# Complex Disordered Systems

Anisotropy and orientational order

Francesco Turci

# What are Liquid Crystals?

- Intermediate phases between **liquids** and **crystals**
- Exhibit **orientational order** without full positional order
- Formed by **anisotropic particles** (rods, ellipsoids, plates)
- Key property: **decoupling** of orientational and translational degrees of freedom

# Types of Order

**Positional order**: Regular arrangement of particle positions (lattice)

**Orientational order**: Angular alignment of particles

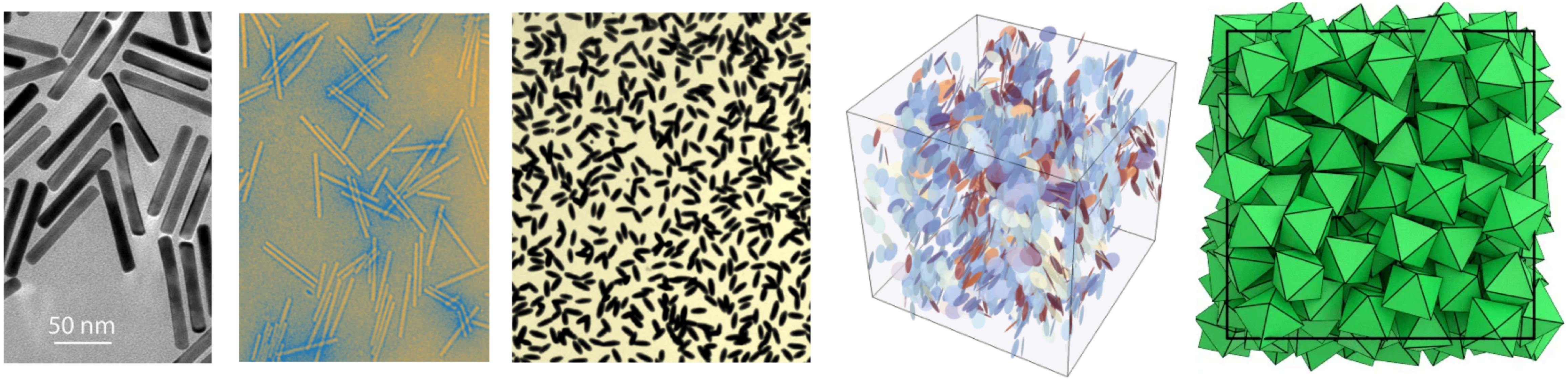
| Phase | Positional | Orientational |
|---|---|---|
| Crystal | Yes (3D) | Yes |
| Liquid | No | No |
| **Liquid Crystal** | **Partial/No** | **Yes** |

The strength of the ordering is determined by the **decay** of correlation functions:

- in liquids we have at best short range order (expoential decay of the oscillations in the $g(r)$)
- in crystals we have long-range order — correlations do not decay (sharp Bragg peaks in $S(\mathbf{k})$ and $g(r)$); this order is only disrupted by defects (dislocations, grain boundaries) on macroscopic scales

# Anisotropic Particles

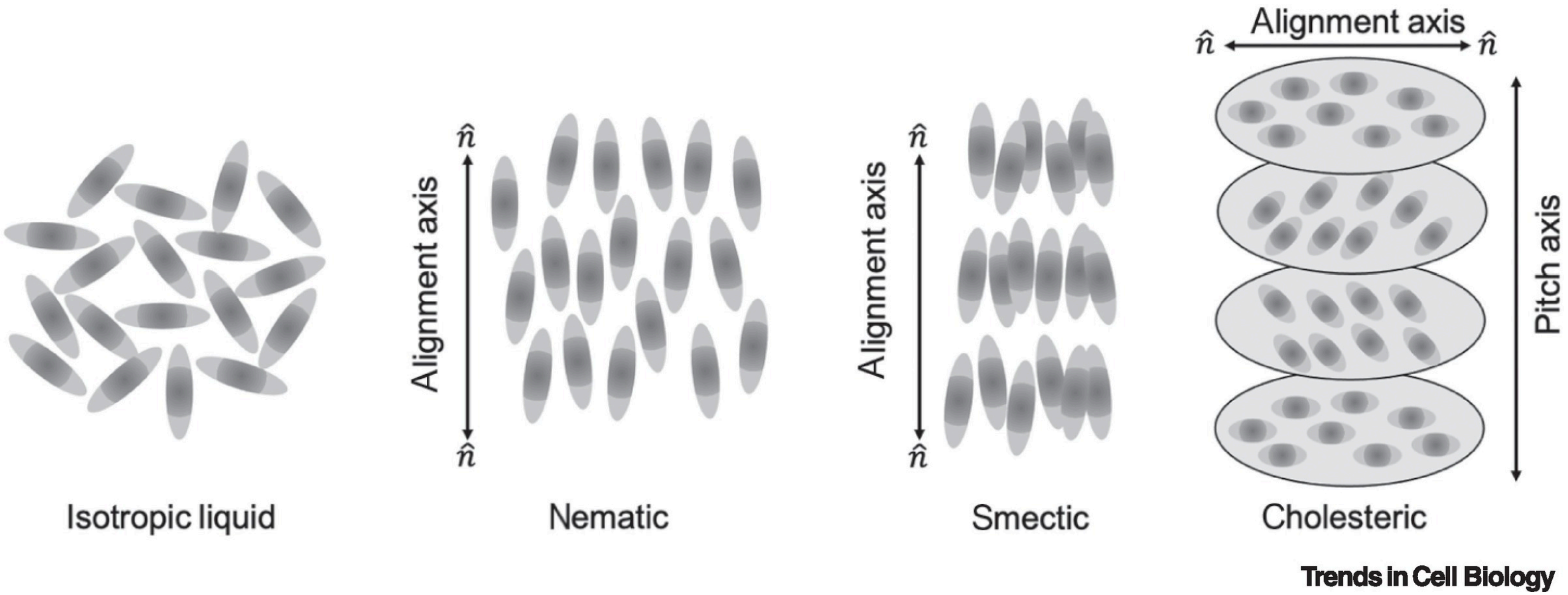
Many natural and artificial systems have anisotropy




Golden nanorods, tobacco virus rods , ellipsoidal silica-coated hematite particles, hard platelets in the isotropic phase, and an arrangement of hard octahedra

# Liquid Crystal Phases

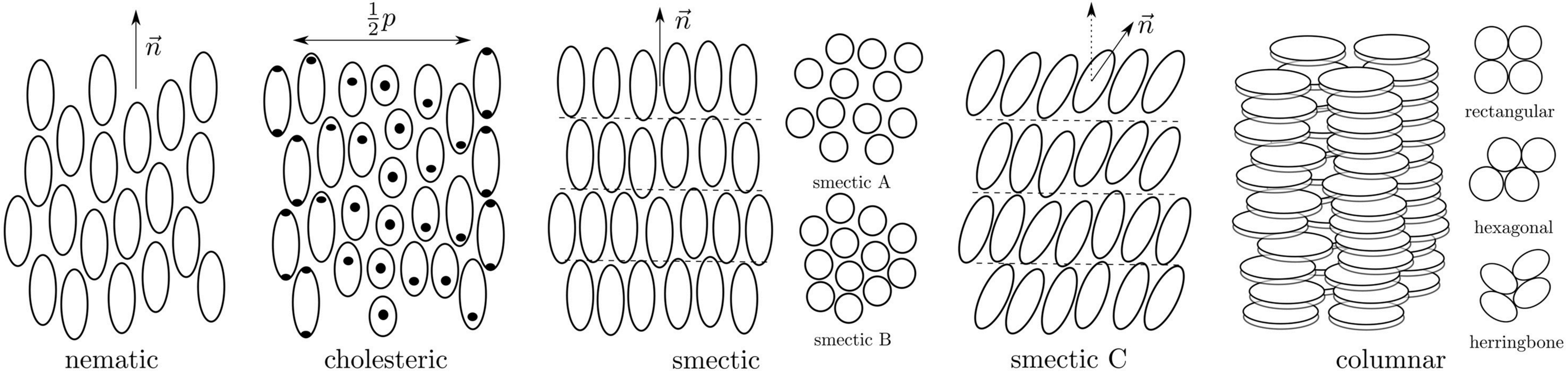
- **Isotropic fluid**: No long-range order (like normal liquids)
- **Nematic phase**: Orientational order, no positional order.
- Particles align along a common direction: the **director $\mathbf{n}$**
- **Smectic phase**: Layered structure with orientational order
  - Positional order in 1D (layers)
  - Liquid-like within layers
- **Columnar phase**: Particles stack into columns
  - 2D positional order
- **Crystal**: Full 3D positional + orientational order
- **Chiral nematic (Cholesteric)**: Director forms a helix




Different liquid crystalline phases, from Doostmohammadi and Ladoux, Trends in Cell Biology (2002)

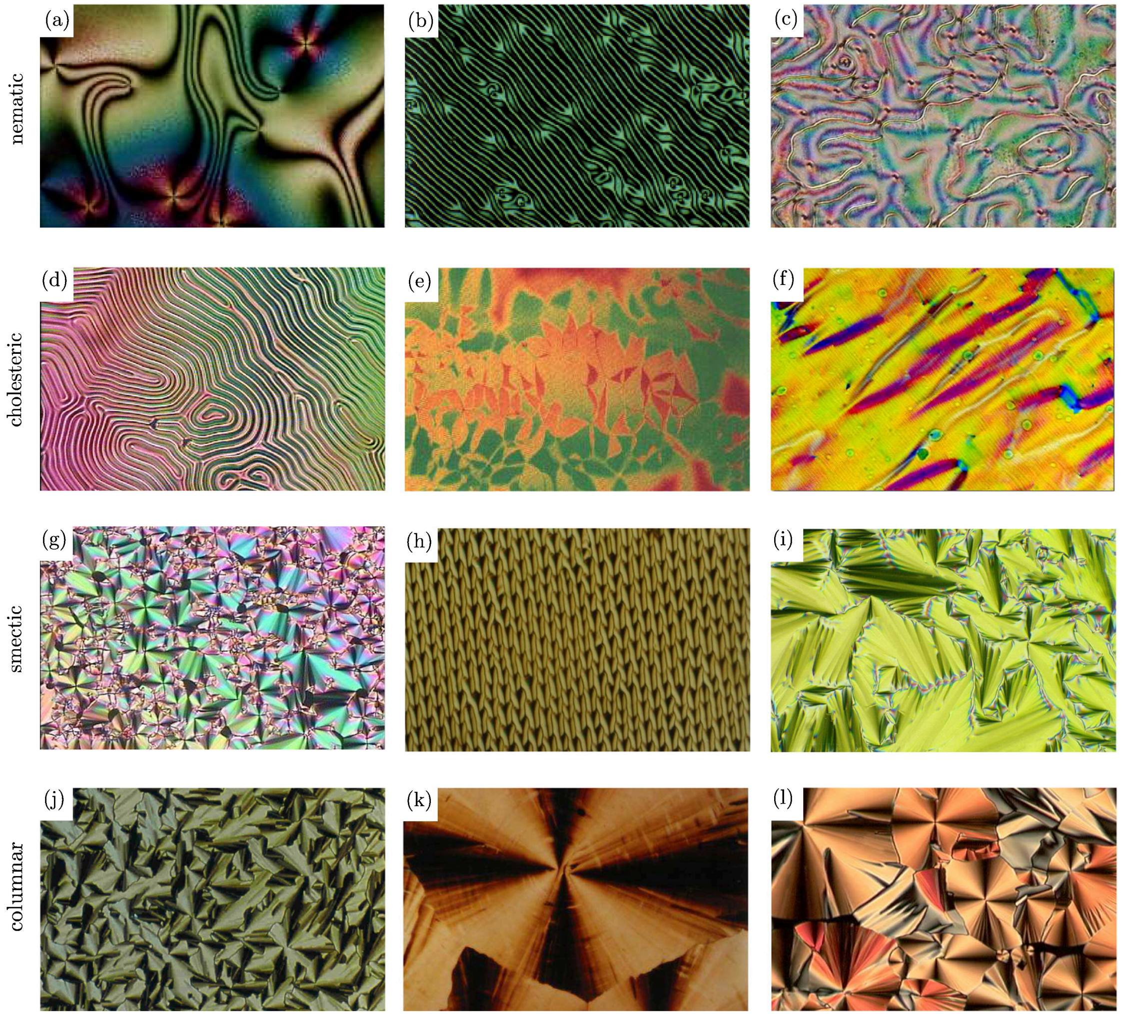
# Phase Comparison

| Phase | Positional Order | Orientational Order |
|---|---|---|
| Isotropic | No | No |
| Nematic | No | Yes (long-range) |
| Smectic | Yes (1D: layered) | Yes |
| Columnar | Yes (2D: columns) | Yes |
| Cholesteric | No | Yes (helical) |
| Crystal | Yes (3D: lattice) | Yes |




Orientation and order in various phases, from Andrienko, Journal of Molecular Liquids (2018)

# Phase Comparison: Textures and Defects




Examples of phases/textures: (a) Nematic with surface point defects. (b) Thin nematic film on isotropic substrate. (c) Thread-like nematic texture. (d) Cholesteric fingerprint (helical axis in plane). (e) Short-pitch cholesteric (standing helix) with vivid colors. (f) Long-range cholesteric DNA alignment in a magnetic field. (g, h) Focal conic textures of chiral smectic A. (i) Focal conic texture of chiral smectic C. (j) Hexagonal columnar spherulitic texture. (k) Rectangular discotic phase. (l) Hexagonal columnar phase. From Andrienko, Journal of Molecular Liquids (2018)

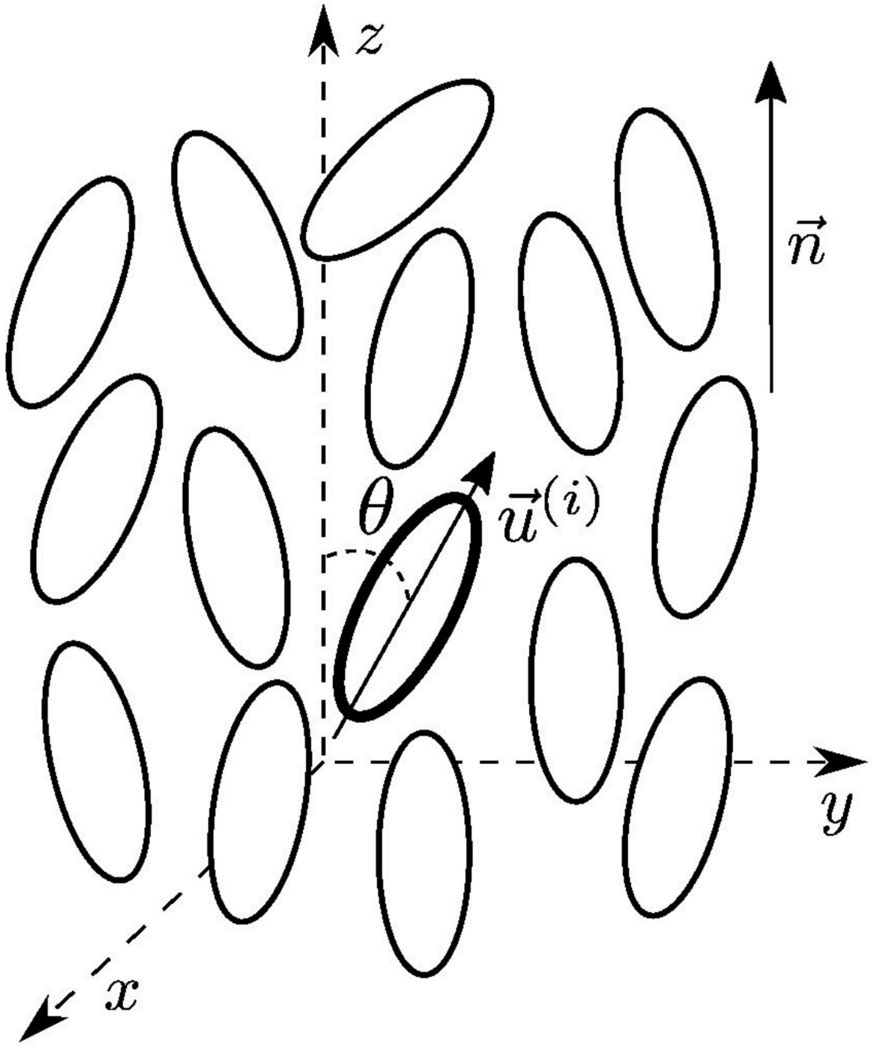
# Orientation and director

- Orientation of a rigid rod is described by a **unit vector $\mathbf{u}$** along its long axis
- The particles are head-tail symmetric, so they have a centre of symmetry
- Because $\mathbf{u}$ and $-\mathbf{u}$ are equiprobable, on average

$$\langle \mathbf{u} \rangle = 0$$

- Vectorial order parameter is zero. The next non-trivial invariant is a **second rank tensor**

| Tensor | Rank | Example order parameter |
|---|---|---|
| Scalar | 0 | Scalar nematic S (degree of alignment), e.g., S = ⟨P2(cos θ)⟩ |
| Vector | 1 | Polarization or magnetization vector P / M (polar order) |
| Second-rank tensor | 2 | Matrices, Alignment tensor $Q_{ij}$ (nematic order) |
| Third-rank tensor | 3 | Octupolar / tetrahedral order $T_{ijk}$ |




The local orientation vector of a molecule $\mathbf{u}$ and the director $\mathbf{n}$

# The Nematic Order Parameter

For **head-tail symmetric** rods, we cannot simply average orientations.

Instead, construct the **alignment tensor**

$$\mathbf{Q} = \frac{d}{2} \left\langle \mathbf{u}_i \otimes \mathbf{u}_i - \frac{1}{d}\mathbf{I} \right\rangle$$

- we make it **traceless** by removing the identity
- we make it include quadratic combinations (it is as **second moment**, essentially the covariances)
- $\otimes$ is the outer product, giving a $d \times d$ matrix:

$$\mathbf{u} \otimes \mathbf{u} = \begin{pmatrix} u_1 u_1 & u_1 u_2 & \cdots & u_1 u_d \\ u_2 u_1 & u_2 u_2 & \cdots & u_2 u_d \\ \vdots & \vdots & \ddots & \vdots \\ u_d u_1 & u_d u_2 & \cdots & u_d u_d \end{pmatrix}$$

where $d$ is dimensionality, $\mathbf{u}_i$ is the unit orientation vector. For us, $d = 2, 3$

# Extracting Order

- Diagonalisation: it extracts the invariants (the properties that do not change wrt a coordinate change or rotations)
- **Largest eigenvalue** $\rightarrow$ scalar order parameter $\mathcal{S}$
- **Corresponding eigenvector** $\rightarrow$ director $\mathbf{n}$

$$\mathcal{S} \in [0, 1]$$

- $\mathcal{S} = 0$: isotropic (random orientations)
- $\mathcal{S} = 1$: perfect nematic order (all aligned)

**Caution**

The nematic order parameter $\mathcal{S}$ should not nbe cconfused with the entropy $S$.

# 2D Nematic Order Parameter

In two dimensions, the director is simply characterised by the angle $\psi$ expressed as

$$\psi = \frac{1}{2}\,\mathrm{atan2}(\sin 2\theta_i, \cos 2\theta_i).$$

and the nematic order parameter is simply

$$\mathcal{S} = \sqrt{\langle\cos 2\theta_i\rangle^2 + \langle\sin 2\theta_i\rangle^2}$$

# 3D Nematic Order Parameter

In 3D, choosing coordinates along director $\mathbf{n}$:

$$\mathcal{S} = \frac{1}{2}\left\langle 3\cos^2\theta_i - 1\right\rangle$$

where $\theta_i$ is angle between particle $i$ and director.

This uses the **Legendre polynomial** $P_2(\cos\theta)$ to enforce head-tail symmetry.

- Lowest nontrivial rotationally-invariant scalar that is even under $\mathbf{n} \to -\mathbf{n}$

| n | Legendre polynomial $P_n(x)$ | Head-tail symmetric? |
|---|---|---|
| 0 | $P_0(x) = 1$ | Yes (even: $P_0(-x) = P_0(x)$) |
| 1 | $P_1(x) = x$ | No (odd: $P_1(-x) = -P_1(x)$) |
| 2 | $P_2(x) = \frac{1}{2}(3x^2 - 1)$ | Yes (even: $P_2(-x) = P_2(x)$) |
| 3 | $P_3(x) = \frac{1}{2}(5x^3 - 3x)$ | No (odd: $P_3(-x) = -P_3(x)$) |
| 4 | $P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$ | Yes (even: $P_4(-x) = P_4(x)$) |