1 Introduction

AKA Soft Condensed Matter Physics (MC mai ghoom phir ke CMP pe aa gya).
Course content

1. Intro to soft matter

2. Viscoelasticity

3. Colloids

4. Polymers

5. Surfactants

6. Liquid Crystals

Books

- Soft Matter Physics (Richard Jones)

- Soft Matter Physics (Masao Doi)

- Introduction to the Theory of Soft Matter (Jonathan Selinger) [liquid crystals]

So, there's three adjectives in front of the word 'Physics'.

1.1 Matter

Composed of atoms or molecules. Matter refers to collections of atoms and molecules. Don't go about referring to a single atom as 'matter'.

It is expected that when we say 'matter', we have a very large ($\approx N_A$) number of building components.

So, how does one go about dealing with such systems? Statistical physics. Your Hamiltonian formalism and Newton's equations will shit the bed.

Solid systems and gaseous systems are easy to deal with for Physicists, because some really neat approximations can be made. In liquids, however potential energy $\approx$ kinetic energy.

[Missed some part of the lecture]

An example of Helium's phase diagram was given. There is a critical pressure below which it cannot exist in the liquid state. Point was $P > 0$ for the existence of liquid, or something like that. You need pressure for the existence of liquids.

You see, the world is not just made up of solid, liquid and gas only. Like what the fuck even is the phase of toothpaste and shampoo??

- Solid

    - Translational order
    - translationally broken symmetry
    - broken rotational symmetry
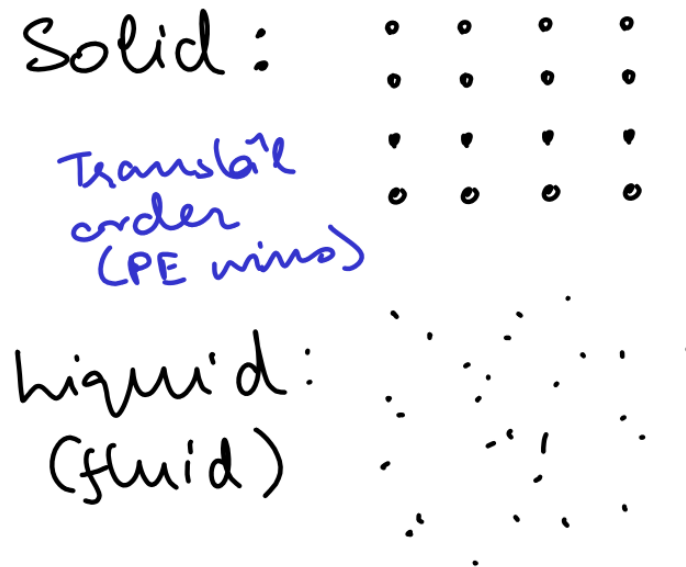
- Fluid

    - Translationally disordered

Figure 1: Fluids vs solids - order

- – translationally symmetric
- – rotational symmetries preserved

Deformations are not energetically favourable in solids and hence any attempts to move particles by shearing, compressing etc will result in strong restoring forces.

Fluids on the other hand have 0 elastic moduli

Then we have soft matter systems, where the elastic moduli are somewhere in between the above two cases.

Systems like liquid crystals are again quite unique because

- Rotational order

- No translational order

BTW time scales matter. Phase diagrams don't show time, only thermodynamic parameters. But, we generally think of different phases like solids, liquids etc in terms of their response funcions - their dynamics. If something is hard, it's solid. If something flows, it's liquid. Phase diagrams do not really capture the dynamics properly.

1.2 Grading

- Home assignments - 33%

- Midsem - 33%

- Endsem - 33%

Intermolecular Forces

Must be attractive at some ranges (else cannot have condensed phases), corresponding potential should achieve minima somewhere.
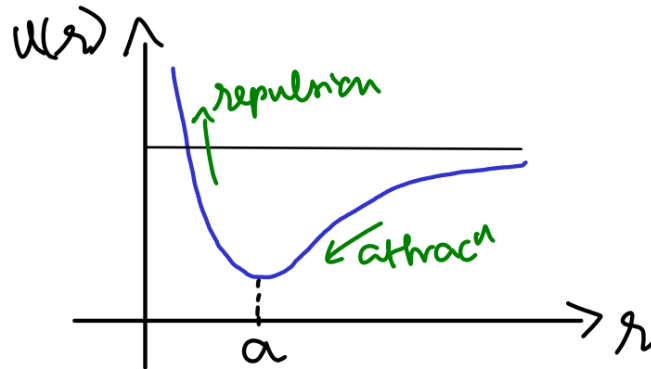

Figure 2: Typical interatomic potentials in condensed matter systems

$$r \to \infty \implies -\frac{dU}{dr} = 0$$
$$r \geq a \implies -\frac{dU}{dr} \leq 0 \tag{1}$$
$$r < a \implies -\frac{dU}{dr} > 0$$

Metallic Bond

A simple minded picture - positive cores form a lattice and negative carriers dispersed throughout the material. Coulomb forces responsible for holding the metallic bulk together.

Typical strength $\approx 10^{-18}$ J ≈ 6 eV, around 300 Kelvin.

Ionic Bonds

Similar bond energy as metallic bonds, bulk formed by interpenetrating lattices of positive and negative charge cores.

Covalent Bonds

Electron sharing and all that jazz. Typically weaker than ionic bonds

Van der Waals interactions

Initiated by spontaneous polarization of a molecule, which then polarizes nearby molecules and the overall medium can be modelled using some empirical potentials that simulate this interaction.

This is typically the weakest interaction, $k_B T \approx$ room temp. $U \sim \frac{1}{r^6}$

Hydrogen Bonds

O, F, N et cetera participate in Hydrogen bonding. refer to CBSE book nothing new here really.
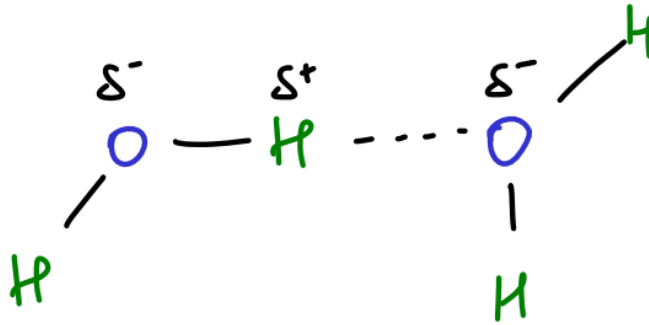

Figure 3: Hydrogen bonding in water

This gives rise to non-trivial properties, like the density of ice being lesser than the density of water. Bond strenth $\sim 20 - 100 k_B$

What is 'soft' matter

We generally think of colloids, liquid crystals etc. The basic building units are mesoscopic in size (somewhere between micro and macro).

Where an atom is typically of the order of a few angstroms, soft matter building blocks are somewhere from a few nanometers to microns.

Consider the act of compressing some bulk material. We define the bulk modulus of the medium as

$$\kappa = \frac{\Delta P}{\Delta V / V} \tag{2}$$

Bulk moduli for condensed matter are very high, because the structure of the bulk material is maintained by the interatomic forces, which typically have a very narrow minimum range. Compressing those solids requires one to reduce the average interatomic distances, thus increasing thus making the restoring force highly repulsive.

Similarly, we could also shear a bulk material. Shear modulus

$$G = \sigma \frac{L}{l} \tag{3}$$

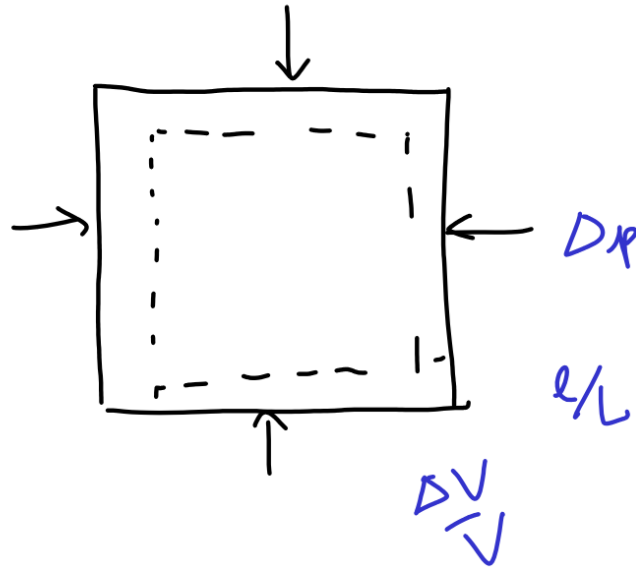where $\sigma = F/A$ is the shear stress and $\gamma = l/L$ or $\Delta L/L$ is the sheer strain (see figure 5)

Figure 4: Doing a bulk compression

Why do soft materials have low G?
Consider the toy model in figure 6 made using springs.
If we try to deform it, then we have

$$F = k(r - a)$$

$$\text{Stress,} \quad \sigma = \frac{F}{A} = \frac{d(r - a)}{a^2}$$

$$\text{Strain,} \quad \gamma = \frac{r - a}{a} \tag{4}$$

$$\text{Young's modulus,} \quad Y = \frac{\sigma}{\gamma} = \frac{k(r - a)}{a^2(r - a)} \cdot a = \frac{k}{a}$$

During deformation that doesn't straight up destroy the whole bulk material, we are essentially moving in a small window around the potential minimum (see fig 2), we can Taylor expand the potential to get some harmonic dynamics.

$$U(r) = U(a) - \frac{1}{2!} \frac{\mathrm{d}^2 U}{\mathrm{d}r^2} (r - a)^2 \tag{5}$$

Some important properties of soft matter systems

1. Disordered matter: energy scales $\approx k_B T$, e.g. granular matter

2. Nonlinear matter

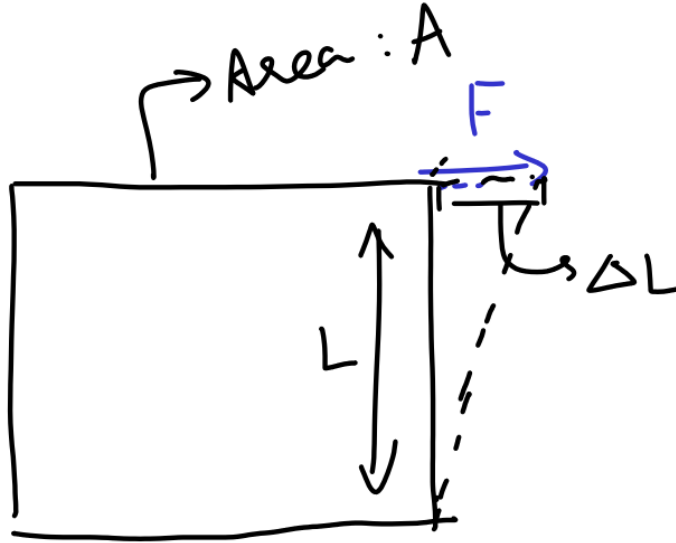3. Far from equilibrium matter

4. Thermal and entropic matter:

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Figure 5: Sheer modulus

5. Observable matter:

Summary: Young's modulus $E \approx \frac{\epsilon}{a^3}$, where $\epsilon \to$ typical bond strength, $a \to$ bond length

Viscous, elastic, and viscoelastic behaviour

- Solid: It resists shear stress and undergoes shear strain without yielding, i.e. original shape et cetera is restored.

- Liquid: Cannot susteain shear stress and yields (i.e. it flows)

Based on this we can define a Hookean solid

$$\sigma = \frac{F}{A} \quad \text{Shear stress} \tag{6}$$

$$\gamma = \frac{\Delta x}{y} \quad \text{Shear strain} \tag{7}$$

$$\text{Shear modulus,} \quad G = \frac{\sigma}{\gamma} \tag{8}$$

is the modulus associated with all Hookean solids.

Similarly we can define a Newtonian liquid

$$\sigma = \frac{F}{A} \tag{9}$$

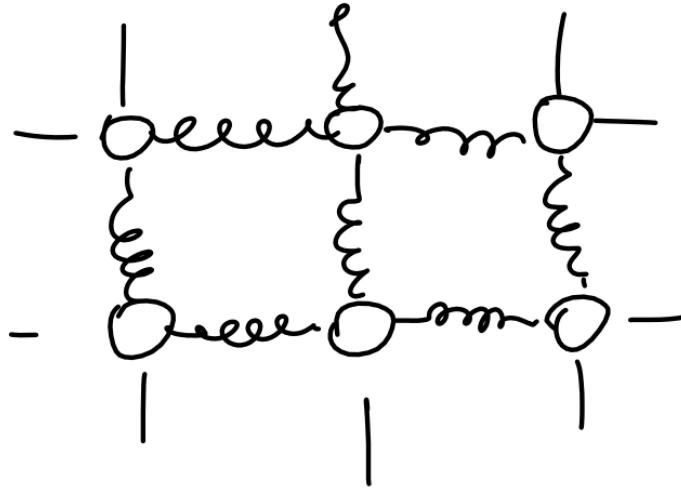$$\text{Shear strain rate,} \quad \dot{\gamma} = \frac{\Delta x}{y \cdot t} = \frac{v}{y} \tag{10}$$

Figure 6:

$$\frac{\sigma}{\dot{\gamma}} = \eta \quad \text{(Shear viscosity)} \tag{11}$$

Why Newtonian? Assumed that η is constant, i.e. not a function of $\dot{\gamma}$
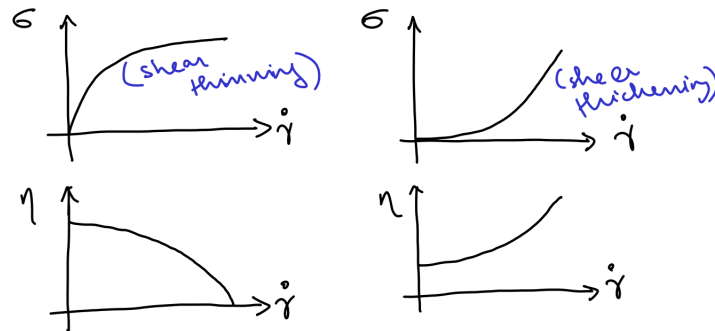

Figure 7: Sheer thickening vs sheer thinning non-Newtonian fluids, driving the system increases and decreased viscosity respectively

- Newtonian $\rightarrow$ Water

- Shear thinning $\rightarrow$ Shampoo, Ketchup

- Shear thickening $\rightarrow$ those corn starch solutions that people keep forwarding on WhatsApp.

Similarly, we can also have non-Hookean solids. For solids, we have $G = \sigma/\gamma$. We know that end of the day, metals also yield, which is why bridges, for example are not meant to last forever.
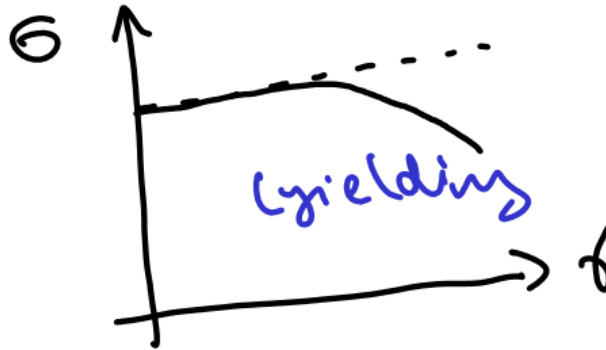

Figure 8: Yielding in solids - nothing is ideal, of course

How do viscoelastic materials respond to stress?

Consider the the rig that is used to apply stress, measure strain and all that. The material being tested could be solid or liquid (or something really in between).
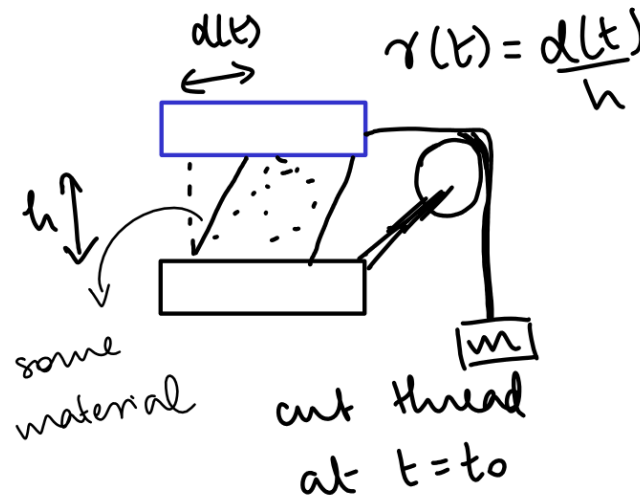

Figure 9: A rig used to apply stress and measure response of the material

Similarly we could compare liquids

Concept of relaxation time

$$
\begin{aligned}
\sigma = G\gamma &\to \text{solid} \\
\sigma = \eta\dot{\gamma} &\to \text{liquid}
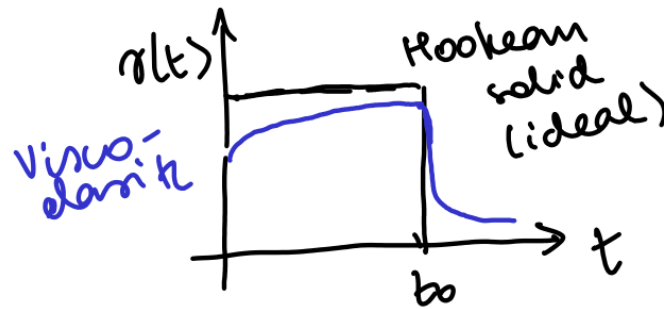\end{aligned}
\tag{12}
$$

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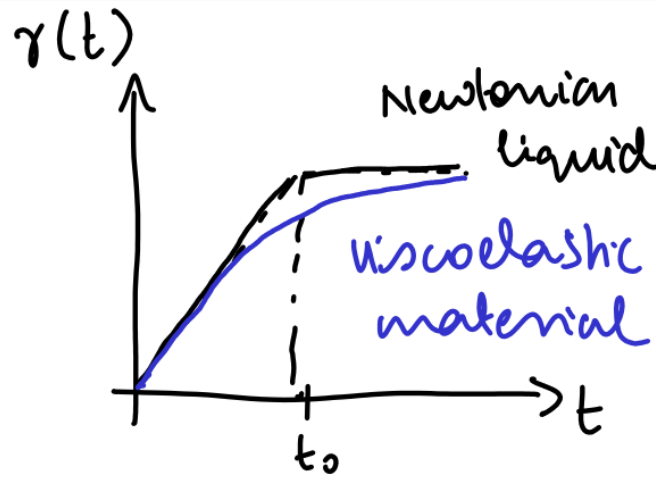Figure 10: Response of ideal (Hookean) and real (non-Hookean) solid

Figure 11: Ideal (Newtonian) vs viscoelastic liquid responses

The relaxation time τ is the time below which system has an elastic response.

Deborah number: It is a way of distringuishing between solids and liquids based on ratio of relaxation time and observation time.

"Even the mountains flow before God"

God can see mountains flow. Nothing religious going on here.

$$\text{Deborah number,} \quad D_e = \frac{\text{Relaxation time}}{\text{Observation time}} \tag{13}$$

$$\begin{aligned} D_e &\rightarrow \text{high} \rightarrow Solid \\ D_e &\rightarrow \text{low} \rightarrow liquid \end{aligned} \tag{14}$$

Everything flows on a long enough time scale. (See the article on Deborah number that appeared in Physics Today in 1964). To have a small D_e you can either have a small relaxation time, or a very large ovservation time for an otherwise long relaxation time.
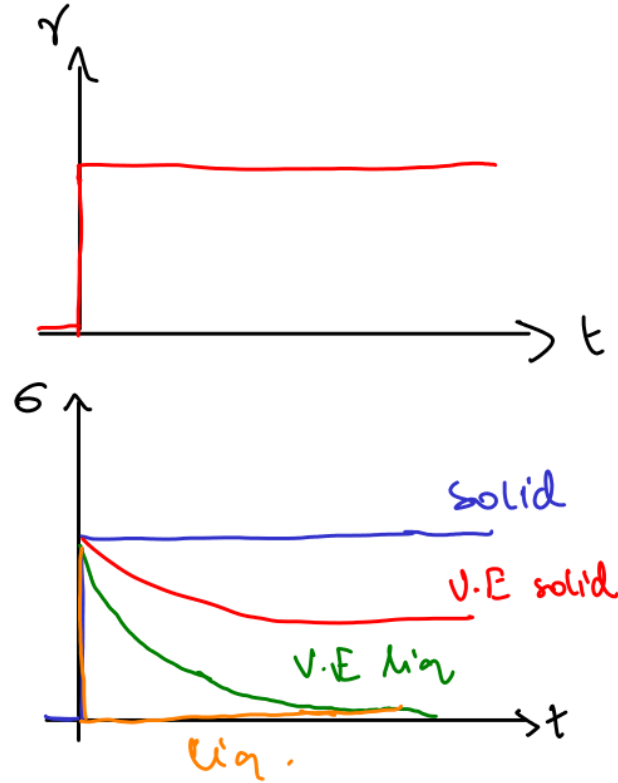
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Figure 12: Comparison between the different classes of condensed matter systems to sheer stress

Linear Viscoelasticity

We want to calculate the response of a soft matter system to some arbitrary strain $\gamma(t)$.

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')\mathrm{d}t' \tag{15}$$

Consider an oscillatory stress

$$\gamma(t) = \gamma_0 \cos \omega t.$$

The response of a linear medium is a superposition of an elastic term. Our response function will be of the form

$$G^*(\omega) = G'(\omega) + iG''(\omega) \tag{16}$$

The first term is the elastic response (storage) and the second one is the viscous response (loss modulus). Note that we are assuming that the system has a single relaxation time.

and a viscour term

$$G'(\omega) = G_e + \frac{G(\omega\tau)}{LOL} \tag{17}$$

So far we are ignoring molecular structure of the soft material. Once we start doing system-specific studies, e.g. polymers, surfactants et cetera, then we'll look at more accurate descriptions. Nevertheless, these approximations give, in many cases, some meaningful insight.

Mechanical Elements

Simple models of linear media are typically constructed using spring-dashpot models. The spring (Young's modulus E) emulates the elastic part of the response while the dashpot (or damper, viscosity η_E) emulates the viscous response.

So, we have

$$\begin{aligned} \sigma &= E\gamma \\ \sigma &= \eta_E \dot{\gamma} \end{aligned} \tag{18}$$

$$\eta_E = \tau E, \tag{19}$$

where τ is the relaxation time of the material.

For a spring-dashpot series model, we have

$$\sigma = \sigma_s = \sigma_d \tag{20}$$

The difference lies in the strain experienced by the two elements

$$\begin{aligned} \gamma &= \gamma_s + \gamma_d \\ \implies \dot{\gamma} &= \dot{\gamma}_s + \dot{\gamma}_d \\ \implies \sigma_s &= E\gamma_s \quad \text{and} \\ \sigma_d &= \eta_E \dot{\gamma}_d \end{aligned} \tag{21}$$

These are the equations for extension, but the same can be done for shear stress.

Creep: Apply tensile stress $\sigma_{E,0}$ which is held constant at later time (i.e. step input)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = 0 \implies \frac{\mathrm{d}\sigma_s}{\mathrm{d}t} = 0 \tag{22}$$

$$\implies \frac{\mathrm{d}\sigma_{E,0}}{\mathrm{d}t} = \tag{23}$$

$$\begin{aligned} \int_0^t \mathrm{d}\gamma &= \int_0^t \frac{\sigma_{E,0}}{\eta_E} \mathrm{d}t \\ \implies \gamma(t) - \gamma(0) &= \sigma_{E,0} \frac{t}{\eta_E} \\ \implies \frac{\gamma(t)}{\sigma_{E,0}} &= \frac{\gamma(0)}{\sigma_{E,0}} + \frac{t}{\eta_E} \end{aligned} \tag{24}$$

Tensile compliance is defined as the inverse of the Young's modulus.

Something-something dynamic experiment.

$$\sigma_E(t) = \sigma_{E,0}^* e^{i\omega t} \tag{25}$$

We have the equation for the Maxwell element

$$\frac{\mathrm{d}\gamma}{\mathrm{d}t} = \frac{1}{E}\frac{\mathrm{d}\sigma_E}{\mathrm{d}t} = \frac{\sigma_E}{\eta_E} \tag{26}$$

$$i\omega\gamma^* t = \frac{1}{E}i^i + \frac{\sigma_{E,0}^*}{\eta_E} \tag{27}$$