BP206T · B.PHARM THEORY

BP206T Physical Pharmaceutics

Unit IV — Rheology

Final Study Notes

Pills & Python Notes

From-zero teaching standard: every technical term is defined before use.

Syllabus coverage: Unit IV (8 hours).

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Chapter 4 — Rheology: Flow Behaviour, Thixotropy, Viscometers and Applications

4.1 Learning objectives

After studying this chapter, you will be able to:

1. Define rheology, viscosity, shear stress, and shear rate.
2. Distinguish Newtonian from non-Newtonian systems, and name the three non-Newtonian types.
3. Explain thixotropy, negative thixotropy, bulges and spurs, and how thixotropy is measured.
4. Classify viscometers into single-point and multi-point types with examples.
5. Define viscoelasticity and psycho-rheology.
6. List pharmaceutical applications of rheology.

4.2 The basic idea — what is rheology?

> **Definition — Rheology:** The science of the **flow and deformation of matter** — how liquids pour, how semisolids spread, and how solids bend. (From the Greek *rheo*, "to flow".)

Two quantities describe any flow:

- **Shear stress (S):** The force applied per unit area — how hard you push. Unit: pascal (Pa).
- **Shear rate (G):** How fast one layer of liquid slides past the next — how fast it flows. Unit: per second (s^{-1}).
- **Viscosity (η):** The resistance to flow = shear stress ÷ shear rate ($\eta = S/G$). Unit: pascal-second (Pa·s). Thick honey has high viscosity; water has low viscosity.

> **Analogy:** Spreading butter. Shear stress = how hard you press the knife; shear rate = how fast the butter spreads; viscosity = how much the butter resists. Cold butter (high viscosity) fights you; melted butter (low viscosity) flows easily.

> **Worked numerical — Newtonian viscosity (all steps): Question:** A liquid experiences a shear stress of 5 Pa at a shear rate of 2.5 s^{-1}. Calculate its viscosity. **Solution:** $\eta = S/G = 5 / 2.5 =$ **2 Pa·s**. (If the same value is obtained at every shear rate, the liquid is Newtonian — see below.)

4.3 Newtonian systems

- **Definition:** A system whose **viscosity stays constant** no matter how fast you shear it — the flow curve (shear stress vs shear rate) is a **straight line through the origin**.
- **Examples:** Water, glycerin, simple syrups, dilute solutions.
- **Worked example:** Water has $\eta \approx 1$ cP whether poured slowly from a glass or pumped fast through a pipe — same viscosity at every shear rate.
- **Analogy:** A honest shopkeeper who charges the same price no matter how much you buy — the "rate" never changes.

4.4 Non-Newtonian systems

Viscosity **changes** with shear rate. Three types are in the syllabus:

4.4.1 Plastic flow (Bingham bodies)

- The material **does not flow at all until a minimum stress — the yield value — is applied**; after that it flows like a Newtonian liquid.
- **Example:** Toothpaste — it sits on the brush (no flow under gravity) but flows when you squeeze (stress above yield value). Also: concentrated suspensions, ointments.
- **Diagram:** Flow curve starts not at the origin but at the yield value on the stress axis, then rises linearly.

4.4.2 Pseudoplastic flow (shear-thinning)

- **Viscosity decreases as shear rate increases** — the faster you stir, the thinner it gets.
- **Example:** Natural gum tragacanth mucilage, methylcellulose solutions, most pharmaceutical suspensions. Shake the bottle (high shear) → thin and pourable; at rest (low shear) → thick and holds particles suspended.
- **Why it happens:** Long polymer chains are tangled at rest; shearing aligns them in the flow direction so they slide past each other easily.
- **Pharmacy gold:** This is the ideal behaviour for suspensions — thin when pouring, thick when standing.
- **Analogy:** A crowd leaving a stadium through a narrow gate — at rest everyone is tangled; once moving in one direction, the crowd streams smoothly.

4.4.3 Dilatant flow (shear-thickening)

- **Viscosity increases as shear rate increases** — the harder you stir, the thicker it gets.
- **Example:** Concentrated suspensions with more than about 50% solids (e.g., starch paste, wet beach sand).
- **Analogy:** Wet sand at the beach — press slowly and your foot sinks; stamp hard and the sand feels rock-solid. Cornflour (cornstarch) mixed with a little water is the classic kitchen demo: stir slowly = liquid; punch it = solid.

System	Viscosity vs shear rate	Flow curve	Example
Newtonian	Constant	Straight line through origin	Water, syrup
Plastic	Flows only above yield value	Line starting at yield value	Toothpaste
Pseudoplastic	Decreases (shear-thinning)	Curve bending down	Gum suspensions
Dilatant	Increases (shear-thickening)	Curve bending up	Concentrated starch paste

> **Common confusion:** Pseudoplastic (thins when sheared) vs dilatant (thickens when sheared) — remember "**P**seudoplastic = **P**ourable when shaken".

4.5 Thixotropy

4.5.1 What is thixotropy?

- **Definition:** A **time-dependent** decrease in viscosity under constant shear, with **slow recovery** when the shear is removed. Stir it → thin; leave it alone → thick again, but the recovery takes time.
- **Rheogram (flow curve):** If you increase the shear rate and then decrease it, the up-curve and down-curve do not overlap — they form a **hysteresis loop**. The **area of the loop measures the degree of thixotropy** (bigger loop = more thixotropic).
- **Example:** Bentonite gels, some ointment bases, ketchup (the classic: shake the bottle, it pours; leave it, it sets again).

4.5.2 Bulges and spurs

- On the **down-curve** of a thixotropic rheogram, the curve may show irregular **bulges and spurs** (little bumps) — these reveal that the internal structure is breaking down unevenly as shear is reduced.
- Their presence and shape help characterise the material's structural breakdown — an exam-favourite detail.

4.5.3 Negative thixotropy (rheopexy / antithixotropy)

- **Definition:** The opposite — viscosity **increases** with time under constant shear.
- **Example:** Certain concentrated clay suspensions.
- **Analogy:** Thixotropy is like a tired crowd that sits down when pushed and slowly stands up again; negative thixotropy is like a crowd that links arms tighter the more you push.

> **Key takeaway:** Thixotropy = thin with time under shear, recovers at rest (hysteresis loop area measures it). Negative thixotropy = thickens with time under shear.

4.6 Determination of rheological properties — viscometers

Viscometers are divided by how many shear-rate points they measure:

4.6.1 Single-point viscometers (one shear rate)

Used for **Newtonian** liquids (one point is enough since viscosity is constant).

- **Capillary viscometer (Ostwald/Ubbelohde):** Liquid flows through a thin capillary under gravity; flow time ∝ viscosity. Simple, cheap, very common in QC labs.
- **Falling-sphere viscometer (Hoeppler):** Time for a ball to fall through the liquid ∝ viscosity.
- **Analogy:** Timing a marble sinking through honey vs water — the slower fall means higher viscosity.

4.6.2 Multi-point viscometers (many shear rates)

Used for **non-Newtonian** systems (viscosity changes, so you need the whole curve).

- **Cup-and-bob (MacMichael / Couette):** Liquid in a cup, a bob (cylinder) rotates inside; measures torque at several speeds.
- **Cone-and-plate:** A cone rotates on a flat plate with a tiny sample between — uniform shear rate, needs very little sample; excellent for semisolids.
- **Brookfield viscometer:** A spindle rotates in the sample; the drag on the spindle gives viscosity at each speed — the workhorse of pharmaceutical QC for creams, gels, and suspensions.

Type	Examples	Points	Best for
Single-point	Ostwald capillary, falling sphere	One	Newtonian liquids
Multi-point	Brookfield, cone-and-plate, cup-and-bob	Many (full curve)	Non-Newtonian systems

Diagram to sketch: A Brookfield viscometer — stand, rotating spindle dipping into a beaker of cream, dial/digital readout; label "torque → viscosity at each rpm". Beside it, a thixotropic rheogram: up-curve and down-curve forming a loop, with a small bulge marked on the down-curve.

4.7 Viscoelasticity

- **Definition:** Materials that show **both** viscous flow (like a liquid) **and** elastic recovery (like a rubber band) at the same time.
- **Example:** Ointment bases and gels — press them and they deform and flow a little, but partly spring back when you release.
- **Simple models:** The **Maxwell model** (spring and dashpot in series — more liquid-like) and the **Voigt model** (spring and dashpot in parallel — more solid-like). A **creep test** (apply constant stress, watch deformation over time) reveals viscoelastic behaviour.
- **Pharmacy link:** An ointment must be viscoelastic — fluid enough to spread on skin, elastic enough to stay in the tube and keep its shape.

4.8 Psycho-rheology

- **Definition:** The study of how rheological properties are **perceived by the user** — the link between measured viscosity/spreadability and what a patient feels.
- **Examples:** A cream that "spreads easily but doesn't feel runny"; a syrup that "pours well but feels rich in the mouth"; toothpaste ribbon that holds its shape on the brush.
- **Why it matters:** A medicine that feels unpleasant will not be used — patient compliance depends on psycho-rheology as much as on the drug itself.

4.9 Applications of rheology in pharmacy

1. **Suspensions:** Pseudoplastic + thixotropic vehicles pour easily yet keep particles suspended (Chapter 2 in action).
2. **Emulsions and creams:** Viscosity controls spreadability, stability against creaming, and skin feel.
3. **Manufacturing:** Pumping, mixing, and filling need known viscosities — too thick clogs the line, too thin splashes.
4. **Syringeability:** Injectable suspensions must flow through a needle — viscosity at high shear (in the needle) is what counts.
5. **QC:** Brookfield viscosity is a routine release test for gels, creams, and lotions in Indian pharma plants.
6. **Patient compliance:** Psycho-rheology — mouthfeel of syrups, spreadability of ointments.

India context: Indian generic companies run Brookfield viscosity as a daily QC test on topical products; the hot climate means formulators must check viscosity at elevated temperatures too, since creams thin out in summer and may cream or leak.

Mnemonic — "NPPD-T": **N**ewtonian, **P**lastic, **P**seudoplastic, **D**ilatant — the four flow types; **T**hixotropy is the time-dependent one on top.

Common mistake: Calling any shear-thinning liquid "thixotropic". Shear-thinning (pseudoplastic) is about shear *rate*; thixotropy is about *time* at constant shear. A pseudoplastic liquid thins instantly; a thixotropic one thins gradually and recovers slowly.

4.10 One-minute revision — Chapter 4

- Rheology = flow science; η = shear stress / shear rate.
- Newtonian: constant viscosity (water). Non-Newtonian: plastic (yield value, toothpaste), pseudoplastic (shear-thinning, suspensions), dilatant (shear-thickening, wet sand).
- Thixotropy: thins with time under shear, recovers at rest; hysteresis loop area measures it; bulges/spurs on down-curve. Negative thixotropy = thickens with time.
- Viscometers: single-point (Ostwald, falling sphere) for Newtonian; multi-point (Brookfield, cone-and-plate, cup-and-bob) for non-Newtonian.
- Viscoelasticity = viscous + elastic (ointments). Psycho-rheology = how flow feels to the patient.
- Uses: suspensions, creams, pumping/filling, syringeability, QC, compliance.

4.11 Practice questions — Chapter 4

MCQs

1. The unit of viscosity is: (a) Pa (b) s^{-1} (c) Pa·s (d) N/m
2. Toothpaste is an example of: (a) Newtonian flow (b) plastic flow (c) dilatant flow (d) turbulent flow
3. The area of the hysteresis loop measures: (a) yield value (b) degree of thixotropy (c) density (d) surface tension
4. A Brookfield viscometer is a: (a) single-point viscometer (b) multi-point viscometer (c) capillary viscometer (d) falling-sphere viscometer
5. Negative thixotropy is also called: (a) rheopexy (b) plasticity (c) dilatancy (d) creep

Short answers

1. Define rheology, shear stress, shear rate, and viscosity.
2. What is a yield value? Give an example.
3. Distinguish pseudoplastic from dilatant flow with examples.
4. What are bulges and spurs?
5. Define viscoelasticity and psycho-rheology with one example each.

Long answers

1. Classify systems based on flow behaviour with flow-curve diagrams and examples.
2. Write a note on thixotropy: definition, measurement, bulges and spurs, negative thixotropy, and pharmaceutical importance.
3. Classify viscometers with examples. Which type would you choose for a non-Newtonian cream, and why?

Numericals

1. A syrup shows shear stress 12 Pa at shear rate 4 s^{-1} and 30 Pa at 10 s^{-1}. Is it Newtonian? Calculate viscosity. (Answer: yes — η = 3 Pa·s at both points.)
2. A gel's viscosity falls from 50 Pa·s to 20 Pa·s after 2 minutes of shearing at constant rate, and recovers to 48 Pa·s after 30 minutes at rest. Name the phenomenon and justify.

Application-based

1. A company wants a calamine-type suspension that pours easily from the bottle but does not settle quickly on the shelf. Which flow behaviour should the vehicle have, and which viscometer would you use to develop it? Justify both choices.

Viva

1. Why is a single-point viscometer not enough for a cream?
2. How does thixotropy help a suspension formulation?

UNIT IV — INFOGRAPHIC CONCEPT (for the PDF designer): A flow-curve gallery titled "How Medicines Flow". Four panels showing shear stress vs shear rate curves: Newtonian (straight line through origin — water drop icon), plastic (line starting at yield value — toothpaste tube), pseudoplastic (curve bending down — shaking suspension bottle), dilatant (curve bending up — wet sand). Below: a hysteresis loop labelled "thixotropy — loop area = degree", with a small bulge marked on the down-curve. Side strip: viscometer icons — capillary tube (single-point) vs Brookfield spindle (multi-point). Bottom banner: "Pseudoplastic + thixotropic = ideal suspension vehicle".

COMBINED REFERENCES — BP206T UNITS III–V

1. Sinko, P.J., *Martin's Physical Pharmacy and Pharmaceutical Sciences* (latest edition).
2. Allen, L.V. and McPherson, T.B., *Ansel's Pharmaceutical Dosage Forms and Drug Delivery Systems* (latest edition).
3. Adejare, A., *Remington: The Science and Practice of Pharmacy* (latest edition).
4. Aulton, M.E. and Taylor, K.M.G., *Aulton Pharmaceutics: The Design and Manufacture of Medicines*, Elsevier (latest edition).