

Soft Matter In and Out of Equilibrium



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- Introduction and motivation
- Critical states of matter
- Smectics
- Cholesterics
- Columnar phase
- Polymerized membranes
- Elastomers



Fluctuations, nonlinearities and phase transitions

Upshot of 50 years of research on fluctuations and critical phenomena:

usually Fluctuations <u>and</u> nonlinearities are only important near isolated critical points (continuous phase transition)



well-known exception: disordered systems, FQHE,...



Properties of critical phases



- spontaneously broken continuous symmetry
- nontrivial fixed point of strongly interacting Goldstone modes (c.f. nonlinear O(N) sigma-model)
- universal power-law correlation functions and amplitude ratios (<u>throughout the phase</u>)
- no fine-tuning to a critical point required
- quantum analogs? road to 3d "Luttinger liquids"?



$$\rho(\mathbf{x}) = \rho_0 + \operatorname{Re}[e^{i\mathbf{q_0}\cdot\mathbf{x}}\psi(\mathbf{x})] = \rho_0 + |\psi|\cos\left[q_0(z-u(\mathbf{x}))\right]$$

Smectics

• elasticity by symmetry or via de Gennes model or :

$$\mathcal{H}_{sm} = \frac{1}{2} J \left[(\nabla^2 \rho)^2 - 2q_0^2 (\nabla \rho)^2 \right] + \frac{1}{2} t \rho^2 - w \rho^3 + v \rho^4 + \dots$$

• express in terms of u(x):

u(x)

 $\psi \sim e^{-i q u}$

$$\mathcal{H}_{sm} = J\rho_0^2 \left[\frac{1}{4} q^2 (\nabla^2 u)^2 + \left(q\mathbf{q} \cdot \nabla u - \frac{1}{2} q^2 (\nabla u)^2 \right)^2 + 4(q^2 - q_0^2) \left(q\mathbf{q} \cdot \nabla u - \frac{1}{2} q^2 (\nabla u)^2 \right) \right]$$

nonlinear strain u_{aq}

• choose the $\mathbf{q} = q_0$ along z:

 $\mathcal{H}_{sm} = \frac{1}{2}K(\nabla^2 u)^2 + \frac{1}{2}B\left(\partial_z u - \frac{1}{2}(\nabla u)^2\right)^2$

Undulation instability on dilation

Strain-induced instability of monodomain smectic A and cholesteric liquid crystals

Noel A. Clark and Robert B. Meyer*

Gordon McKay Laboratory, Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 9 February 1973)

A mechanism is proposed for the observed mechanical instability of monodomain smectic A and cholesteric liquid crystals subjected to uniaxial dilative stress. The threshold conditions for the instability are derived, and the possible roles of dislocations in controlling the instability and in producing large plastic distortions are discussed.

$\mathcal{H}_{sm} = \frac{1}{2}K(\nabla^2 u)^2 + \frac{1}{2}B\left(\partial_z u - \frac{1}{2}(\nabla u)^2\right)^2$





 $E[u_0(\mathbf{r})] = 0,$ for $u_0(\mathbf{r}) = z(\cos \theta - 1) + x \sin \theta$

FIG. 1. Periodic undulation of the layers of a dilated smectic A liquid crystal. Regions of maximum dilation are marked S.

• harmonic approximation: $H_{sm} = \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \left(Kk_{\perp}^4 + Bk_z^2 \right) |u_{\mathbf{k}}|^2$,

u(x) Sm harmonic properties

$$\begin{split} \langle u^2 \rangle_0^T &= \int_{L_{\perp}^{-1}}^{\Lambda_{\perp}} \frac{d^d k}{(2\pi)^d} \frac{T}{Bk_z^2 + Kk_{\perp}^4}, & \text{power-law disordered smectic} \\ & \text{for } x > \xi, \text{ with } u_{\text{rms}} \sim a \\ & \approx \begin{cases} \frac{T}{2\sqrt{BK}} C_{d-1} L_{\perp}^{3-d}, \ d < 3, \\ \frac{T}{4\pi\sqrt{BK}} \ln q_0 L_{\perp}, \ d = 3, \end{cases} & \xi_{\perp} \approx \begin{cases} \frac{a^2\sqrt{BK}}{T} \sim \frac{K}{Tq_0}, & d = 2, \\ ae^{4\pi a^2\sqrt{BK}/T} \sim ae^{\frac{cK}{Tq_0}}, & d = 3, \end{cases} \\ & \text{with } \eta = \frac{q_0^2 T}{8\pi\sqrt{BK}}. \end{split}$$

• density is uniform:

$$egin{aligned} &\langle
ho_q(\mathbf{x})
angle_0 &= 2
ho_0 \langle \cos\left[\mathbf{q}_0 \cdot \mathbf{x} - qu(\mathbf{x})
ight]
angle_0, & \textit{with} \ &= 2
ho_0 e^{-rac{1}{2}q_0^2 \langle u^2
angle_0} \cos\left(\mathbf{q}_0 \cdot \mathbf{x}
ight), & ilde{
ho}_0(L_\perp) &=
ho_0 \left\{ egin{aligned} e^{-L_\perp / \xi_\perp}, & d = 2, \ \left(rac{a}{L_\perp}
ight)^{\eta/2}, & d = 3, \end{aligned} \ &= 2 ilde{
ho}_0(L_\perp) \cos\left(\mathbf{q}_0 \cdot \mathbf{x}
ight), & o 0, & \text{for } L_\perp \to \infty, \end{aligned}$$

• harmonic approximation: $H_{sm} = \frac{1}{2} \int \frac{d^d k}{(2\pi)^d} \left(Kk_{\perp}^4 + Bk_z^2 \right) |u_{\mathbf{k}}|^2$,

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S(q)

0

0

2Q

30

• quasi-Bragg peaks (3d), Lorentzian (2d):

$$S(\mathbf{q}) = \int d^3x \langle \delta \rho(\mathbf{x}) \delta \rho(0) \rangle e^{-i\mathbf{q}\cdot\mathbf{x}},$$

$$\approx \frac{1}{2} \sum_{q_n} |\rho_{q_n}|^2 \int_{\mathbf{x}} \langle e^{-iq_n(u(\mathbf{x})-u(0))} \rangle_0 e^{-i(\mathbf{q}-q_n\hat{z})\cdot\mathbf{x}},$$

$$\approx \frac{1}{2} \sum_n \frac{|\rho_{q_n}|^2}{|q_z - nq_0|^{2-n^2\eta}}, \text{ for } d = 3,$$





Smectic nonlinearities

Grinstein-Pelcovits '81, L.R. '13

• renormalize elastic moduli in length-dependent ways:

 $\delta B \approx -\left[T\left(\frac{B}{K^3}\right)^{1/2} L_{\perp}^{3-d}\right] B \to \delta B \approx -\frac{1}{8}gB\delta\ell$ $\delta K \approx \frac{1}{16}gK\delta\ell$ $\frac{dg(\ell)}{d\ell} = (3-d)g - \frac{5}{32}g^2$





- color selective Bragg reflection from cholesteric planes
- temperature tunable pitch -> wavelength









number of Goldstone modes = dim[G/H] e.g., classical ferromagnet: $SO(3) \rightarrow SO(2) \rightarrow G/H = S_2$

• Exceptions:

- <u>quantum ferromagnet</u>: noncommuting symmetry generators $[S_x, S_y] = i S_z$
- <u>Higgs mechanism</u>: some of the GMs are "eaten" by gauge fields, e.g., superconductor, Standard model, crystals

Goldstone modes in a helical state

- Isotropic state: G = T × SO(3)
- Helical state: $H = T_x \times T_y \times U(1) = Diagonal[T_z,O_z(2)]$

--> <u>naively</u> 3 = dim[G/H = SO(3)] Goldstone modes

--> <u>actually</u> 1 phase (ϕ) = phonon (u) mode, defining "layers"



--> smectic elasticity (proposed by deGennes '72)?

Goldstone modes via symmetry

u

Q"

• small angle θ rotational invariance

--> cholesteric <--> smectic elasticity (deGennes '72)

$$\twoheadrightarrow \mathcal{H} = \frac{B}{2} (\partial_z u)^2 + \frac{K}{2} (\partial_{\perp}^2 u)^2$$

- derivation?
- consequences?
- differences?



Derivation of Goldstone modes theory

- Frank chiral elasticity or Dzyaloshinkii-Morya interaction $\mathcal{H} = K_s (\nabla \cdot \hat{n})^2 + K_b (\hat{n} \times \nabla \times \hat{n})^2 + K_t (\hat{n} \cdot \nabla \times \hat{n} + q_0)^2$ $= K \left[(\nabla \hat{n})^2 + 2q_0 \hat{n} \cdot \nabla \times \hat{n} \right] + \dots$
 - Helical background: $\hat{e}_1(\mathbf{r}) \times \hat{e}_2(\mathbf{r}) = \hat{e}_3(\mathbf{r}) \in S_2$ $\hat{n}(\mathbf{r}) = \hat{e}_1(\mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r} + \phi(\mathbf{r})) + \hat{e}_2(\mathbf{r}) \sin(\mathbf{q} \cdot \mathbf{r} + \phi(\mathbf{r}))$
 - U(1) gauge theory:

 $\mathcal{H} = \frac{K}{2} (\nabla \phi + \mathbf{a} + \mathbf{q} - q_0 \hat{\mathbf{e}}_3)^2 + \frac{K}{4} \left[(\nabla \hat{e}_3)^2 + 2q_0 \hat{e}_3 \cdot \nabla \times \hat{e}_3 \right]$ --> spin connection: $\mathbf{a} = \hat{e}_2 \cdot \nabla \hat{e}_1$



Derivation of Goldstone modes theory

- U(1) gauge theory of helical state: $\mathcal{H} = \frac{K}{2} (\nabla \phi + \mathbf{a} - q_0 \delta \hat{\mathbf{e}}_3)^2 + \frac{K}{4} \left[(\nabla \hat{e}_3)^2 + 2q_0 \hat{e}_3 \cdot \nabla \times \hat{e}_3 \right]$
- integrate out $\hat{e}_3 = \hat{e}_{3\perp} + \hat{z}\sqrt{1 \hat{e}_{3\perp}^2} \approx \hat{e}_{3\perp} + \hat{z}(1 \frac{1}{2}\hat{e}_{3\perp}^2)$:

--> Locking helical frame to pitch axis ("Higgs mechanism") $\hat{e}_{3\perp} pprox \left(
abla_\perp \phi + \mathbf{a}_\perp
ight) / q_0$

$$\mathcal{H} \approx \frac{K}{2} \left[\partial_z \phi + a_z + \frac{1}{2} (\nabla \phi + \mathbf{a})^2 \right]^2 + \frac{K}{4} \left[(\nabla (\nabla \phi + \mathbf{a}))^2 + 2q_0 \hat{z} \cdot \nabla \times (\nabla \phi + \mathbf{a}) \right]^2$$

helical state no defects --> single-valued u and curl-free a

$$\mathcal{H} \approx \frac{B}{2} \left[\partial_z u + \frac{1}{2} (\nabla u)^2 \right]^2 + \frac{K}{2} (\nabla^2 u)^2$$

- phonon $u(r) = -\phi(r)/q_0$, $B = K q_0^2$, $\overline{K} = K/2$



Rotational invariance of helical state

nonlinear Goldstone modes

$$\mathcal{H} \approx \frac{B}{2} \left[\partial_z u + \frac{1}{2} (\nabla u)^2 \right]^2 + \frac{\overline{K}}{2} (\nabla^2 u)^2$$

- encodes <u>large</u> rotational invariance

 $E[u_0(\mathbf{r})] = 0,$ for $u_0(\mathbf{r}) = z(\cos \theta - 1) + x \sin \theta$



- important at long length scales --> anomalous elasticity





Melting by dislocation unbinding into Isotropic

Membranes everywhere



biological membranes

graphene

2d polymers and gels

 MoS_2 , ZrP sheets







 fascinating interplay of statistical mechanics, field theory and geometry



- vanishing surface tension
- bending rigidity

in-plane elasticity





• in-plane order: anisotropy, hexatic,...



heterogeneity



Kantor, Kardar, Nelson '86





$$H = -\kappa \sum_{\langle ij \rangle} \hat{n}_i \cdot \hat{n}_j + \sum_{ij} V(|\mathbf{r}_i - \mathbf{r}_j|)$$

- want Landau description
- O(D) x O(d) order parameter:

$$\dot{\alpha} = \partial_{\alpha} \vec{r}$$



$$F[\vec{r}] = \int d^{D}x \left[\kappa (\partial^{2}\vec{r})^{2} + \tau_{\alpha} (\partial_{\alpha}\vec{r})^{2} + g(\partial_{\alpha}\vec{r})^{4} \right] + v \int d^{D}x d^{D}x' \delta^{(N)}(\vec{r}(\mathbf{x}) - \vec{r}(\mathbf{x}'))$$

bending rigidity self-avoidance

bending rigidity



ignore k_BT, minimize:

- Crumpled phase (τ_x > 0, τ_y > 0): $\langle \vec{t}_x \rangle = \langle \vec{t}_y \rangle = 0$ $\vec{r}_c = 0$
- Tubule phase (T_x > 0, T_y < 0): $\langle \vec{t}_x \rangle = 0, \langle \vec{t}_y \rangle > 0$ $\vec{r}_t = (0, t_y y, 0)$
- Flat phase (τ_x < 0, τ_y < 0): $\langle \vec{t}_x \rangle > 0, \langle \vec{t}_y \rangle > 0$



 $\vec{r_t} = (t_x x, t_y y, 0)$

*k*_B*T*, self-avoidance, heterogeneity, nonlinearities: ???





$$\frac{Crumpled phase}{F_c[\vec{r}] = \tau \int d^D x (\partial_\alpha \vec{r})^2 + v \int d^D x d^D x' \delta^{(N)}(\vec{r}(\mathbf{x}) - \vec{r}(\mathbf{x}'))}$$

- short-range order in normals $n_i \,.\, n_j \approx e^{-|i\,-j|/\xi}$
- disordered by k_BT

$$R_G \sim L^{\nu}$$

- analog of PM state of the normals
- fractal $M \sim R_{G}^{d_{F}}$ (Flory)



- $d_F = D/v \approx D(d+2)/(D+2) = 2.5, v \approx 0.8$
- self-avoiding interaction important: $R_G^0 \sim \sqrt{\ln L} \longrightarrow R_G \sim L^{4/5}$







- long-range order in the normals, breaks O(3) symmetry
 - geometric analog of 2D ferromagnet in the normals
 - "circumvents" Hohenberg-Mermin-Wagner-Coleman theorem, via order-from-disorder
- characterized by power-law roughness, $\zeta \approx 0.59$

LeDoussal, L.R. '92

"critical phase" with universal anomalous elasticity:
 κ(L) ~ L^η , μ(L) ~ L^{-η}u , σ = -1/3 (η_u = 4 - D - 2η) (agrees well with MC simulations by Bowick, Falcioni et al, '96, '97)



- free-energy density: $f[u_{\alpha}, \vec{h}] = rac{\kappa}{2} (\partial^2 \vec{h})^2 + \mu u_{\alpha\beta}^2 + rac{\lambda}{2} u_{\alpha\alpha}^2$
- nonlinear strain: $u_{\alpha\beta} = \frac{1}{2}(\partial_{\alpha}u_{\beta} + \partial_{\beta}u_{\alpha} + \partial_{\alpha}\vec{h} \cdot \partial_{\beta}\vec{h}) = \frac{1}{2}(g_{\alpha\beta} \delta_{\alpha\beta})$

• integrate out u_{α} : $f_{\text{eff}}[\vec{h}] = \frac{\kappa}{2} (\partial^2 \vec{h})^2 + \frac{1}{4} (\partial_{\alpha} \vec{h} \cdot \partial_{\beta} \vec{h}) K_{\alpha\beta,\gamma\delta} (\partial_{\gamma} \vec{h} \cdot \partial_{\delta} \vec{h})$

Gaussian curvature interaction: $R \frac{1}{\nabla^4} R$



• need a fully nonlinear treatment; physical interpretation?



- length-scale dependent moduli: $\kappa(k) \sim k^{-\eta}, \ \mu(k), \lambda(k) \sim k^{\eta_u}$
- Ward identity O(3) symmetry $(\partial u + \frac{1}{2}\partial h\partial h) \rightarrow \eta_u = 2 2\eta_{\kappa(L)} = \mu(L)h_{rms}(L)^2$
- RG with ε = 4-D, 1/d expansions (Aronovitz-Lubensky, David-Guitter, '88)



• SCSA exact: O(ϵ ,d), O(1/d,D), at d=D: $\eta = 0.82$, $\zeta = 0.59$, $\sigma = -1/3$



Tubule phase

L.R., Toner '97, '99



- long-range orientational order in 1d, breaks O(3) symmetry: $\langle \theta^2 \rangle \sim L^{-\eta} \ll 1 \longrightarrow {
 m stable to} \ k_B T > 0$
- nontrivial anomalous fixed point (with SA): $h_{rms}\sim L^{1/4}, R_G\sim L^{3/4}, \kappa(L)\sim L^{3/2}$



 $\kappa(L) \sim \mu(L) R_G(L)^2$

 $\rightarrow 2\nu = z(\eta_{\kappa} + \eta_{\mu})$



Tunable spontaneous anisotropy X. Xing, L.R. '04

 <u>spontaneous</u> in-plane nematic order (e.g., nematic elastomer membrane) -> reentrant flat phase:





- proteins, nano-pores, holes, network defects, ...
 - -> random distribution of interstitials, dislocation, disclinations, grain-boundaries, ...

L.R., LeDoussal '91, '92
Local heterogeneity
random stresses, preferred curvature:

$$f = \frac{\kappa}{2} (\partial^2 h - c(\mathbf{x}))^2 + \mu u_{\alpha\beta}^2 + \frac{\lambda}{2} u_{\alpha\alpha}^2 - u_{\alpha\beta} \sigma_{\alpha\beta}(\mathbf{x})$$

$$\eta = 0.45$$

$$\eta = 0.45$$

$$\zeta = 0.775$$
• "crumpled glass" ground state, anomalous elasticity:

$$\zeta = 0.775$$
• "crumpled glass" ground state

Open questions and implications

• systematic quantitative measurements e.g., graphene

- realization of the crumpling transition
- sheets with tunable anisotropy
- nature of glassy phases
- statistical mechanics of membranes with nontrivial background strain and topology (see e.g., vesicles: Nelson, et al.)

• redoing deformation analysis (Euler, Lame, crumpling,...) for free energy







Terentjev Finkelmann Ratna

"Solid" Liquid-Crystal



Thermal response and stress-strain relation



Properties: • spontaneous distortion (~ 400%) at T_{IN} , thermoelastic

- "soft" elasticity
- giant electrostriction

- Applications: *plastic displays*
 - switches
 - actuators
 - artificial muscle

Terentjev, et al

Nematic elastomer as heat engine



 monodomain nematic LCE

• 5cm x 5mm x 0.3mm

 lifts 30g wt. on heating, lowers it on cooling

large strain (>400%)

 $\eta \simeq 10^5 Pa$

H. Finkelmann, Shahinpoor, et al



Elastic theory of NE

• Construct rotationally invariant elastic theory of deformations about $\underline{\underline{u}}_0$ • Study fluctuations and heterogeneities about $\underline{\underline{u}}_0$

Must incorporate underlying rotational invariance of the nematic state

some distortions cost no energy: "soft" uniaxial solid $f[\vec{R}(\mathbf{x})] = f[O_T \vec{R}(O_R \mathbf{x})] \qquad u' \approx \frac{(r-1)}{2\sqrt{r}} \begin{pmatrix} 0 & \theta \\ \theta & 0 \end{pmatrix} = (\Lambda_0^T)^{-1} \, \delta u \, \Lambda_0^{-1}$

• Vanishing energy cost for: $\delta \underline{\underline{u}} = \underline{\underline{O}} \cdot \underline{\underline{u}}_0 \cdot \underline{\underline{O}}^T - \underline{\underline{u}}_0$

- <u>Harmonic</u> elasticity about nematic state: $\underline{\varepsilon} = \underline{u} \underline{u}_0$ $\mathcal{H}_{NE}^0 = \mu_{zi} \varepsilon_{zi}^2 + B_z \varepsilon_{zz}^2 + \mu_\perp \varepsilon_{ij}^2 + \lambda \varepsilon_{ii}^2 + \lambda_{zi} \varepsilon_{zz} \varepsilon_{ii}$ 0, required by rotational invariance
- <u>Nonlinear</u> elasticity about nematic state: $\mathcal{H}_{NE} = B_z w_{zz}^2 + \mu_{\perp} w_{ij}^2 + \lambda w_{ii}^2 + \lambda_{zi} w_{zz} w_{ii}$ $w_{zz} = \partial_z u_z + \frac{1}{2} (\nabla u_z)^2 \qquad w_{ij} = \frac{1}{2} (\partial_{(i} u_{j)} - \partial_i u_z \partial_j u_z)$

Fluctuations and heterogeneity



• Thermal fluctuations: $\mathcal{Z} = \operatorname{Trace}_{u}[e^{-\beta \mathcal{H}[u]}]$

• Heterogeneity random torques and stresses: *nematic elastomers are only <u>statistically</u> homogeneous and isotropic*

$$\mathcal{H}_{NE}^{real} = \mathcal{H}_{NE}[\underline{\underline{u}}] - \underline{\underline{\underline{u}}} \cdot \underline{\underline{\sigma}}(\mathbf{r}) - (\hat{n} \cdot \vec{g}(\mathbf{r}))^2$$

encodes heterogeneity Elastic "softness" leads to strong qualitative effects of thermal fluctuations and network heterogeneity

Predictions

Xing + L.R., PRL (2003)

 δu_{ij}

- <u>Universal</u> elasticity: $\overline{\langle |\delta u(q)|^2 \rangle} \sim q_{\perp}^{-4+\eta}$, for $r_{\perp} > \xi_{\perp} \sim K^2/\Delta$
- Non-Hookean elasticity: $\sigma_{zz} \sim (u_{zz})^{\delta}$, $\delta > 1$ (cf. non-Fermi liquid) σ_{ij} vanishing slope no linear response

- Length-scale dependent elastic moduli: $K_{\text{eff}}(L) \sim L^{\eta}, \quad \mu_{\text{eff}}(L) \sim L^{-\eta_{\mu}}, \quad B_{\text{eff}}(L) \sim B_0$
- Macroscopically incompressible: $\kappa_{\text{eff}} \sim \mu_{\text{eff}}(L) / B_{\text{eff}}(L) \rightarrow 0$
- $u_{xx} > 0 \Longrightarrow \begin{cases} u_{yy} = \frac{5}{7}u_{xx} \\ u_{zz} = -\frac{12}{7}u_{xx} \end{cases}$ • Universal Poisson ratios: $u_{zz} > 0 \implies u_{xx} = u_{yy} = -\frac{1}{2}u_{zz}$



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- spontaneously broken continuous symmetry
- nontrivial fixed point of strongly interacting Goldstone modes (c.f. nonlinear O(N) sigma-model)
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