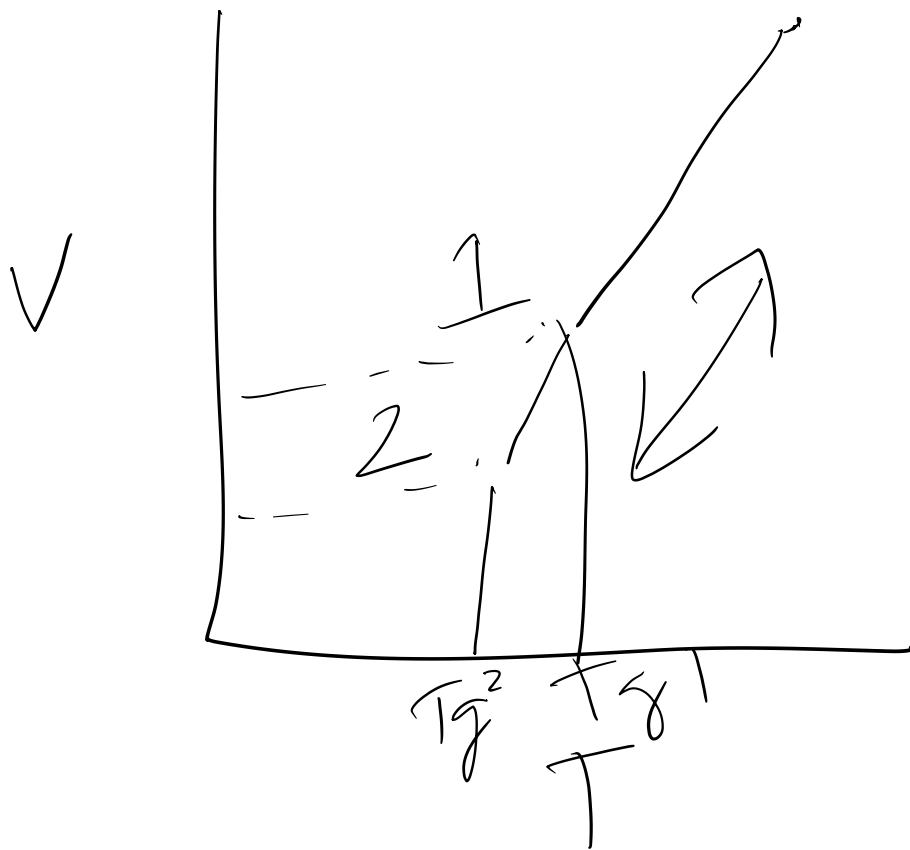


TXL211

Lecture 9



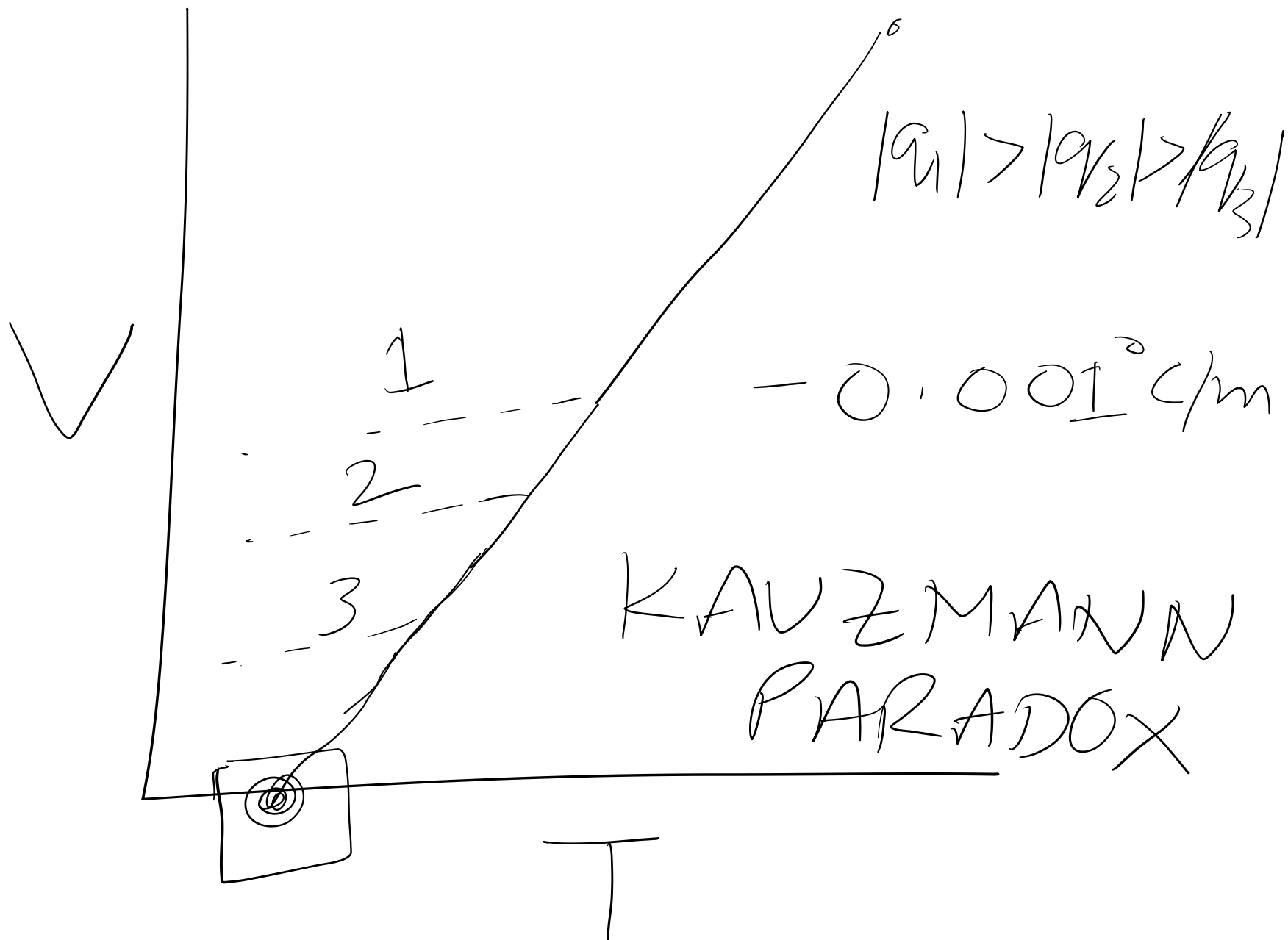
$$|q_1| > |q_2|$$

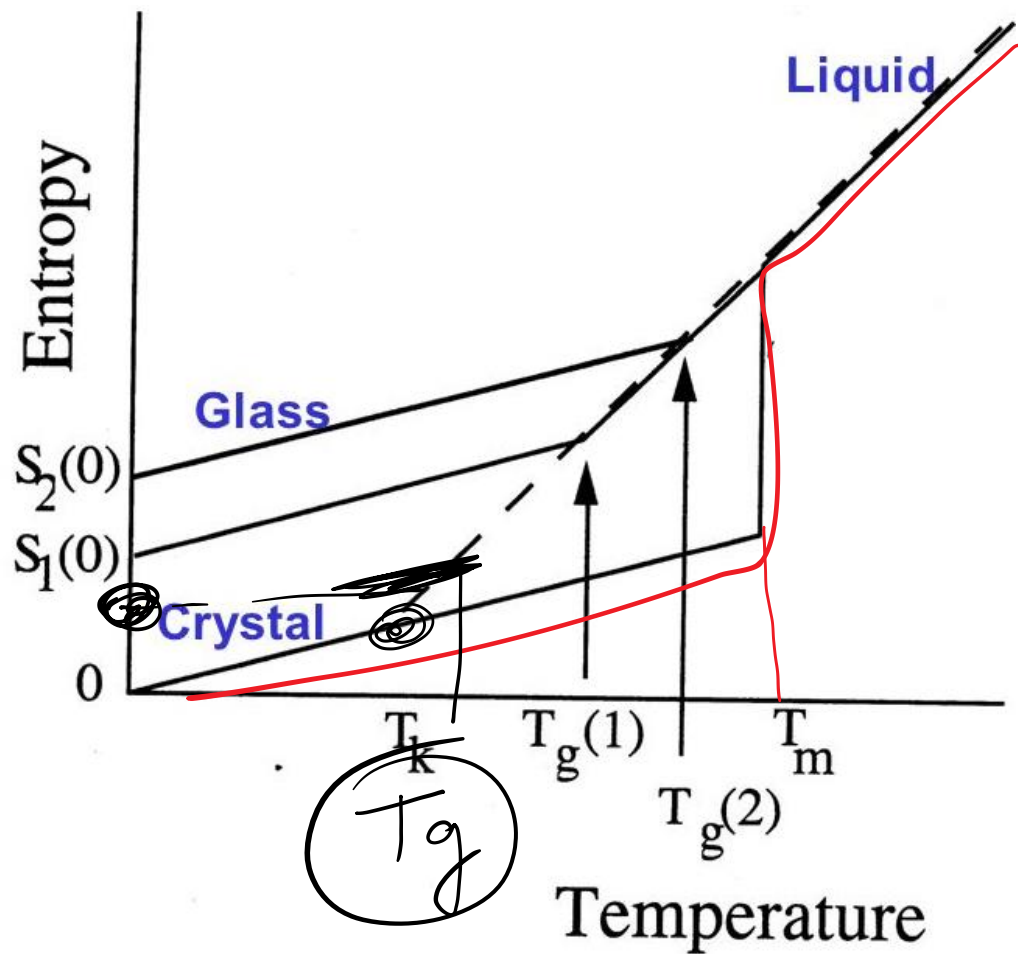
WLF

$a_T$

$C_1$

$C_2$





THERMODYNAMIC THEORY

$$\Rightarrow S_{total} = \cancel{S_{rot}}^{\circ} + S_{vib}$$

The **thermodynamic** theory was formulated by Gibbs and DiMarzio (1958) who argued that, although the observed glass transition is a kinetic phenomenon, the underlying true transition can possess equilibrium properties. The thermodynamic theory attempted to explain the Kauzmann paradox, which can be stated as follows. If the equilibrium properties of a material, entropy ( $S$ ) and volume ( $V$ ), are extrapolated through the glass transition, the values of  $S$  and  $V$  for the glass will be lower than for the corresponding crystals. The equilibrium theory resolves the problem by predicting a thermodynamic glass transition reached when the conformational entropy takes the value zero

SVIB

# Thermodynamic Theory

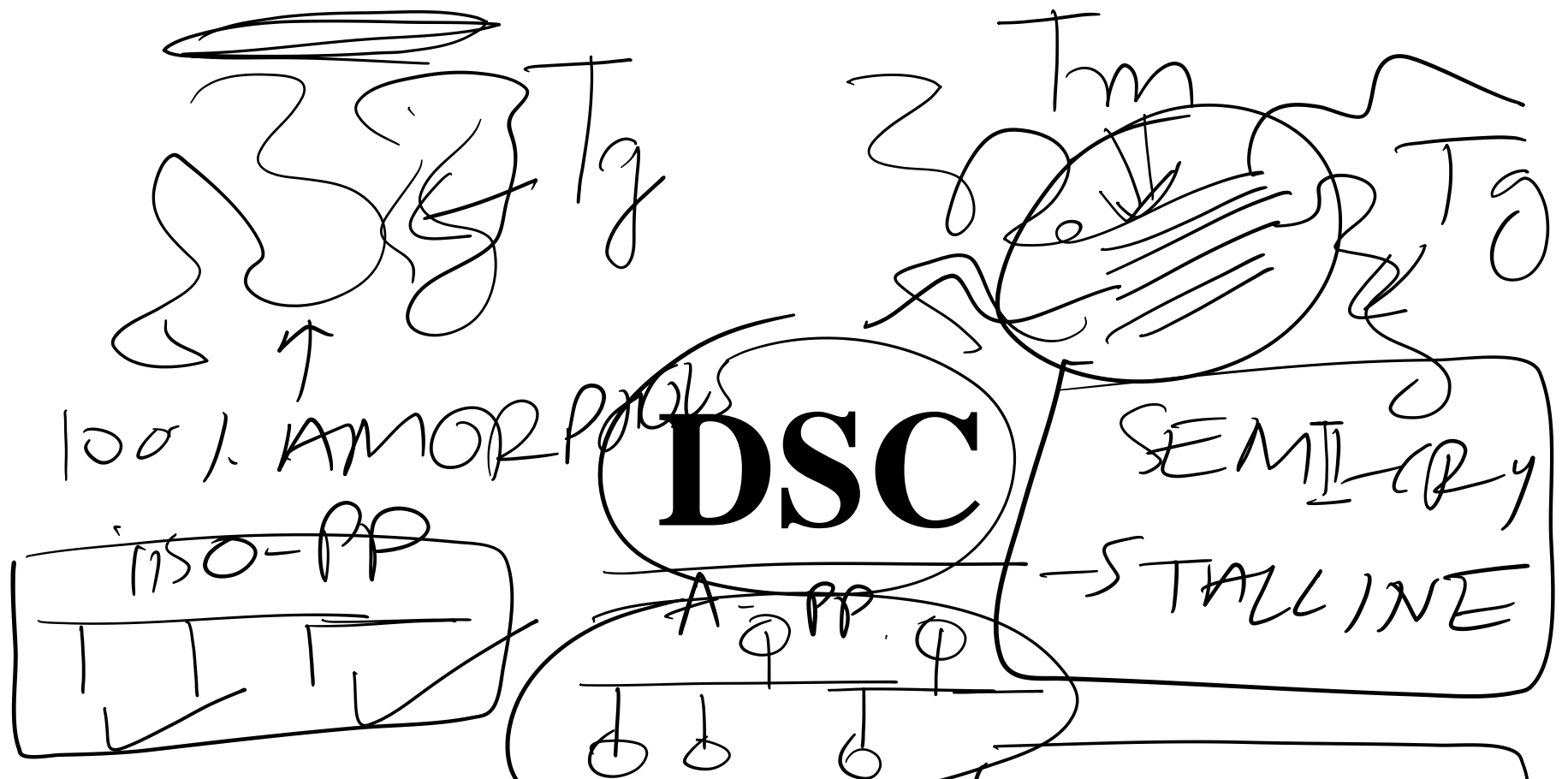
**What about infinite time allotted to establish  
a quiet equilibrium?**

**The Gibbs and DiMarzio Theory: In infinitely slow experiments a glassy phase will eventually emerge whose entropy is negligibly higher than that of crystal.**

# Summary of the Theories

MOL WT, X LINK, BRANCHING

- Free-Volume theory provides relationships between coefficients of expansion below and above  $T_g$  and yields equations relating viscoelastic motion to the variables of time and temp.
- The kinetic theory defines  $T_g$  as the temp. at which the relaxation time for the segmental motions in the main polymer chain is of the same order of magnitude as the time scale of experiment.
- The thermodynamic theory introduce the notion of equilibrium and the requirements for a true second-order transition.

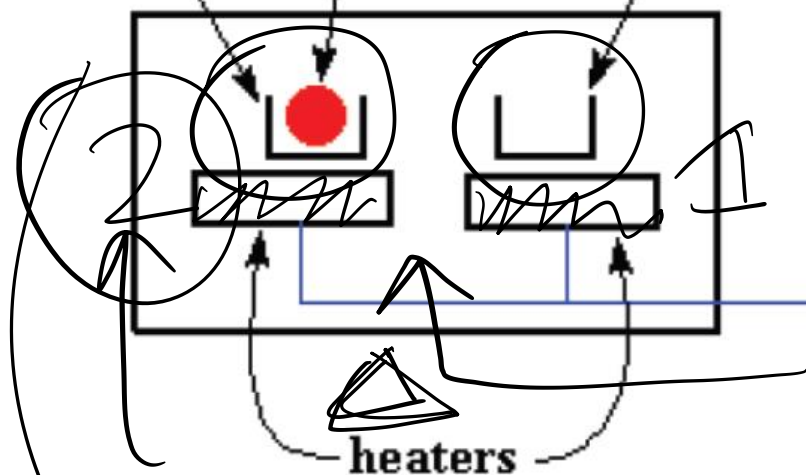


## Differential Scanning Calorimetry

- MOL WT. / PDI
- CHAIN REGULARITY
- ~~SEMI~~ INTER-CHAIN INTERACTIONS



sample pan      polymer sample      reference pan



10°C/min.

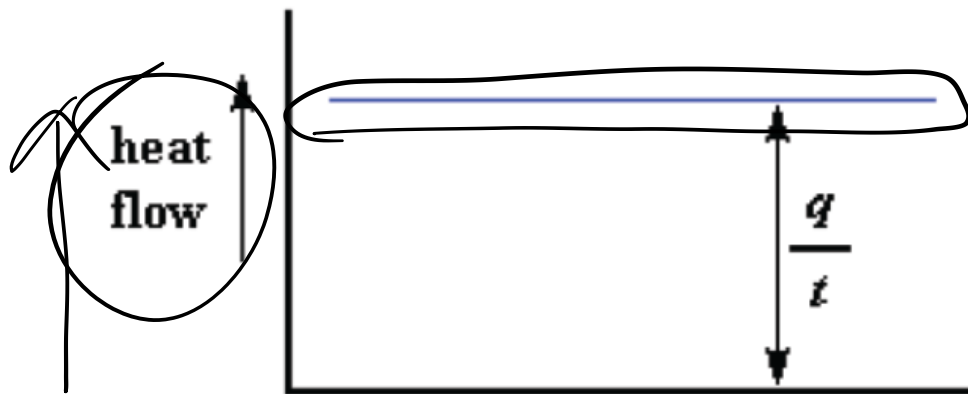
computer to monitor temperature  
and regulate heat flow





HEAT FLOW

$$= \frac{q}{t} = \frac{\text{heat}}{\text{time}}$$

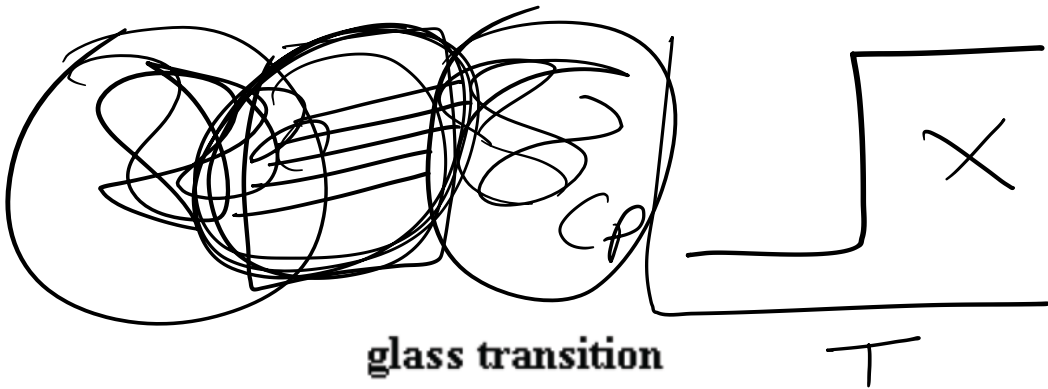


HEATING RATE

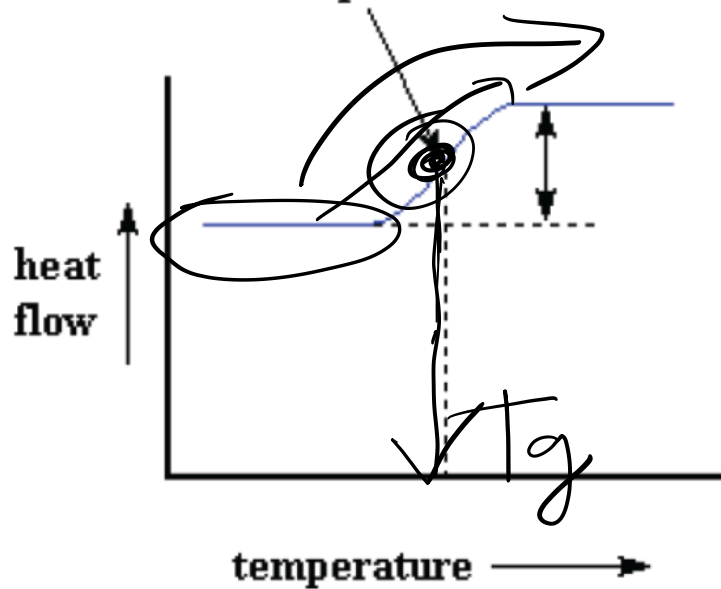
temperature →

$$\frac{q/t}{\Delta T/t} = \frac{q}{\Delta T} = C_p$$

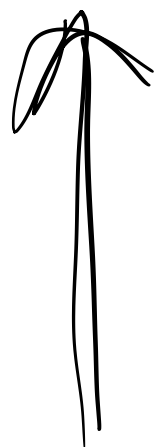
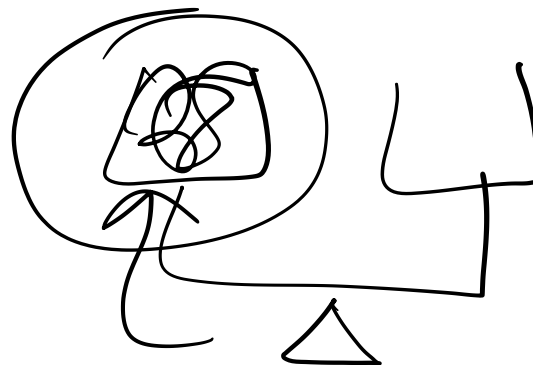
↗



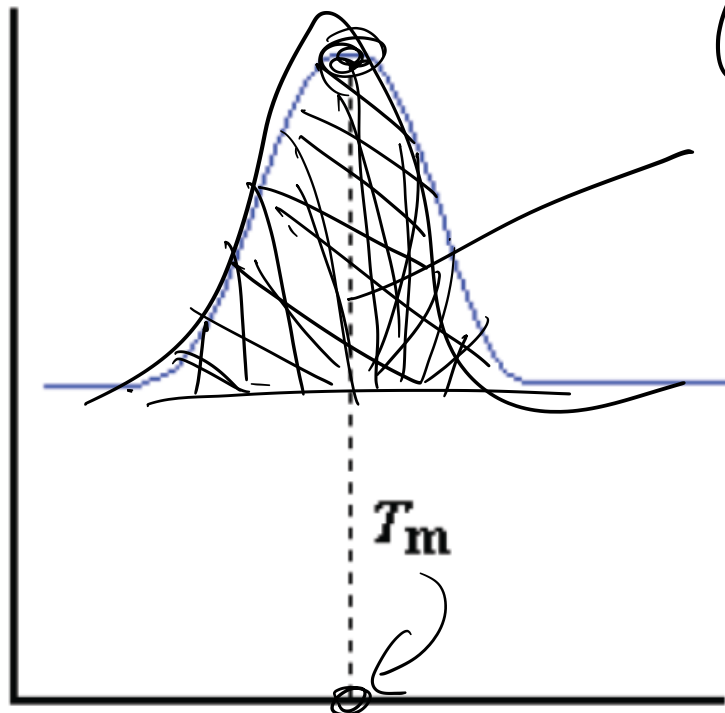
glass transition  
temperature



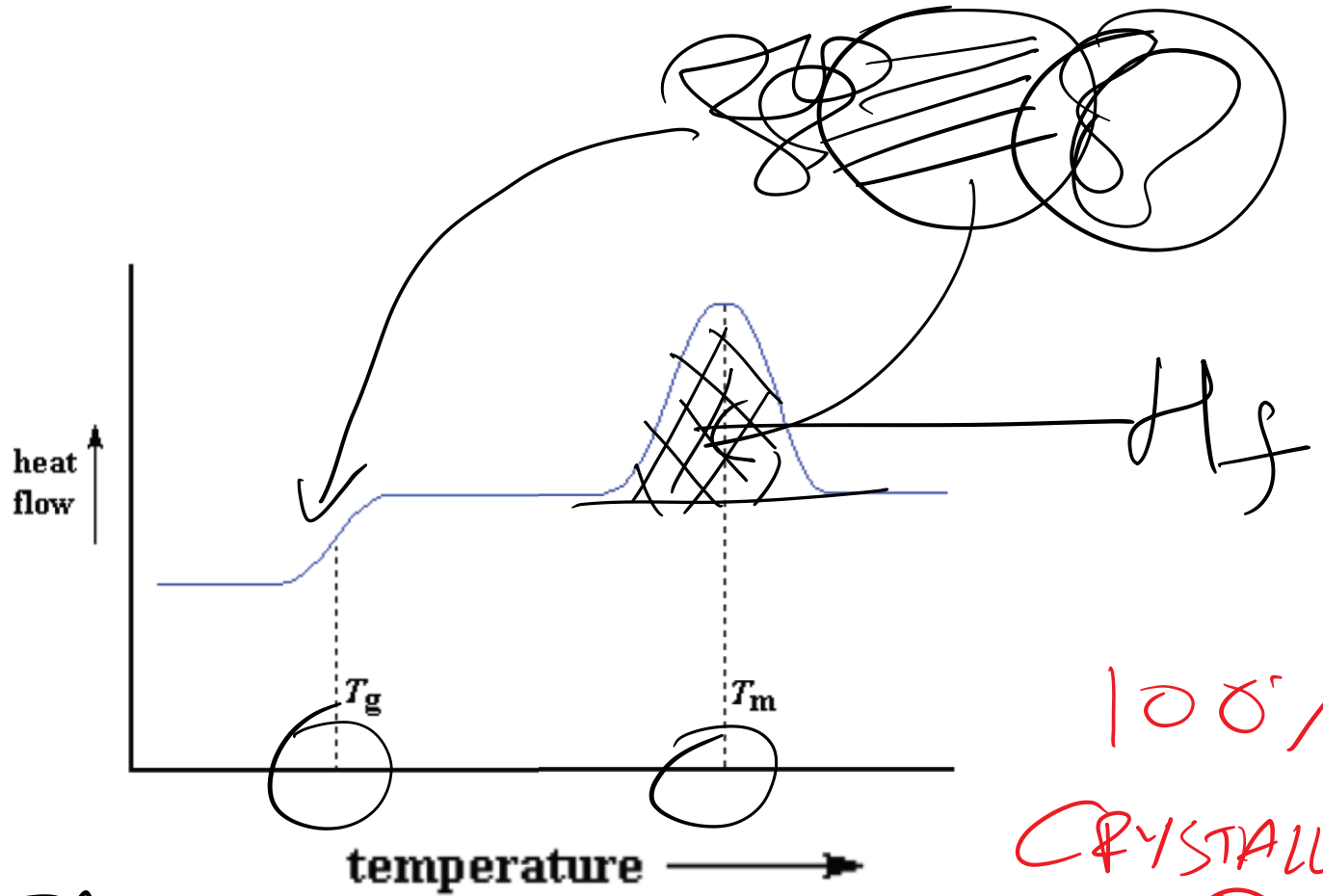
LIQUID  
SOLID



heat  
flow



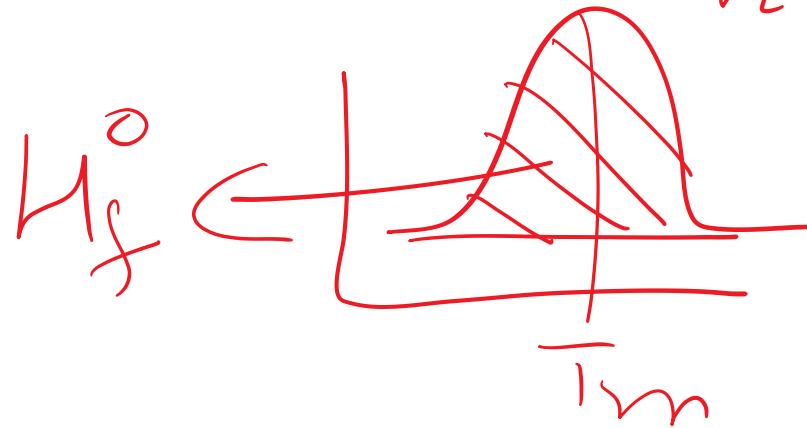
temperature

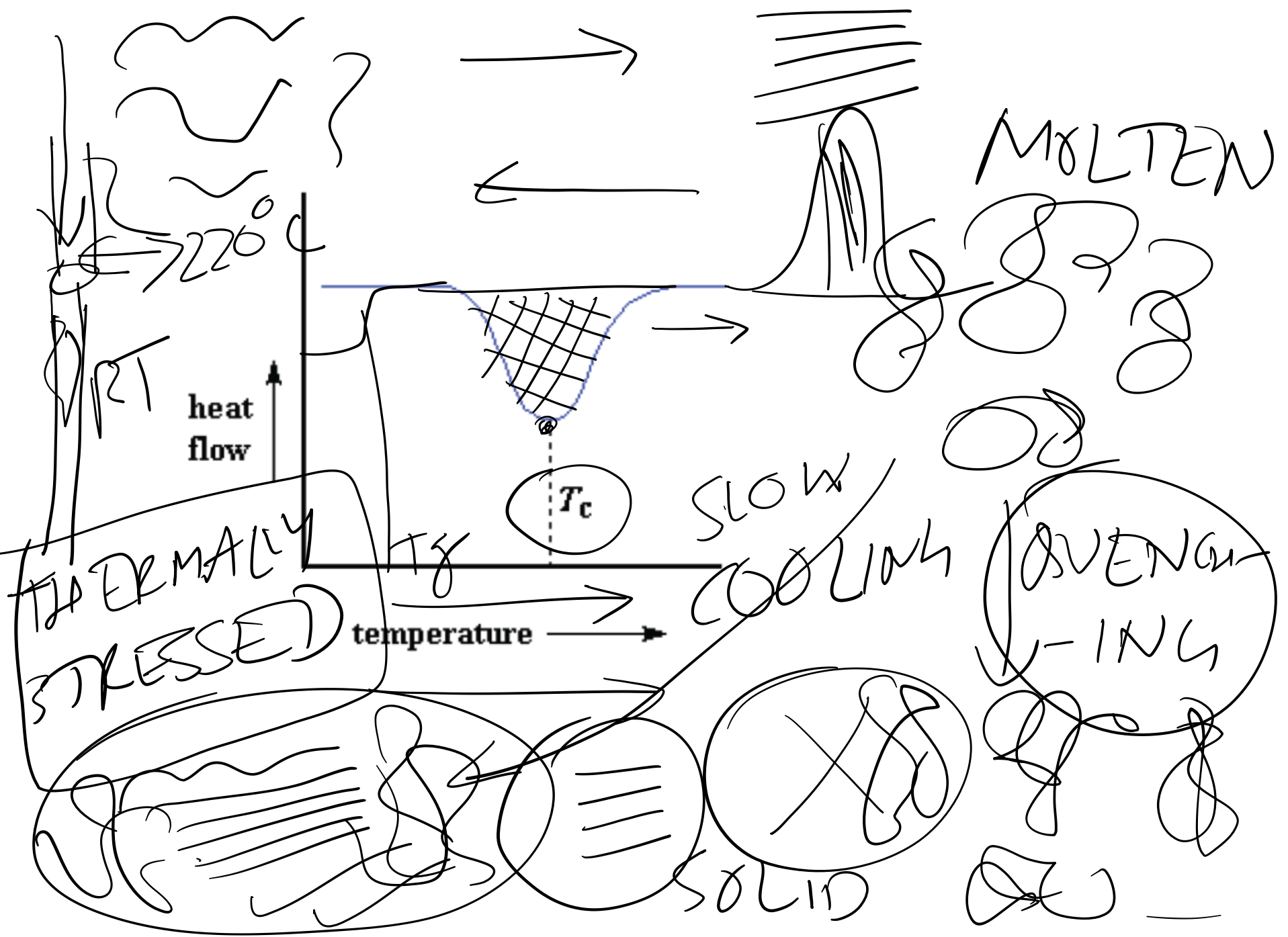


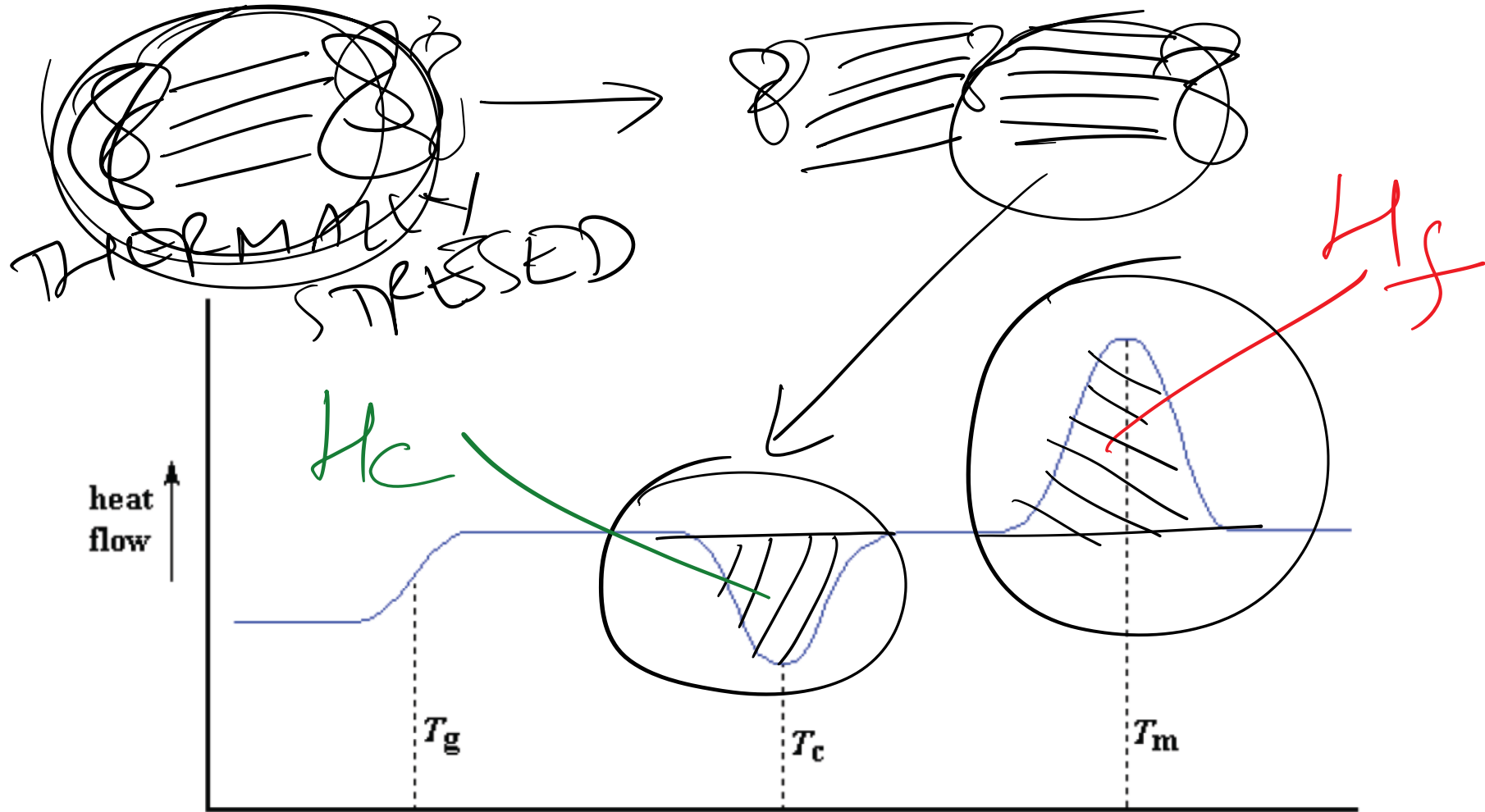
% CRYSTALLINITY

$$= \frac{H_f}{H_f^0} \times 100$$

100%  
CRYSTALLINE



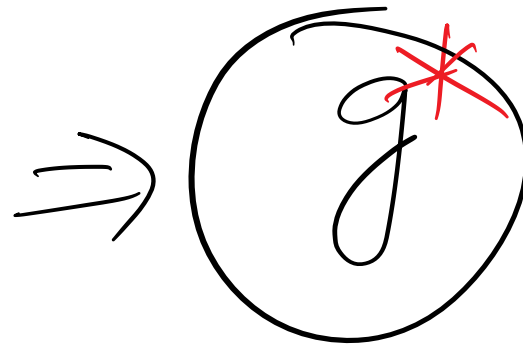




$$H_c < H_f$$

$$H_f - H_c = \Delta H$$

$$\frac{H'}{H_m^*} \quad J \quad J/g$$



IN THE  
THERMALLY  
STRESSED  
SAMPLE

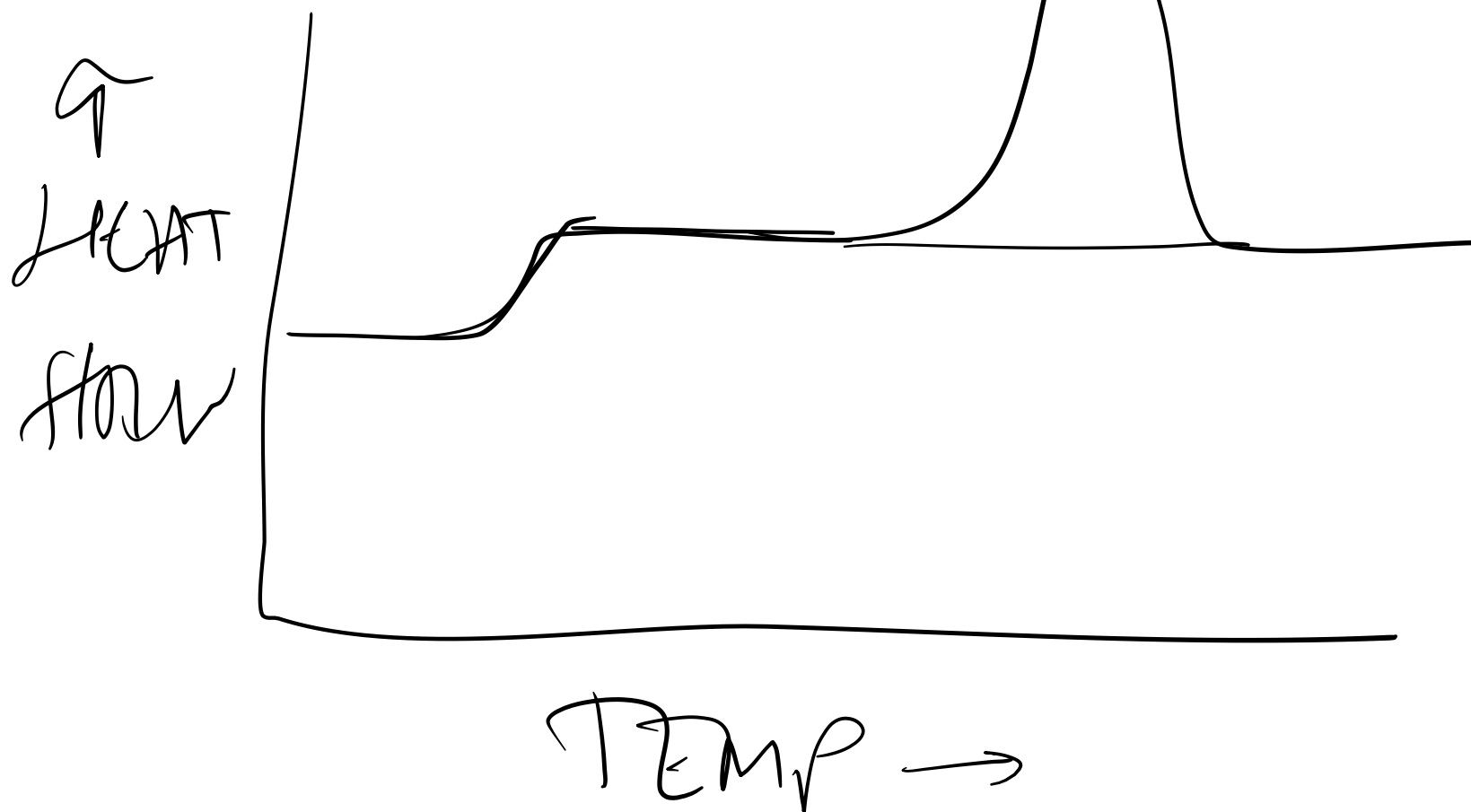
→ SPECIFIC HEAT OF

MELTING

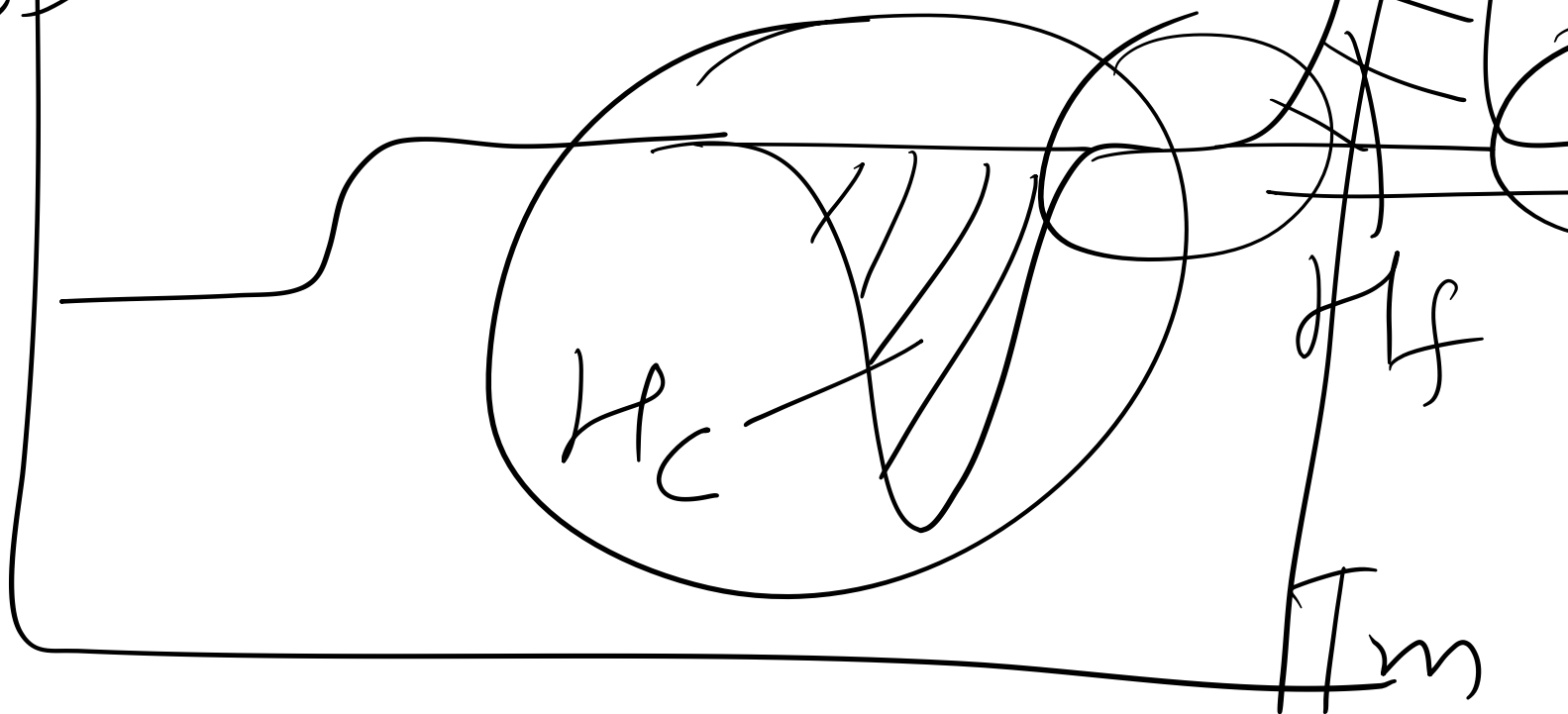
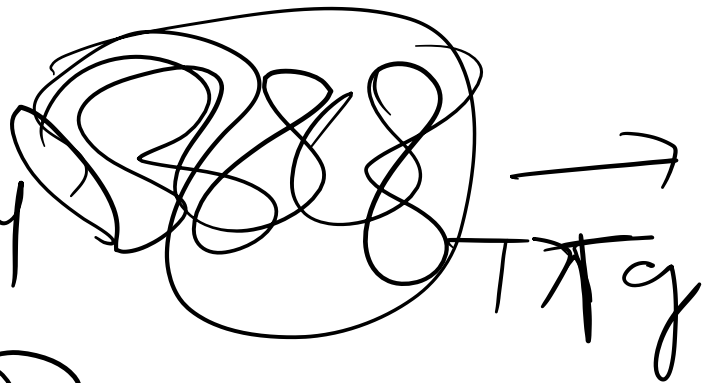
$$\frac{g^*}{g_{total}}$$

ORIGINAL  
CRYSTALLINE  
= CONTENT





100%  
THERMALLY  
STRESSED



$$H_c = H_f$$

