

LAB UNIT 4: Force Modulation Microscopy

Specific Assignment: Thermomechanical Viscoelastic Response Study

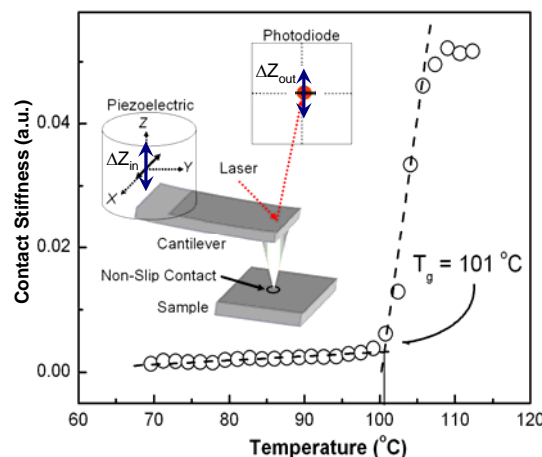
Objective This lab unit introduces a scanning force microscopy (SFM) based mechanical (sinusoidal) perturbation method referred to as force modulation microscopy, to explore thermomechanical properties in polymers around the glass transition.

Outcome Learn about the basic principles of contact mechanics and polymer viscoelasticity, and conduct force modulation studies as a function of temperature below and above the polymer glass transition.

Synopsis Force modulation microscopy provides surface sensitive local information about nano-mechanical properties, such as material stiffness (moduli), hardness, elastic-plastic yield points, and viscosity. As SFM based methods operate with nanoscale probing areas, perturbation-induced material activation into metastable configurations can be to a great part avoided, which makes force modulation microscopy very sensitive to “true” (equilibrated) material properties. This is illustrated with this project utilizing with small amplitude normal modulations at a variety of temperatures around the glass transition of poly-t-butylacrylate and polystyrene thin films.



Force Modulation Spectroscopy applied to Local Glass Transition at Polymer Surface



Materials Poly-t-butylacrylate spin-coated film (> 100 nm) on silicon substrates.

Technique SFM force modulation microscopy

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1. Assignment

The assignment is to locally investigate the nano-thermomechanical properties of thin film polymers utilizing normal force modulation microscopy, and to employ the theories and background information to discuss the experimental results. The steps are outlined here:

1. Familiarize yourself with the background information provided in Section 4.
2. Test your background knowledge with the provided Quiz in Section 2.
3. Conduct the force modulation experiments in Section 3. Follow the experimental step-by-step procedure.
4. Analyze your data as described in Section 3
5. Finally, provide a report with the following information:
 - (i) Result section: In this section you show your data and discuss instrumental details (i.e., limitations) and the quality of your data (error analysis).
 - (ii) Discussion section: In this section you discuss and analyze your data in the light of the provided background information.
It is also appropriate to discuss section (i) and (ii) together.
 - (iii) Summary and outlook: Here you summarize your findings and provide an outlook on how one could proceed.

The report is evaluated based on the quality of the discussion and the integration of your experimental data and the provided theory. You are encouraged to discuss results that are unexpected. It is important to include discussions on the causes for discrepancies and inconsistencies in the data.

2. Quiz – Preparation for the Experiment

Theoretical Questions

- (1) (3pts) Determine the contact area for a JKR contact at which the contact becomes unstable.
- (2) (3pts) Describe the two terms *solid-like* and *liquid-like* using the two simple models of Hooke's law of elasticity and Newton's law of viscosity.
- (3) (3pts) List methods that are used to determine the glass transition temperature. What property are they actually sensitive to?
- (4) (3pts) At the glass transition temperature, the response signal of SM-FM that is proportional to the contact stiffness is increasing noticeably. Considering that the modulus for many polymers decreases by orders of magnitude from the glassy state to the rubbery state (e.g., in the case of polystyrene PS by about 4 orders of magnitude from 10^9 N/m^2 to 10^5 N/m^2), the probing contact area of SM-FM has to increase substantially to compensate for the reduction in the material stiffness. This is based on the Hertzian relationship between the contact stiffness and the modulus, i.e., $k_c = 2aE$ (for normal distortion), or $k_c = 8aG$ (for lateral distortion). Evaluate with the Hertzian model, the relative degree of contact area increase for polystyrene.
- (5) (3pts) Glass transition and Gibbs free energy.
 - (a) Show in a V(T) diagram the distinct difference between melt/freezing transition and a glass transition
 - (b) How are changes related to the specific heat and volume obtained from Gibbs free energy.

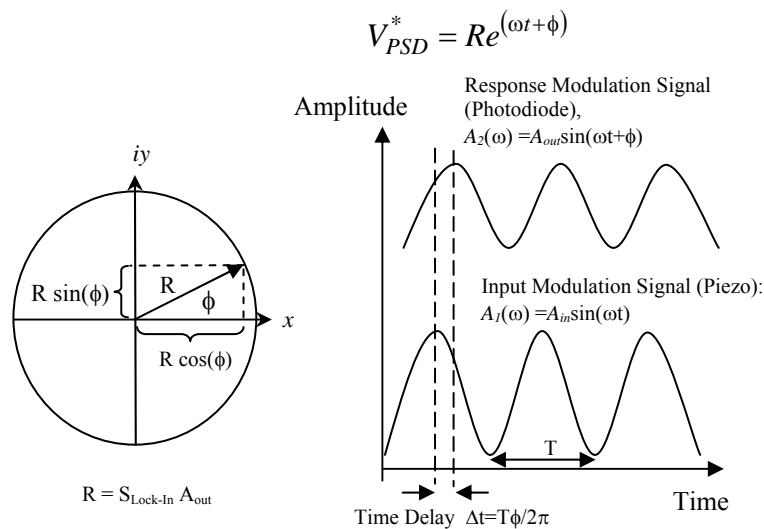
Prelab Quiz

- (1) (10 pts) For a sinusoidal FM microscopy experiments, the input modulation amplitude A_{in} and the output signal amplitude A_{out} shall be known in volts that are applied to the piezo (PZ) and received from the photo diode (PD), respectively. The conversion sensitivity factors S_{PZ} and S_{PD} are used to convert the two signals into nanometer.
 - (a) Determine formally the root mean square (RMS) amplitudes in nanometer.
 - (b) With the appropriate RMS amplitudes determine the force that is acting on a cantilever with spring constant k_L .
 - (c) Assuming an ideal spring model as depicted in Figure 3, what is the force acting on the sample?
 - (d) Provide an expression for the sample deformation δ as function of A_{in} and A_{out} .
 - (e) Express the contact stiffness as function of δ , A_{in} , A_{out} and k_L .

(2) (10 pts) FM microscopy utilized a function generator with a sinusoidal input modulation to the piezo. The cantilever response modulation signal $A_{out}\sin(\omega t + \phi_{out})$ is detected with a laser detection scheme by the photodiode. Because the signals are very small, i.e., within the noise level of the signal, a lock-in technique is used. The lock-in amplifier, a phase sensitive detector (PSD), compares the photodiode signal with the input signal to the piezo, $A_{in}\sin(\omega t + \phi_{in})$, as a reference signal. Note that both signals are not only defined by their amplitude and frequency but also by their phase ϕ . The output signal of the lock-in amplifier V_{psd} is the product of two sine waves, i.e.,

$$V_{PSD} = A_{in}A_{out} \sin(\omega t + \phi_{in}) \sin(\omega t + \phi_{out})$$

This signal is composed of two AC signals, one with frequency $\omega_{in} + \omega_{out}$ and $\omega_{in} - \omega_{out}$ and is heavily low pass filtered. Consequently, as in our case, only a non-zero DC signal comes through for $\omega_{in} = \omega_{out} = \omega$. In other words the lock-in technique is frequency discriminating the signal it receives based on the reference signal. The quantities that matter are the amplitudes, and the phase shift $\phi = \phi_{out} - \phi_{in}$. As the phase of the phase signal of the input signal to the piezo is arbitrary, we will define it generally as zero, i.e., $\phi_{in} = 0$. The situation described here, is illustrated in the figure below, expressing the frequency discriminated signal V_{PSD} in complex form, i.e.,



Describe the operation of the function generator. How would you expect the phase angle to differ between solid-like and liquid-like materials?

3. Experimental Assignment

Goal

Following the step-by-step instruction below, determine the glass transition temperature of the polystyrene film. Analyze and discuss the data with the background information provided in Section 4. Provide a written report of this experiment.

Specifically provide answers to the following questions:

- (1) What is the observed glass transition temperature for poly (t-butyl acrylate)? Does this value correlate with the literature value? What factors would cause the observed T_g value to be different from the literature?
- (2) Why is Modulated Force Microscopy effective at determining the glass transition temperature?
- (3) What is the magnitude of the cantilever modulation?
- (4) What is the relationship between contact stiffness and normal load? Does this relationship depend on temperature?
- (5) What is the relationship between contact stiffness and adhesion force?

Safety

- Wear safety glasses.
- Refer to the General rules in the AFM lab.
- The heating module should be off when it is not in use.

Instrumental Setup

- Easy Scan 2 AFM system with long contact Mode SFM tip with 0.2 N/m spring constant with NO Aluminum coating.
- Heating stage with controller.
- Lock-in amplifier with two long BNC cables

Materials

- Samples: 2 pieces of $\sim 1\text{cm}^2$ Spin-coated PtBA film on silicon substrate, stored in sealed Petri dishes until ready for the experiment. The sample PtBA ($M_w = 137.3\text{k}$) is spin cast onto an organic contaminant-cleaned (possibly also oxide treated) silicon wafer and annealed above its glass transition temperature in a vacuum oven. Preferred film thicknesses are between 100 to 500 nm. Recommended pretreatments of the silicon substrate: (i) sonication, (ii) UV/ozone cleaning, and (iii) hydrofluoric acid treatment. More information is provided at the end of the experimental procedure.

Experimental Procedure

Read carefully the instructions below and follow them closely. They will provide you with information about (i) preparation of the experiment, (ii) the procedure for force modulation microscopy and temperature control, (iii) the procedure for closing the experiment, and (iv) on how to conduct the data analysis.

(i) Preparation of the experiment

- (1) System Set-up: (This part will be performed with a TA) Place BT00250 silicon sample grid on heater stage
- (2) Follow the start up procedure **step 1 – 8**, in Easy Scan 2 AFM System SOP (Standard Operational Procedure).
 - a. Place a CONTR cantilever with the spring constant of 0.2 N/ m.
- (3) Connect BNC cables:
 - a. from Function Generator *Function* output to *Excitation* Input on Nanosurf Break Out Box
 - b. from Function Generator *Function* output to Lock-In *REF IN* signal (reference)
 - c. from *Current or Deflection* Output on Nanosurf Break Out Box to Oscilloscope Signal *I*
 - d. From Oscilloscope Signal *I* to Lock-In Signal *A*

(ii) Determining Probe/Photodiode Sensitivities

- (1) Under **Positioning Window:Approach Options** uncheck **Auto. Start imaging**
- (2) Under **Positioning Window:Video Options** set **Illumination, Brightness** and **Contrast** to 0, 0 and 0 respectively
- (3) Come in to contact with the sample and scan enough lines to clearly see grid pattern
- (4) Under **Z-Controller:Z-Controller Mode** set **Z-Feedback algorithm** to **Standard PID**
- (5) Under **Z-Controller** set **Set point** to 100nN
- (6) Under **Z-Controller** set **P-Gain**, **I-Gain** and **D-Gain (PID)** to 0,0 and 0 respectively
- (7) On the oscilloscope, determine in mV the height of the grid step (corresponds to 100nm actual height)
- (8) Stop the scan
- (9) Turn on the function generator
 - a. Set frequency: Push **FREQ – 50 – Hz/V_{pp}**
 - b. Set Amplitude: Push **AMPL – 5 – Hz/V_{pp}**
- (10) On the oscilloscope measure the peak to peak height of the probe oscillation (in mV)
- (11) Repeat for multiple frequencies, filling out the following table (use result from **ii-6** to determine displacement)

Frequency (Hz)	Amplitude (mV)	Sensitivity(nm/mV)	Displacement (nm)
50			
100			
150			
200			
300			
500			
750			
1000			

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- (12) Withdraw probe and set function generator amplitude to 0
- (13) Set **Illumination, Brightness** and **Contrast** to 50, 50 and 50 respectively

(iii) Determining PtBA Glass Transition

- (1) Replace Si grid with PtBA sample
- (2) Reset **PID** gains to 10,000 , 1000 and 0 respectively
- (3) Under **Approach Options** set **Tip-Position** to 4 μ m advanced
- (4) Set **Illumination, Brightness** and **Contrast** to 0, 0 and 0 respectively
- (5) Approach sample and come into contact
- (6) Scan sample surface and identify a clean, smooth area between 1 μ m and 5 μ m in size
- (7) **Zoom** in on smooth area
- (8) After ~5 scan lines, stop scan and set **PID** gains to 0, 5 and 0 respectively
- (9) Set function generator amplitude to 5V and frequency to 200 Hz
- (10) Open heater software at **Desktop:contactlab:HEATER-CONTROL: TC-36-25RS232rev.A.exe**
- (11) Initialize Heater in Heater program
 - a. Set **FIXED SET TEMP** to 25.00
 - b. Set **SELECT COMM PORT** to COM2
 - c. Click **CommCheck** (if system ready, proceed. Otherwise seek TA)
 - d. Click **INITIALIZE**

Verify that **OUTPUT ON/OFF** is now **ON**
- (12) Wait 4-5 minutes for equilibrium
- (13) By hand, record for ~30 seconds the **R** value from the lock-in
- (14) For the first (25°C) and last (45°C) temperatures record **R** as a function of load (**Set point**) (make sure to use 100nN for all other temperatures)

Load (nN)	R _{25°C} (mV)	R _{45°C} (mV)
20		
40		
60		
80		
100		

- (15) By changing **FIXED SET TEMP** in the heater program, repeat steps 11-15 for temperatures from 27 to 45°C in increments of 2°C
- (16) Cool system back to 25°C
- (17) Obtain a force-distance curve for each temperature:
 - a. Set modulation amplitude to 0
 - b. Set **PID** gains to 10000, 1000 and 0 respectively
 - c. Scan image for at least 15 lines
 - d. Follow Easyscan2 AFM F-D SOP to determine F_{ADH}
 - e. If F_{ADH} exceeds the range of the z-piezo, a value can be extrapolated
- (18) Fill in all data in the table below

Temperature (°C)	R (mV)	F _{ADH} (nm)
25		
27		
29		
31		
33		
35		
37		
39		
41		
43		
45		

- (19) Withdraw tip, set heater temperature to 25°C, set function generator amplitude to 0
- (20) Shut down the AFM system by following the shutdown procedure described in Easy Scan 2 AFM system SOP

(iv) Instructions for Data Analysis

- (1) *T_g* analysis
 - a. Plot R vs temperature and the identify transition onset.
 - b. How large is the change in R as the sample goes through its transition?
 - c. What other parameters could be investigated to maximize *T_g* sensitivity?
- (2) Contact mechanics analysis
From the back ground:

$$\frac{k_c(\omega)}{k_c(\omega)|_{L=0}} = \left[\frac{1 + \sqrt{1 - L / F_{adh}}}{2} \right]^{2/3}$$

- a. Using the load dependence data above and below *T_g*, determine the limiting value of R as load goes to 0 (i.e. plot R vs Load and determine R intercept). Do you observe a difference in load dependence below and above *T_g*? Why might the behavior differ above and below *T_g*? Is your data consistent with this rationale?
 - b. Given that R is proportional to contact stiffness, plot R vs

$$\left[\frac{1 + \sqrt{1 - L / F_{adh}}}{2} \right]^{2/3}$$

What is the nature of the observed trend? If the above equation were perfectly obeyed, how should the plot appear? Sketch this expectation on your same plot. Do you think the equation is valid for describing you system below *T_g*? Above *T_g*?

- c. Plot R vs *F_{adh}* and describe the observed trend.

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(v) Silicon Pretreatment Prior to Spin Coating

The pretreatment of silicon addresses (A) organic contamination and (B) and control of the oxide surface via HF treatment. Best treatment is achieved with (A) and (B). As HF surface treatment has to follow very strict safety requirements, it might be better that the procedure is conducted by a well trained TA instead of undergraduate students.

Safety

- (1) Follow the general rules for Nanotechnology Wet-Chemistry Lab at your Institution.
- (2) This lab uses **Hydrofluoric Acid (HF)**. Exposure to HF is extremely dangerous. Prior to the use of HF, read the **emergency procedures for HF exposure in the appendix and consult the safety regulations in your institution**, and receive a **formal HF handling training** prior to working with HF.
- (3) The UV/Ozone cleaner should be **OFF** before opening the sample tray.
- (4) Always handle silicon wafers with tweezers, not with your fingers. Wafer edges can be very sharp.
- (5) All solvent wastes are disposed into designated waste bottles located under the hood.
- (6) All silicon waste are disposed into the sharp object waste box.

(A) Removal of Organic Contaminants

Depending on the degree of contamination solvent cleaning and UV/Ozone treatment are recommended.

Materials

- (1) 4 pieces of Silicon wafers (~1cm² size pieces)
- (2) Millipore H₂O
- (3) Acetone
- (4) Methanol
- (5) A 150 ml beaker, a caddy and a watch glass for sonication
- (6) A waste beaker for organic solvent
- (7) A plastic waste beaker.
- (8) Fine point tweezers
- (9) N₂ gas with 0.2 micron filter.
- (10) 3 Petri dishes and para-film for finished samples.
- (11) UV/Ozone cleaner.
- (12) Sonicator
- (13) DI water

Procedure

- (1) **Solvent cleaning:** Removes organics off of the silicon surfaces.
 - a. Place silicon wafers in the caddy fitted in a 150 ml beaker and pour Acetone to fill upto~ 60 ml.
 - b. Fill the sonicator with water. Place the beaker and adjust amount of water so that the water in the sonicator is about at the surface level of Acetone in the beaker.
 - c. Cover with the watch glass.
 - d. Turn on the sonicator and run for 15 minutes.
 - e. Turn off the sonicator and remove the beaker.
 - f. Lift up the caddy (with silicon wafers) and drain the acetone into a waste beaker. Place the caddy back into the beaker.
 - g. Pour small amount of methanol for rinsing. Drain the methanol into the waste beaker. Repeat once.
 - h. Fill the beaker with Methanol upto ~ 60 ml.
 - i. Place the beaker back in to the sonicator. Cover with the watch glass.
 - j. Sonicate for 30 minutes. Take the beaker out when done.

- k. Lift the caddy and pour out the methanol into the waste beaker. Rinse with Millipore water at least three times. Return the caddy back into the beaker and fill with Millipore water.
 - l. Pick up a piece of wafers with tweezers and rinse with flowing Millipore water. Blowdry it with N₂ gas.
 - m. Place the dried silicon wafers in a Petri dish. Cover the Petri dish.
 - n. Transfer the waste solvent mixture (of acetone, methanol and water) into the designated solvent waste bottle. Rinse the waste beaker with DI water. The spent water is also drained into the waste bottle. Note: Don't use this waste beaker for the HF process.
 - o. Empty out the sonicator and allow drying.
- (2) **UV/Ozone treatment:** Removes any trace of organics off of the surface.
- a. Make sure the UV/Ozone cleaner is OFF.
 - b. Open the sample tray and place two of the silicon wafers. Leave the other two for HF treatment.
 - c. Close the tray.
 - d. Turn on the power switch.
 - e. Set a timer to 30 minutes and start.
 - f. Turn of the power switch when done. Open the sample tray and take the silicon wafers out and place them into a Petri dish and seal it with parafilm.

(B) HF Treatment

Hydrofluoric acid (HF) is used to remove the oxide layer and hydrogen passivate the surface, i.e., generates a hydrophobic surface. This surface is known to still grow an oxide layer (~ 2 nm thick over ½ hour).

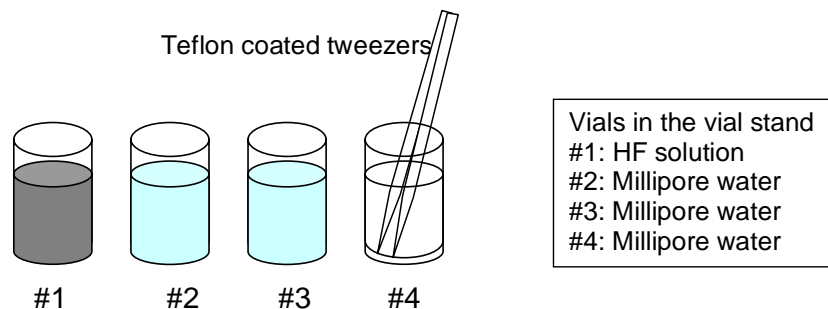
Additional Materials for HF treatment

- (14) HF and HF handling tool kit (vials, vial stand, teflon coated tweezers)
 (15) An extra large (~1000ml) waste beaker for HF

Procedure

- Be well prepared for the HF procedure. Wear TWO LAYERS of NITRILE gloves, a lab coat and a goggle. Make sure to be covered as much as possible. If you have long hair, tie it back. If you have facial hair, you might want to wear a mask.
 - Decide who is operating the main HF procedure (Leader) and who is operating the sub-tasks around the main HF procedure (Assistant).
 - Alert others that you are about to work with HF.
 - Have the third person ready for any assistance. This person can remind you and your partner the steps in the procedure, interact with others in the lab, open and close the N₂ gas tank, etc.
- g. Clear the working surface in the hood.
 - h. Fill an extra large waste beaker with water filled 70%. Place it under the hood.
 - i. Place a plastic waste beaker under the hood.
 - j. Have Millipore water and DI water filled in squeeze bottles. Place them under hood.
 - k. From this point on, separate tasks as directed.
 - l. **Leader** Place the HF tool kit basket under the hood. Places the vials in the vial stand in front of the basket.
 - m. **Leader** pours the Millipore water into the 4 HF vials up to the 15 ml mark.
 - n. **Leader** places the Teflon coated tweezers into the #4 vial. Note that the Teflon coated tweezers will be placed in the #4 vial whenever it is not used.
 - o. **Leader** opens the HF bottle. The mouth should be facing the back of the hood, not you. Add 5-6 drops of HF in the vial #1.

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- p. **Assistant** places a silicon wafer in HF vial #1 using a tweezers. Don't submerge the tweezers in the HF solution. Wait for 5 minutes or more.
- q. **Leader** takes the silicon wafer out using the Teflon coated tweezers and place it in the vial #2, and transfer it into the vial #3.
- r. **Leader** takes the silicon wafer in the vial #3 out. Hold it over the plastic waste beaker for rinsing with copious amount of flowing Millipore water.
- s. **Assistant** takes over the silicon piece with a tweezers. Blow Dry it with N_2 gas. Make sure it is completely dry. Place it in a Petri dish.
- t. Repeat for the second silicon piece.
- u. HF treatment is done. Follow the **cleaning procedure**.
- v. **Leader** pours the HF solution out of the vial #1 into the extra large waste beaker. Rinse it with copious amount of flowing DI water.
- w. **Leader** places the clean vial back to the vial stand.
- x. Repeat for the vial #2, #3, and #4. Rinse the Teflon coated tweezers likewise. Lay on the vial stand.
- y. **Leader** places the vial stand into the HF tool kit basket. Place the basket into a designated storage location. Ask the third person for opening drawers/doors.
- z. **Assistant** Transfer the extra large waste beaker and the plastic waste beaker into a sink with flowing water. Let it rinse it for 5 minutes.
- aa. **Leader and Assistant** take the top layer of the gloves off. Through them out INSIDE OUT in a regular trash can.
- bb. While **Leader** wipes the working surfaces with wet/dry paper towels, **Assistant** finish washing the waste beakers.
- cc. Make sure to clean everywhere Leader and Assistant touched: the N_2 gas nozzle tube, water squeeze bottles, the water faucet.
- dd. When done, take the second layer of gloves off INSIDE OUT. Through it in a regular trash can.

4. Background: Contact Mechanics and Viscoelastic Phenomena of Polymers

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Contact Mechanics – Fully Elastic Models

Hertz analyzed the stresses at the contact of two elastic solids, and thereby assumed small strains within the elastic limit. The contact radius a is considered significantly smaller than the radius of curvature R , and the two contacting surfaces, as depicted in Figure 1, assumed to be non-conformal. Furthermore, creep at the interface is neglected; i.e., a frictionless contact assumed.

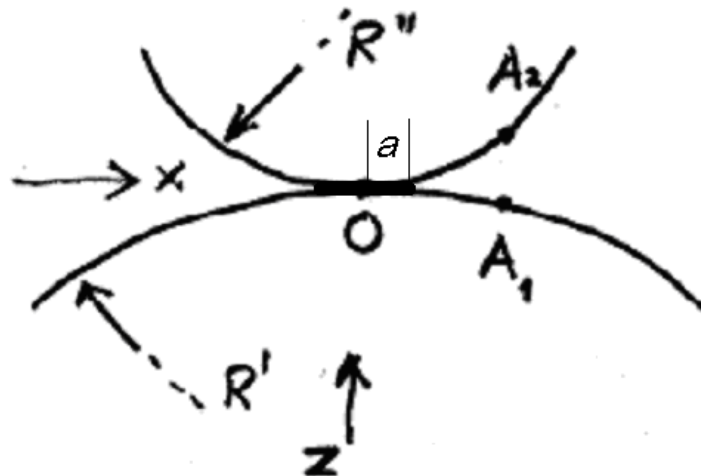


Figure 1: Contact of two elastic spheres.

Based on this assumption, the contact radius a , the contact area A , and both the maximum pressure p_{max} and the mean pressure p_m can be determined with an elastic infinite half-space analysis as:

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$$\text{Hertz contact radius: } a = \left[\frac{3LR}{4E^*} \right]^{1/3}$$

$$\text{Hertz area of contact: } A = \pi a^2 = \pi \left[\frac{3LR}{4E^*} \right]^{2/3}$$

$$\text{Mutual approach: } \delta = \frac{a^2}{R} \left[1 - \frac{2}{3} \left(\frac{a_o}{a} \right)^{3/2} \right] \text{ with } a_o = a|_{L=0}$$

$$\text{Hertz pressure: } p_{max} = \frac{3L}{2\pi a^2} = \frac{3}{2} p_m \left[\frac{6L(E^*)^2}{\pi^3 R^2} \right]^{1/3}$$

with the applied normal force (load) L , and the combined Young's modulus and radius of curvature of the two materials (1 and 2), i.e.,

$$E^* = \left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)^{-1} \text{ and } R = \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^{-1}$$

where ν is the Poisson ratio ($\nu \approx 0.5$ for polymers). Neglected in the Hertz model are adhesive interactions, as seen at zero loads where the contact area vanishes.

The adhesion force between two rigid spheres can be expressed as

$$F_{adh} = -2\pi R^* \Delta\gamma; \quad \Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{12}$$

where $\Delta\gamma$ is called the "work of adhesion" per unit area. This force-adhesion relationship is named after *Bradley*. Neither elastic nor plastic deformations are considered in Bradley's model. Johnson, Kendal and Roberts introduced a very successful elastic model - named JKR model. Based on this model, the area of contact $A = \pi a^2$ can be easily deduced from the JKR contact radius, i.e.,

$$a = \left[\frac{3R}{4E^*} \left(L + 3\pi R \Delta\gamma + \sqrt{6\pi R \Delta\gamma L + (3\pi R \Delta\gamma)^2} \right) \right]^{1/3}.$$

Note, for vanishing work of adhesion, the JKR expression for a corresponds to the Hertzian contact radius. For non-zero adhesion forces, the significant difference of the two models is illustrated in Figure 2. With the JKR model, a negative loading regime between $L = 0$ and the instability load, i.e., the adhesion force

$$L = F_{adh}^{JKR} = -\frac{3}{2} \pi R^* \Delta\gamma, \text{ is possible.}$$

Considering that the JKR adhesion force equation is seemingly independent of any elastic modulus, there seems to be an inconsistency, if compared to the Bradley model above. The apparent discrepancy was resolved by David Tabor (1977) who introduced the following parameter:

$$\mu = \frac{(R^*)^{1/3} (\Delta\gamma)^{2/3}}{\sigma (E^*)^{2/3}}, \quad \text{"Tabor Coefficient"}$$

where E^* and R^* are the combined curvature and modulus, respectively, and σ the characteristic atom-atom distance. The Tabor coefficient μ expresses the relative

importance of the adhesive interaction versus the elastic deformation. For $\mu > 5$, which is typical for soft organic materials, the JKR model is appropriate.

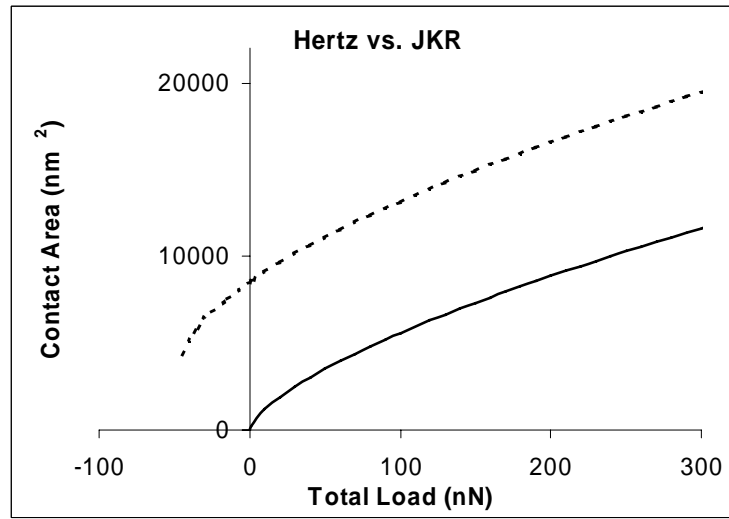


Figure 2: Hertzian elastic contact and JKR adhesive-elastic contact as function of load.

Force Modulation SFM and Hertzian Theory

The Hertzian theory of elastic circular point contact for a planar surface and an assumed spherically capped tip, Fig. 3, describes the contact radius as

$$a = \left[\frac{3LR}{4E} \right]^{1/3},$$

where R is the radius of curvature of the probing SFM tip, and E is the modulus of the sample only, if the sample material stiffness is much smaller than the modulus of the cantilever material. The mutual relative approach of distant points δ between the sample and probing tip, i.e., the sample indentation for an incompressible tip material, is given by the Hertzian theory as

$$\delta = \left[\frac{9L^2}{16RE} \right]^{1/3}$$

For a fully elastic sample and a incompressible stiff probing SFM tip, δ reflects the elastic strain deformation (indentation) of the sample material. For a force modulated relative approach, the load varies around the equilibrium load L_o as

$$L = L_o + \frac{\partial L}{\partial \delta} \delta$$

As we consider only the sample being deformed, a one-dimensional sample stiffness (generally referred to as contact stiffness) can be introduced as the derivative of the load, i.e.,

$$k_c \equiv \frac{\partial L}{\partial \delta} = \left(6E^2 L_o R \right)^{1/3}.$$

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The equation above is synonymous with the non-adhesive Hertzian expression

$$k_c = 2aE .$$

Higher order derivatives provide anharmonic distortions (dissipation) that can be neglected. The equilibrium load can be expressed by the normal spring constant of the cantilever k_L and the equilibrium deflection z_o as $L_o = k_L z_o$.

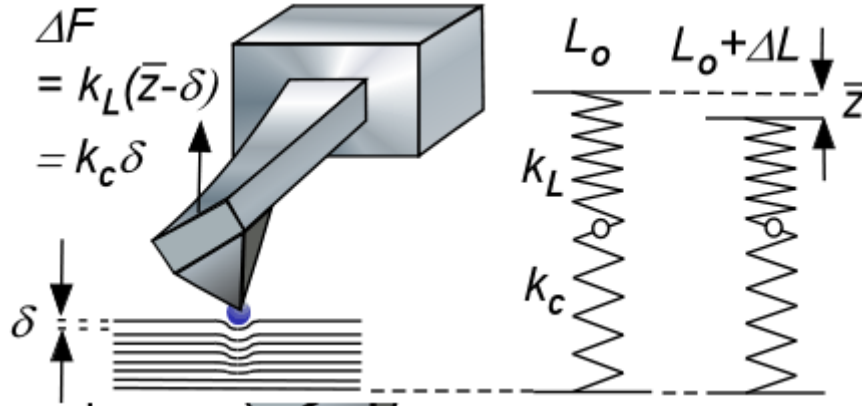


Figure 3: Elastic sample deformation involving rigid SFM tip.

Thus, for a sinusoidal normal stress disturbance, $z = A \sin(\omega t)$, with a root mean square amplitude

$$\bar{z} = \frac{1}{\sqrt{2}} A$$

the dynamic force acting on the cantilever is proportional to the net displacement (input modulation minus sample deformation), i.e.,

$$\Delta F = k_L (\bar{z} - \delta) .$$

Analogous, the force modulation can also be described from the sample perspective as

$$\Delta F = k_c \delta .$$

The "normal force", ΔF , acting on the SFM lever in the process of an indentation can be expressed in Hooke's limit as

$$\Delta F = k_{sys} \bar{z} = k_c \delta = k_L \Delta z_L \quad \text{with} \quad \Delta z_L = \bar{z} - \delta ,$$

as illustrated in Figure 3. The system combined spring constant, k_{sys} , is then given as

$$k_{sys} = \left(\frac{1}{k_c} + \frac{1}{k_L} \right)^{-1} .$$

Analogous relationships exist also for elastic shear modulation.

Contact Stiffness

In the previous paragraph, we have assumed that only the sample is deformed and the material response is rate independent. If both bodies are compliant, the non-adhesive Hertzian contact stiffness is given as

$$k_c = 2aE^* \text{ with } E^* = \left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)^{-1}$$

where E_i and ν_i ($i = 1,2$) are the reduced material Young's moduli and Poisson ratios, respectively. This equation has also been found to be applicable for viscoelastic materials, i.e.,¹

$$k_c(\omega) = 2aE^*(\omega).$$

where $k_c(\omega)$ and $E(\omega)$ reflect effective stiffnesses.

If we consider now also adhesion to take place in the contact area the Hertzian theory would have to be replaced by the JKR theory, which leads to the following expression for a normalized contact stiffness to zero load:¹

$$\frac{k_c(\omega)}{k_c(\omega)|_{L=0}} = \left[\frac{1 + \sqrt{1 - L / F_{adh}}}{2} \right]^{2/3}, \text{ with}$$

$$k_c(\omega)|_{L=0} = 2a_o E^*(\omega) = 2E^*(\omega) \left[\frac{9\pi R^2 \Delta\gamma}{2E^*|_{\omega \rightarrow 0}} \right]^{1/3}$$

FM and Polymer Relaxation Properties

Controlled temperature experiments involving force modulation microscopy, provides the opportunity to investigate relaxation properties of polymeric and organic materials. Thereby, the contact stiffness is monitored as a function the temperature, as illustrated below with shear modulation force microscopy (SM-FM) employed to thin polystyrene films. Due to the small probing area even the smallest changes in the polymer internal pressure, modulus and surface energies can be detected. SM-FM is allows for accurate determination of transition properties, such as the glass transition temperature,^{*} T_g , of nanoconstrained systems, such as ultrathin polymer films with a thickness below ~100 nm, Fig. 4(a).

The SM-FM method is briefly described as follows: A nanometer sharp SFM cantilever tip is brought into contact with the sample surface, Figure 4(b). While a constant load is applied, the probing tip is laterally modulated with a "no-slip" nanometer amplitude, ΔX_{IN} . The modulation response, ΔX_{OUT} , is analyzed using a two-channel lock-in amplifier, comparing the response signal to the input signal. The modulation response, i.e., the effective stiffness, is a measure of the contact stiffness. Thermally activated transitions in the material, such as the glass transition, T_g , are determined from the "kink" in the response curve, as shown in Figure 4(b).

Conceptually, the force modulation FM approach is a nanoscopic analogue to dynamic mechanical analysis (DMA). In essence, mechanical responses to external shear forces with varying temperature entail a material's viscoelastic properties, such as the modulus.

* Background information regarding the glass transition of viscoelastic material is provided below.

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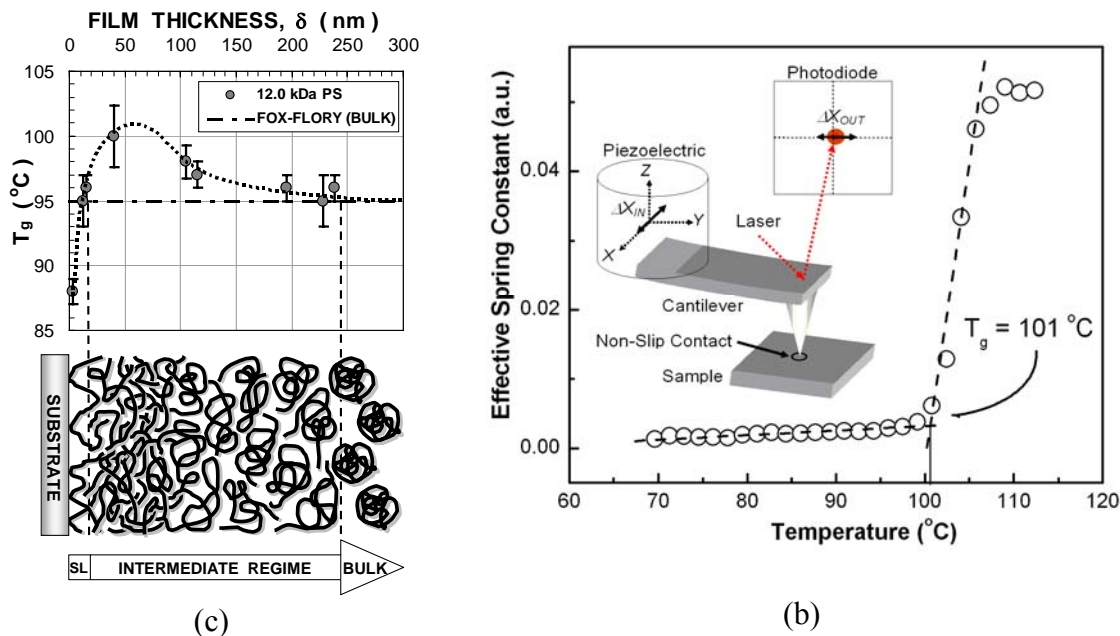


Figure 4. (a) Nanoscale constrained glass transition profile below 100 nm thick polymer films. (b) Working principle of Shear Modulation Force Microscopy (SM-FM)

Transition and Viscoelasticity

It is hard to imagine life without plastics, looking at water bottles, car bumpers, backpacks, computer casings, and many more products that involve synthesized organic materials – called polymers. There are numerous reasons to list why the last one hundred years can be called the *Plastic Age*. Polymers are light weight, formed in any shapes and colors, and can be produced with a simple scheme at low cost. One major advantage of polymers over traditional materials such as metals is their versatility in their mechanical property. Polymers can be soft and flexible like rubber bands and chewing gums, but also stiff and tough like the aircraft body of the new Boeing 787.

One critical parameter in designing polymeric product is the glass transition temperature T_g . The glass transition can be pictured, although with some caution, as a structural order-disorder transition that is observed in non-structured (amorphous) solids. One of the main features of the glass transition is the change in the mechanical and diffusive properties of the material below and above T_g . For instance, below T_g the material starts to act stiff and is brittle (i.e., glass like), and above T_g , still in the solid (condensed) phase, it exhibits high mechanical flexibility due to the existence of molecular chain mobility. Despite the importance of the glass transition of polymeric materials, the glass transition phenomena and its underlying viscoelastic behavior are not completely understood. These shortcomings have however not stopped mankind from designing continuously new polymer based products on a macroscopic level. However, the ambiguity in our current fundamental understanding of the glass forming process in polymers is being challenged by the recent nanotechnology spurt. As the dimension of solid systems approach the nanoscale, a dimension that is comparable to the size of polymer chains, it matters from an effective design perspective to grasp the exact relaxation mechanism behind the glass transition process.

One of today's most common ways to determine the glass transition temperature is the measurement of the change in the specific heat capacity $C_p(T)$ as a function of temperature by differential scanning calorimetry (DSC). Although widely used because of its convenience, DSC is also known for its inaccuracy. One of the main reasons is that the glass transition process takes place not only at a specific temperature, like a typical first order phase transition, but over a range of temperatures². Thus, T_g as determined by DSC has to be assigned, to some degree arbitrarily within a critical temperature range, as illustrated in Figure 5. Another reason for the difficulties in determine T_g originates from the viscoelastic nature of polymers, which makes the material temperature rate dependent with a high possibility of aging during the characterization process. DSC information is usually obtained from the polymer in powder form, to reduce effects based on thermal history and process engineered properties.³ In other words for T_g determination, DSC is restricted to the characterization of bulk materials, like other widely used techniques, as the dynamic mechanical analysis (DMA), Fig. 5. DMA is sensitive to changes in the in-phase G' and out-of-phase modulus response G'' . The ratio of these two moduli components, define the loss modulus (also referred to as loss tangent $\tan\delta$), with which T_g can be identified. Due to imposed macroscopic mechanical constraints this value is often different from the DSC calorimetric glass transition.

There is currently not only a need for new techniques to provide a more fundamental understanding of the glass transition process, but also for methods that are applicable to small scale systems; e.g., thin films, and polymeric heterosystems (e.g., polymers blends and polymer nanocomposites). A technique that has been found to address the experimental shortcomings of DSC and DMA is shear modulation force microscopy (SM-FM), as introduced above.

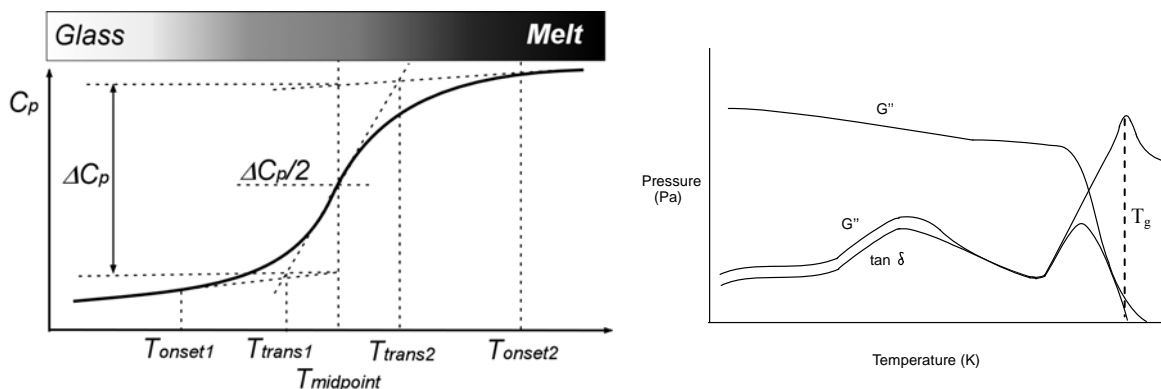


Figure 5 : (left) Schematic thermogram of $C_p(T)$. Shows the various distinct temperatures used to define the midpoint temperature T_g . (right) Schematic thermomechanical results, as obtainable by DMA.

Introduction to Linear Viscoelasticity

The science that deals with the mechanical properties of condensed phases under external stresses is called Rheology. We will limit our discussion to a subdiscipline of rheology, i.e., linear viscoelasticity, with which we conceptually separate the *liquid-like* (viscous) behavior from the *solid-like* (elastic) behavior. Thereby, a material that exhibits

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ideal solid-like behavior under stress can be described with a simple stress-strain relationship, and a material with *ideal liquid-like* behavior shows a simple stress-strain-rate dependence. With *stress* we define the external force per unit area that is imposed on the condensed phase. The resulting deformation (e.g., length or angular deformation (ΔL or γ) for a uniaxial length extension, or simple shear, respectively) defines a strain ratio (e.g., $(L_0 + \Delta L)/L_0$ or $\tan \gamma$). It is convention to use for uniaxial stress and strain the Greek symbols σ and ε and for the shear stress and strain τ and γ . Strain rates reflect the time derivative of the strain.

Ideal solid-like and ideal liquid-like

Ideal solid-like materials deform and relax instantaneously with changes in the applied external stresses. *Hooke's Law* is a manifestation of a solid-like behavior. Thus, an ideal solid-like behavior is synonymous with *ideal elastic*. Mechanical energy is stored in an ideal elastic material without exhibiting any form of energy dissipation. The energy is instantaneously regained with the discharge of the external stresses. Note, with this definition of a material behaving ideal solid-like, no structural arrangements, such as for instance "*crystallinity*", were imposed. In ideal elastic materials the stress is linearly related to the strain and the proportionality factor is called a *stiffness modulus*. In the case of a uniaxial elongation/compression in x-direction or simple shear in y-direction of an isotropic material, Hooke's law has the following simple form:

$$\begin{aligned}\sigma_{xx} &= E\varepsilon_{xx} \quad (\text{unaxial deformation}) \\ \tau_{xy} &= G\gamma_{xy} \quad (\text{simple shear deformation})\end{aligned}$$

with the modulus of elasticity (Young's modulus) E and the shear modulus G . The forces per unit area, i.e., $F_x/A = \sigma_{xx}$ and $F_y/A = \tau_{xy}$ are the normal and lateral stresses, respectively, which are imposed on the elastic solid. ε and γ are the corresponding strains; i.e., normalized dimensionless displacements.

The conceptual counter behavior to ideal solid-like is ideal liquid-like as found in a *Newtonian liquid*. The basic equation of simple flow is described one-dimensionally by *Newton's law of viscosity*,

$$\tau_{yx} = -\eta \frac{dv_x}{dy},$$

which relates proportionally the shear force per unit area, $F_x/A = \tau_{xy}$, to the negative of the local velocity gradient (time derivative of the deformation) with a constant viscosity value, η . The velocity gradient represents a strain rate. If a stress is applied to a Newtonian liquid no strain is built up. The material is incapable of mechanical energy storage. Once the stress is removed the material does not relax. The material resistance to shear manifests itself in the rate with which the stress is imposed. In a perfect liquid we find a linear relationship between the stress and the strain rate. The proportionality factor is called *viscosity*.

In general, any realistic liquid and solid matter will behave in a mixed manner, solid-like and liquid-like, depending on the degree and time scale over which external stresses are acting.

Linear Viscoelasticity

Mixed liquid-like and solid-like characteristics of viscoelastic materials suggest that the external forces applied are partially stored and partially dissipated. This is nicely described by a simple constitutive equation based on a periodic deformation process. If the viscoelastic behavior is in a linear region, a shear sinusoidal stress that is applied to a viscoelastic body exhibits a sinusoidal strain with a phase lag that is expressed as follows:

$$\begin{aligned} \gamma &= \gamma_0 \sin(\omega \cdot t), \\ \sigma &= \sigma_0 \sin(\omega \cdot t + \delta), \end{aligned}$$

ω is the angular frequency, and δ is the phase lag, and γ_0 and σ_0 are the maximum magnitudes of the strain and the stress. The expression of the sinusoidal stress can be expanded to elucidate the two components, i.e., in phase component and out of phase component,

$$\sigma = \sigma_0 \sin(\omega \cdot t) \cos(\delta) + \sigma_0 \cos(\omega \cdot t) \sin(\delta).$$

The in phase component, $\sigma_0 \cos(\delta)$ is referred to as the storage modulus G' , and the out of phase component, $\sigma_0 \sin(\delta)$ is called the loss modulus G'' . The stress relationship then writes as

$$\sigma = \gamma_0 \cdot G' \cdot \sin(\omega \cdot t) + \gamma_0 \cdot G'' \cdot \cos(\omega \cdot t),$$

Expressed in complex notation the strain and stress are:

$$\begin{aligned} \gamma &= \gamma_0 \exp(i \cdot \omega \cdot t), \\ \sigma &= \sigma_0 \exp(i \cdot (\omega \cdot t + \delta)), \end{aligned}$$

and thus, we can introduce a complex modulus G^* as,

$$\frac{\sigma}{\gamma} = G^* = \frac{\sigma_0}{\gamma_0} (\cos \delta + i \cdot \sin \delta) = G' + i \cdot G'',$$

The *storage modulus* G' represents the storage capability of the systems and the *loss modulus* G'' describes the dissipation character of the system in form of plastic deformation or flow. The ratio of the loss and the storage component is referred to as the loss tangent,

$$\tan \delta = \frac{G''}{G'},$$

and reflects the relative viscous and elastic properties. The smaller the loss tangent is the more elastic is the material. $\tan \delta$ is often the most sensitive indicator of various molecular motions within the material. Figure 6 provides a response visualization of a simple shear phenomenon.

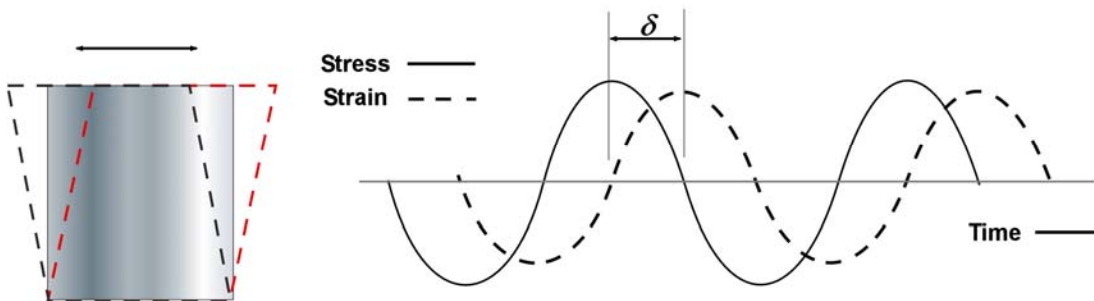


Figure 6: Dynamic shear stress-strain visualization.

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The response of a viscoelastic material can be described by a simple combination of dashpots (dissipative) and springs (elastic). The simplest model of a spring and a dashpot in series is the Maxwell's model (Figure 7(a) with

$$\frac{d\gamma}{dt} = \frac{1}{G} \frac{d\sigma}{dt} + \frac{1}{\eta} \sigma$$

where η is the viscosity, we have introduced above. The solution to this differential equation is,

$$\sigma(t) = \gamma_0 \cdot G \cdot \exp\left(-\frac{t}{\eta/G^*}\right)$$

with $G^* = \sigma/\gamma$. This model predicts a time sensitive modulus, i.e.,

$$G(t) = G \cdot \exp\left(-\frac{t}{\tau_\gamma}\right),$$

where τ_γ is the characteristic relaxation time, and t is the observation time. Thus, if the deformation process is very fast compared to the material relaxation time, i.e., $t \gg \tau_\gamma$ the elastic behavior will dominate. For very slow deformation ($t \ll \tau_\gamma$), the system's viscous behavior dominates. Another basic viscoelastic setup is obtained by operating a spring in parallel with a viscous dashpot. (Kelvin-Voigt Model, Fig. 2(b)) The Kelvin-Voigt model provides the following relationships:

$$\sigma = G \cdot \gamma + \frac{\eta \cdot d\gamma}{dt}$$

and the solution with a constant stress σ_0 is,

$$\gamma(t) = \frac{\sigma_0}{G} \left[1 - \exp\left(-\frac{t}{\tau_\sigma}\right) \right]$$

where τ_σ is the retardation time of the strain.

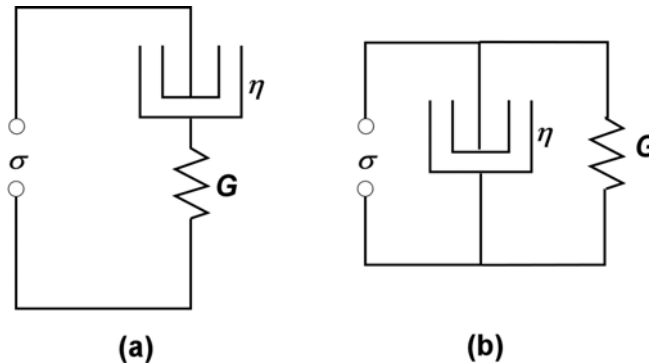


Figure 7: Dashpot spring model of (a) Maxwell Model (b) Kelvin-Voigt Model.

While the Maxwell model describes the stress relaxation but not creep, the Kelvin-Voigt model describes creep but not stress relaxation. For viscoelastic material, the simplest model would be the combination of the two,⁴

$$\sigma + \left(\frac{\eta_1 + \eta_2}{G_1} + \frac{\eta_2}{G_2} \right) \frac{d\sigma}{dt} + \frac{\eta_1 \eta_2}{G_1 G_2} \frac{d^2 \sigma}{dt^2} = \eta_2 \frac{d\gamma}{dt} + \frac{\eta_1 \eta_2}{G_1} \frac{d^2 \gamma}{dt^2}$$

as G_1 , G_2 , η_1 and η_2 are corresponding to two springs and two dashpots, Fig. 8. If this is solved with the sinusoidal stress,

$$\frac{G' - G_0}{G_\infty - G_0} = \frac{\omega^2 \cdot \tau_\gamma^2}{1 + \omega^2 \cdot \tau_\gamma^2}$$

$$\frac{G''}{G_\infty - G_0} = \frac{\omega \cdot \tau_\gamma}{1 + \omega^2 \cdot \tau_\gamma^2}$$

$$\tan \delta_m = \frac{G_\infty - G_0}{G_0 + G_\infty \omega^2 \cdot \tau_m^2}$$

where G_0 and G_∞ are *relaxed* and *unrelaxed* moduli, respectively, and τ_m is derived as:

$$\tau_m = (\tau_\sigma \tau_\gamma)^{1/2} = \left(\frac{\eta_1}{G_1} \frac{\eta_1}{G_1 + G_2} \right)^{1/2}$$

The maximum of the loss curve then corresponds to $\tau_m \omega_0 = 1$. The product $\tau_m \omega_0$ is referred to in the literature as the Deborah number, and reflects the ratio of the externally imposed time disturbance and the intrinsic relaxation time⁴

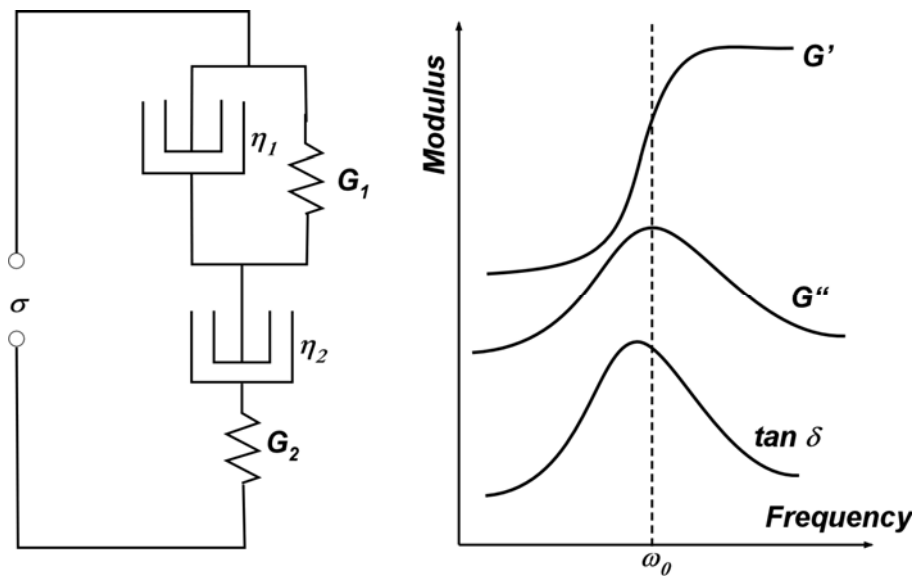


Figure 8: A combination of the Maxwell and Kelvin-Voigt Model.

Many more combinations of springs and dashpots are possible and in detail described in the literature.³

Time-Temperature Equivalence of Viscoelastic Behaviors

We showed in the previous section that the viscoelastic behavior is strongly affected by the temperature and the observation time (frequency). Here the concept of time-temperature equivalence is introduced. Consider a glass window. Glass windows are made with an amorphous inorganic (silica mixture) material that appears in daily life to be “solid-like. However, it is more appropriate to consider glass to be in a highly viscous condensed phase that appears to be at equilibrium in a solid-like state during the

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time of observation. By controlling the temperature without imposing any transitions we can accelerate or slow down the flow process. In that sense, the viscoelastic behavior of the material is affected similarly by either changes in the temperature and or time. This is called a time-temperature equivalence and is illustrated in Figure 9. Figure 9(a) and 9(b) reflect the modulus in a time (i.e., frequency) domain, and in a temperature domain, respectively. Valuable information about the viscoelastic behavior of materials can be deduced from such measurements and will be discussed in the following sections.

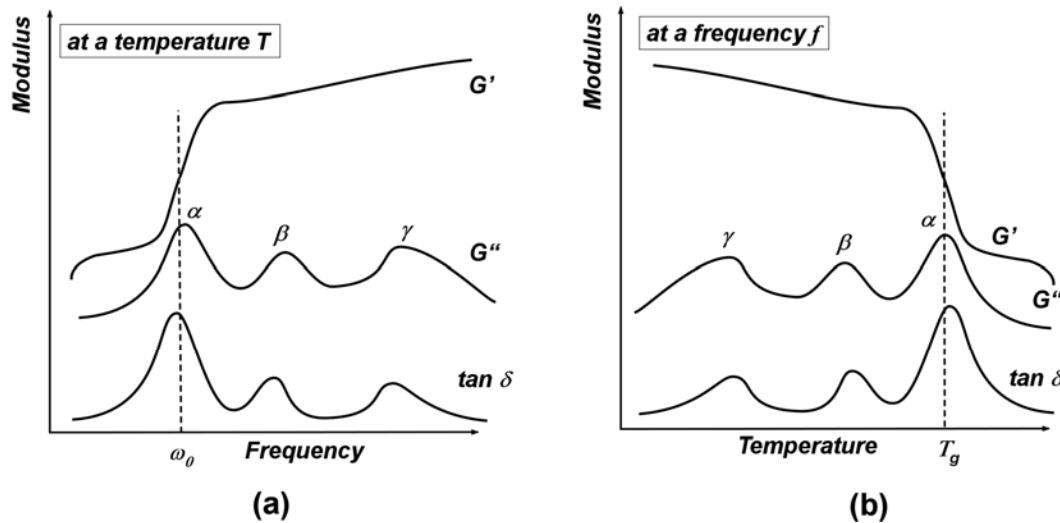


Figure 9: Modulus spectrums in (a) time domain, and in (b) temperature domain.

Glass Transition

The *glass transition* T_g is defined as the reversible change in an amorphous material (e.g., polystyrene) or in amorphous regions of a partially crystalline material (e.g., polyethylene), from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.⁵ As shown in the previous section, Fig. 9(b), this transition corresponds to a temperature at which the modulus drastically changes. Above the glass transition temperature the material, still a solid, reveals a strongly rubbery behavior that is to part liquid-like. Below the transition temperature the material behaves like a brittle solid-like material. The glass transition itself, as illustrated in Figure 10, exhibits a strong cooling rate dependence and is in appearance significantly different from melting (first order phase) transition. Also the frequency of the applied macroscopic stresses is affecting the temperature of the transition.

Force Modulation Microscopy

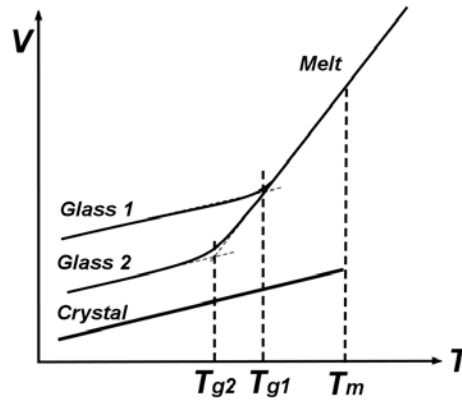


Figure 10: Specific volume change as function of temperature. Depending on the cooling rate any liquid can freeze into a glass phase (fast quenching; e.g. of metallic glasses). Depending on the cooling rate, T_g can significantly shift as indicated with Glass 1 and Glass 2. In polymers, the transition from a melt to a glass is not discontinuous as the first order phase transition (indicated with melting temperature T_m). Hence the assignment of a single transition value for T_g seems to be ambiguous on first sight.

Thermodynamically, the free energy changes between equilibrium states are usually identified by a discontinuity in the first partial derivatives of the Gibbs free energy $G = H - TS$, with respect to the relevant state variable (pressure P and temperature T), as illustrated Figure 11. Discontinuities, as expressed in the first partial derivatives of the Gibbs free energy

$$\left(\frac{\partial G}{\partial P}\right)_T = V,$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S,$$

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H,$$

are found in the property-temperature relationships, i.e., the volume V , the entropy S and enthalpy H .

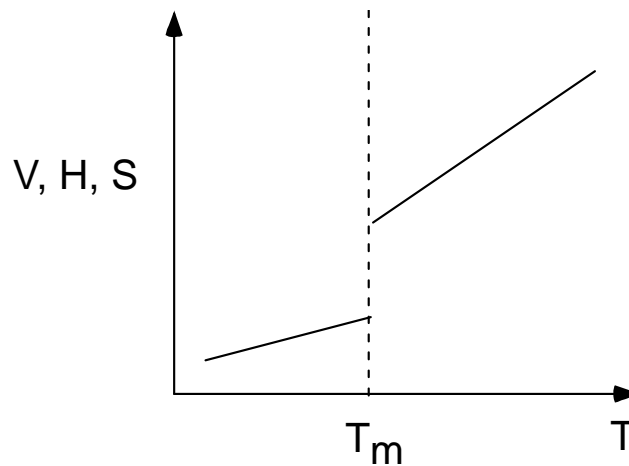


Figure 11: Volume discontinuity. First-order transition between liquid and solid. (T_m melting temperature).

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The second derivatives of the Gibbs free energy introduces the heat capacity C_p , compressibility κ and thermal expansion coefficient α .

$$\text{Heat Capacity, } C_p : \quad -\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial(G/T)}{\partial(1/T)} \right)_P \right]_P = \left(\frac{\partial H}{\partial T} \right)_P = C_p$$

$$\text{Compressibility, } \kappa : \quad \left(\frac{\partial^2 G}{\partial P^2} \right)_T = \left(\frac{\partial V}{\partial P} \right)_T = -\kappa V$$

$$\text{Therm. Expansion Coeff., } \alpha : \quad \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right]_P = \left(\frac{\partial V}{\partial T} \right)_P = \alpha V$$

Figure 12 provides a rough classification based on the changes of the free energy and derivatives with temperature. While, column (i) illustrates the qualitative behavior of a first-order phase transition (i.e., a melting/freezing transition), column (ii) and (iii) are found for second order and glass transitions, respectively. A second order phase transition (e.g., an order-disorder transition) exhibits no discontinuity in V and H , and S . But there are discontinuities in C_p , κ and α .

First and second order transitions are illustrated in Figure 12. If compared to property changes in glasses around the glass transition temperature, one finds some similarity between the glass transition and the second order transition. There are however significant differences. C_p , κ and α values are always smaller and closely constant below the glass transition temperature, T_g , if compared to the values above T_g . This is in contrast to the second-order transition.

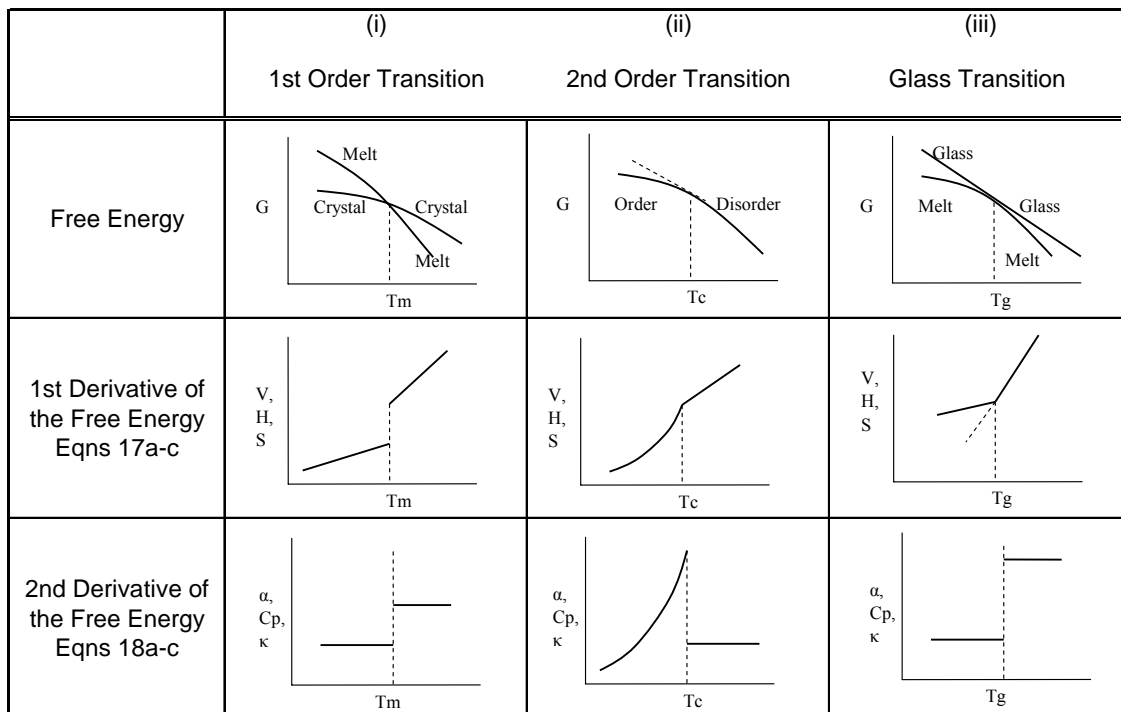


Figure 12: Schematic representation of the changes with temperature of the free energy and its first and second derivatives for (i) first order, (ii) second order and (iii) glass transition.

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Recommended Reading

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- Mechanical Properties of Solid Polymers* by I. M. Ward, Wiley-Interscience Publication, London, 1971.
- Nanoscience: Friction and Rheology on the Nanometer Scale* by E. Meyer, R. M. Overney, K. Dransfeld, and T. Gyalog, World Scientific Publ., Singapore, 1998.

**Appendix: EMERGENCY PROCEDURES FOR HYDROFLUORIC ACID (HF)
EXPOSURE**

**SEEK IMMEDIATE MEDICAL ATTENTION
CALL 911**

SERIOUS TISSUE DAMAGE WITH DELAYED ONSET
BEGIN FIRST AID IMMEDIATELY

FIRST AID FOR SKIN CONTACT

1. IMMEDIATELY (within seconds) proceed to the NEAREST SAFETY SHOWER. While showering REMOVE ALL CONTAMINATED CLOTHING and WASH THE AFFECTED AREA FOR 5 MINUTES.
2. USING NITRILE 22 MIL (MFG> RECOMMENDED) GLOVES MASSAGE CALCIUM GLUCONATE GEL into the affected area. If calcium gluconate gel is not available, wash area for at least 15 minutes or until emergency medical assistance arrives.
3. RE-APPLY CALCIUM GLUCONATE GEL and massage it into affected area EVERY 15 MINUTES until medical assistance arrives or pain disappears.

FIRST AID FOR EYE CONTACT

1. IMMEDIATELY (within seconds) proceed To THE NEAREST EYEWASH STATION.
2. Thoroughly WASH EYES WITH WATER FOR AT LEAST 15 MINUTES while holding eyelids open.
3. DO NOT APPLY CALCIUM GLUCONATE GEL TO EYES.

FIRSTS AID FOR INHALATION

GET MEDICALASSISTANCE by calling 9-911.

ASK THE MEDICAL ASSISTANCE TO TAKE YOU TO A **MEDICAL BURN CENTER
FOR TREATMENT, NOT ANYWHERE ELSE.**