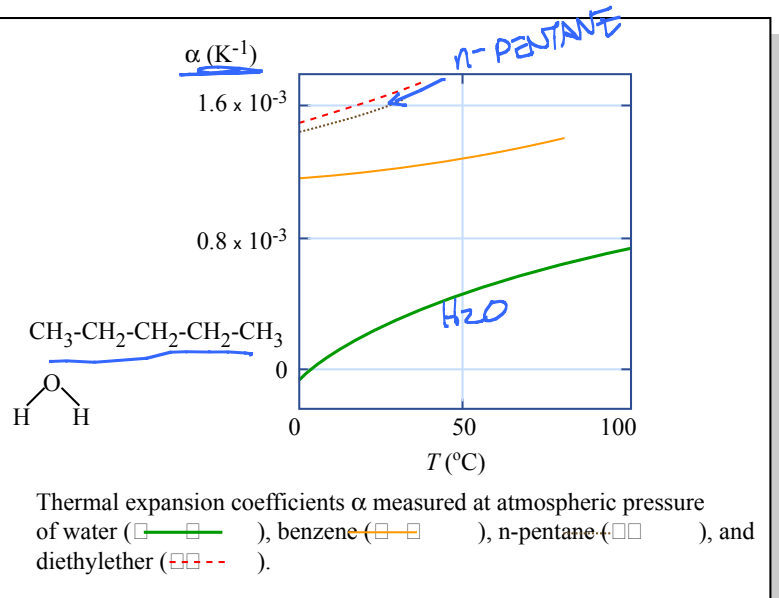


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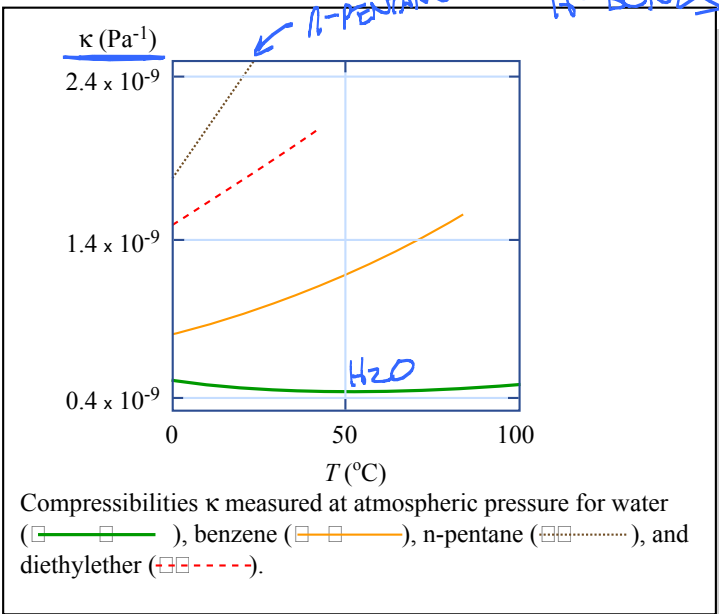
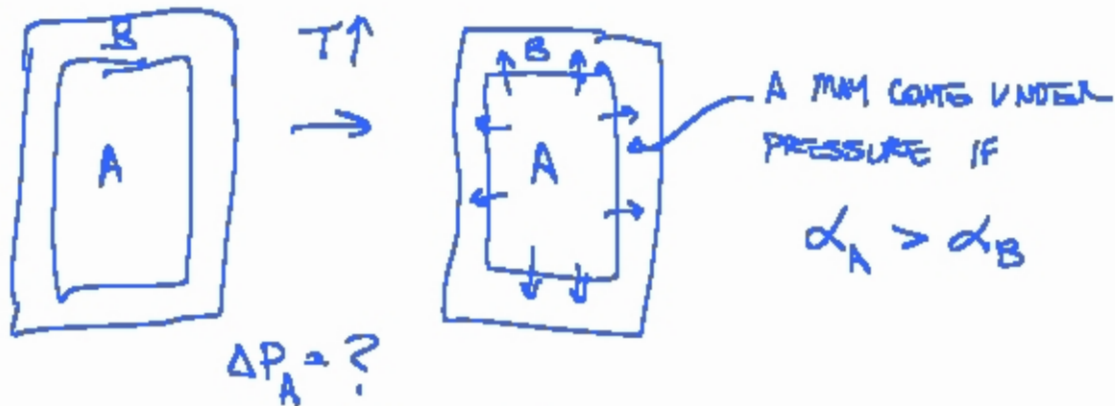


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Calculations using thermal expansion and compressibility: Example of calculating the pressure of a confined sample



RECALL IDEAL GAS: $P = \frac{nRT}{V}$ IF n IS FIXED: $P = P(T, V)$
 ↓ STATE FUNCTION!

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

STATE FUNCT.

CYCLIC RULE: $\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = -1$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T} = \frac{\alpha}{\kappa}$$

$\frac{1}{\alpha V}$ $-KV$

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{1}{KV}$$

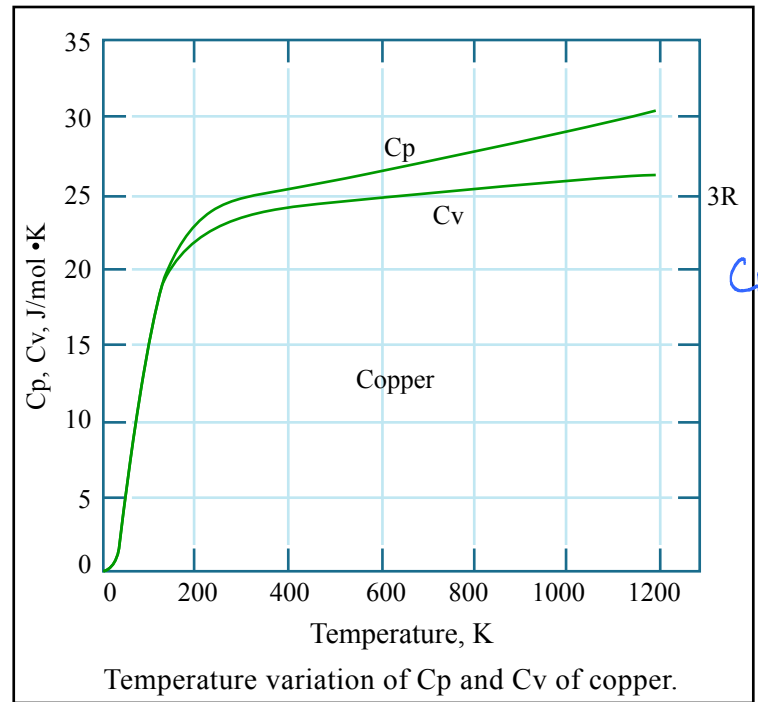
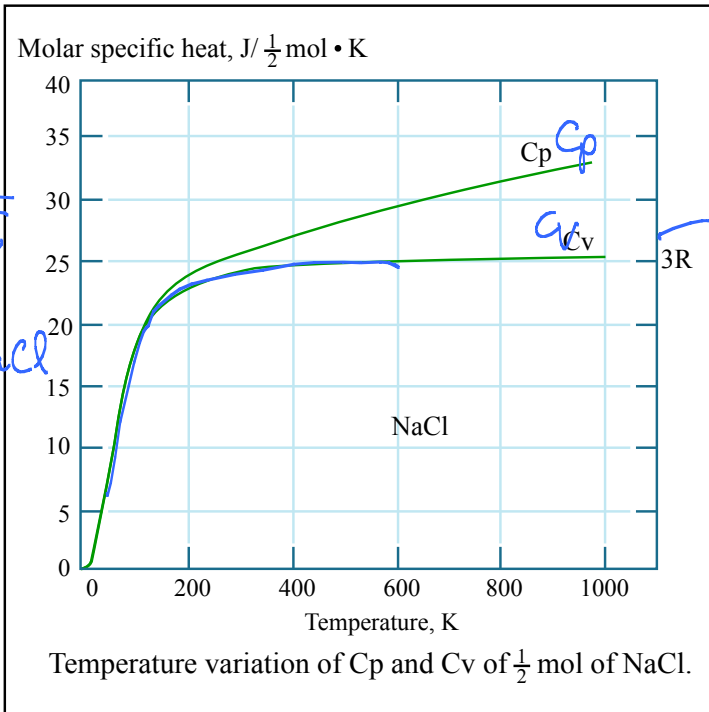
CALCULATE PRESSURE CHANGES FOR A CONFINED SAMPLE:

$$\Delta P = \int_{T_i}^{T_f} \frac{\alpha}{\kappa} dT - \int_{V_i}^{V_f} \frac{1}{KV} dV$$

$$dP = \frac{\alpha}{\kappa} dT - \frac{1}{KV} dV$$

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.



- C_p contains the effect of thermal expansion:

$$C_v \implies \Delta U \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

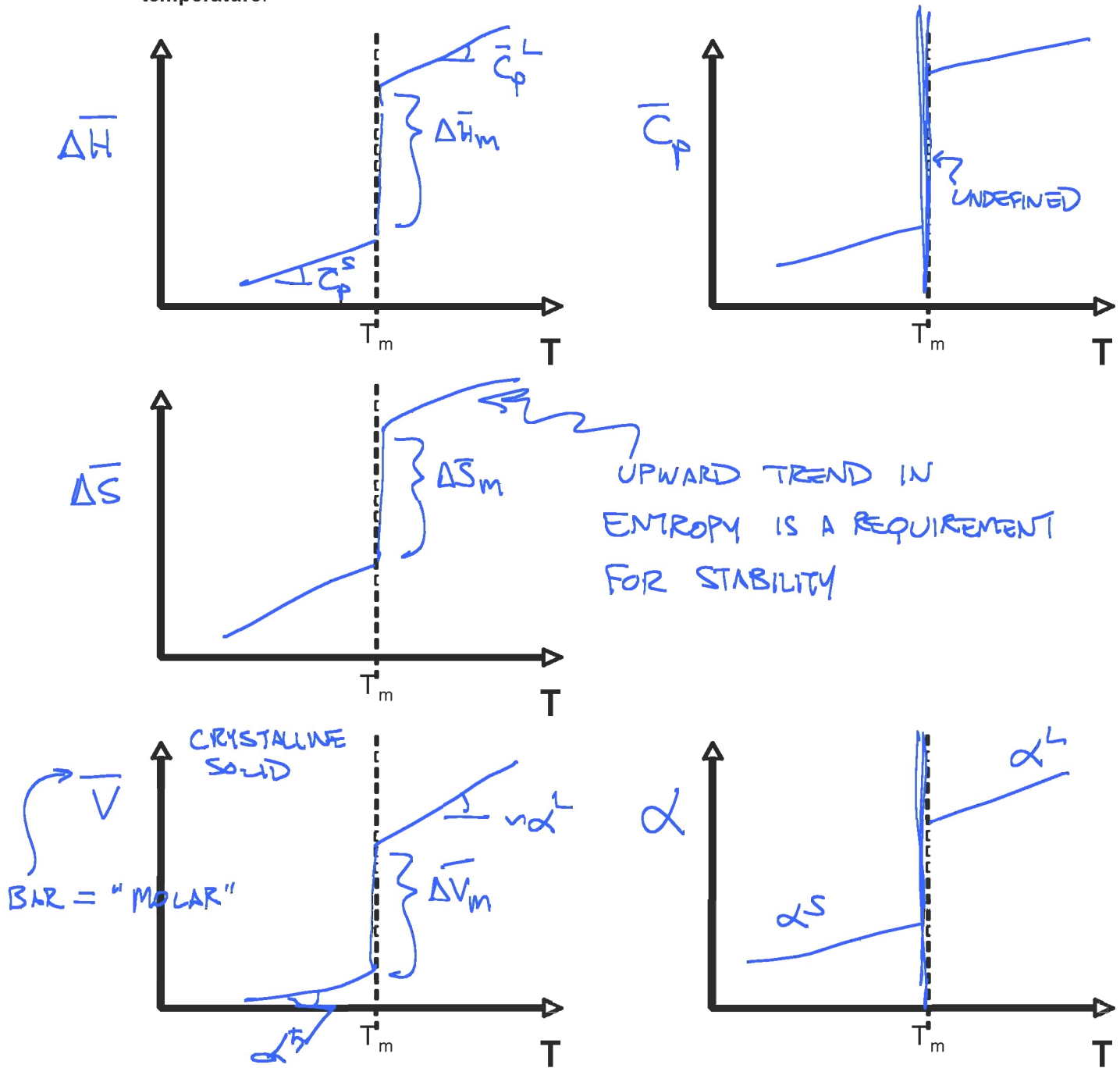
$$C_p - C_v = -T \underbrace{\left(\frac{\partial V}{\partial T}\right)_P^2}_{(\alpha V)} \underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{-K_V}$$

$$C_v = C_p - \frac{T \alpha^2 V}{\kappa}$$

- V_{sp} is the specific volume (cm^3/g) of the material. Thus, from 3 measurable quantities- C_p , α , and κ , we can indirectly arrive at the constant volume heat capacity. The difference $C_p - C_v$ is zero at zero K, but increases as T goes up. Knowledge of C_v 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 C_v extremely challenging- enormous pressures are required to prevent a material from expanding over even small temperature increases. Thus, in practice, one usually determines C_p and uses the connection between C_p and C_v to calculate C_v 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 (maximima or minima) when the system is at equilibrium- e.g. the entropy will be maximized at equilibrium. When U and S are written as 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:

References

1. Blaber, M. (1999).
2. Dill, K. & Bromberg, S. *Molecular Driving Forces* (New York, 2002).
3. Zallen, R. *The Physics of Amorphous Solids* (John Wiley & Sons, New York, 1983).
4. Zemansky, M. W. & Dittman, R. H. *Heat and Thermodynamics* (McGraw-Hill, New York, 1997).