Anomalous elasticity of 2D flexible materials

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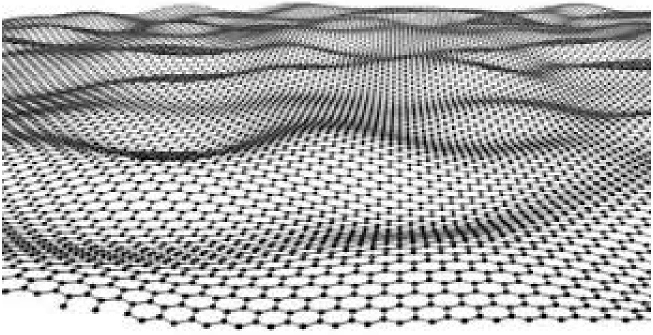
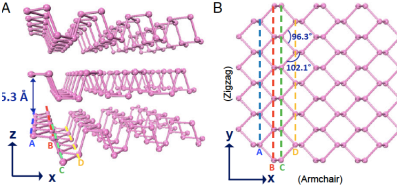
- flexural fluctuations of a 2D crystalline material



[adopted from Meyer et al. (2007)]

- the first and mostly known example is graphene

- 2D materials with orthorhombic crystal structure
    - single layer black phosphorous (phosphorene)

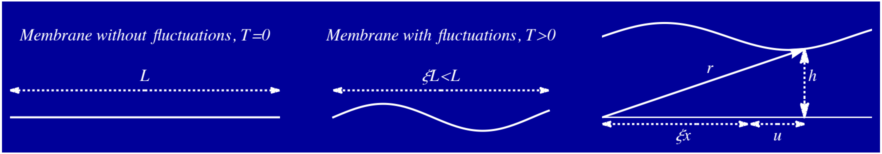


orthorhombic crystal structure with D_{2h} (Pmna) point group

a figure adopted from Ling, Wang, Huang, Xia, Dresselhaus, PNAS (2015)

- metal monochalcogenide monolayers (SiS, SiSe, GeS, GeSe, SnS, SnSe)
- monolayers $GeAs_2$, WTe_2, $ZrTe_5$, Ta_2NiS_5

[for a review, see Li et al., InfoMat (2019)]



- parametrization of the surface 3D vector $\vec{R}(\boldsymbol{x})$ depending on 2D vector $\boldsymbol{x}$.

- surface is characterized by the internal metric tensor and curvature

$$g_{\alpha\beta}(\boldsymbol{x}) = \frac{\partial R_a}{\partial x^\alpha}\frac{\partial R_a}{\partial x^\beta}, \qquad K_{\alpha\beta} = n_a \frac{\partial}{\partial x^\alpha}\frac{\partial R_a}{\partial x^\beta}$$

where $\boldsymbol{n}$ is a normal vector to the surface.

NB EXERCISE: to find the curvature tensor $K_{\alpha\beta}$ for the sphere.

- free energy of the membrane

$$F = \int d^2\boldsymbol{x}\sqrt{\det g}\Big[\frac{w}{2}(\mathrm{tr}\,K)^2 + \tilde{w}\det K + \frac{t}{2}\,\mathrm{tr}\,g + u\,\mathrm{tr}\,g^2 + v(\mathrm{tr}\,g)^2 + \ldots$$

[Paczuski, Kardar, Nelson (1988)]

- uniform stretching of the membrane $\boldsymbol{r} = \xi_0\boldsymbol{x}$:

$$g_{\alpha\beta} = \xi_0^2\delta_{\alpha\beta}, \qquad K_{\alpha\beta} = 0, \qquad F/L^2 = t\xi_0^2 + 2(u+2v)\xi_0^4$$

- mean-field Landau-type transition

$$\xi_0^2 = \begin{cases} -t/(u+2v), & t < 0 \quad \text{flat phase} \\ 0, & t > 0 \quad \text{crumpled phase} \end{cases}$$

$$F_0/L^2 = t^2/(u+2v)$$

- free energy of the membrane

$$F = \int d^2\boldsymbol{x}\sqrt{\det g}\Big[\frac{w}{2}(\operatorname{tr} K)^2 + \tilde{w}\det K + \frac{t}{2}\operatorname{tr} g + u\operatorname{tr} g^2 + v(\operatorname{tr} g)^2 + \dots$$

- parametrization of the position on the membrane $\boldsymbol{R} = \xi_0 \boldsymbol{r}$:

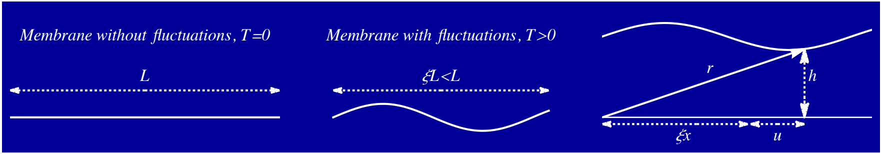
$$F = F_0 + \int d^2\boldsymbol{x}\Big[\frac{\varkappa}{2}(\operatorname{tr} K)^2 + \tilde{\varkappa}\det K + \mu\operatorname{tr} U^2 + \frac{\lambda}{2}(\operatorname{tr} U)^2\Big]$$

where $\varkappa = w\xi_0^2$, $\tilde{\varkappa} = \tilde{w}\xi_0^2$, $\mu = 4u\xi_0^4$, $\lambda = 8v\xi_0^4$, and deformation tensor

$$U_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial r_a}{\partial x^\alpha}\frac{\partial r_a}{\partial x^\beta} - \delta_{\alpha\beta}\right), \qquad K_{\alpha\beta} = n_a \frac{\partial}{\partial x^\alpha}\frac{\partial r_a}{\partial x^\beta}$$

NB $\int d^2\boldsymbol{x}\det K = \text{const}$ due to Gauss-Bonet theorem.

- membrane's free energy $F = \int d^2\boldsymbol{x}\left[\frac{\varkappa}{2}(\mathrm{tr}\,K)^2 + \mu\,\mathrm{tr}\,U^2 + \frac{\lambda}{2}(\mathrm{tr}\,U)^2\right]$



- parametrization of the position on the membrane $\boldsymbol{r} = \xi\boldsymbol{x} + \boldsymbol{u} + h\boldsymbol{e_z}$:

$$\mathrm{tr}\,K = \boldsymbol{n}\Delta\boldsymbol{r} \simeq \Delta h, \qquad U_{\alpha\beta} = \frac{\xi^2-1}{2}\delta_{\alpha\beta} + u_{\alpha\beta},$$

$$u_{\alpha\beta} = \frac{1}{2}(\xi\partial_\alpha u_\beta + \xi\partial_\beta u_\alpha + \partial_\alpha u_\gamma\partial_\beta u_\gamma + \partial_\alpha h\partial_\beta h)$$

- final form of the free energy

$$F = L^2(\lambda+\mu)\frac{(\xi^2-1)^2}{2} + (\lambda+\mu)\frac{\xi^2-1}{2}\int d^2\boldsymbol{x}[\partial_\alpha h\partial_\alpha h + \partial_\alpha u_\beta\partial_\alpha u_\beta]$$
$$+\int d^2\boldsymbol{x}\left[\frac{\varkappa}{2}(\Delta h)^2 + \mu u_{\alpha\beta}u_{\beta\alpha} + \frac{\lambda}{2}u_{\alpha\alpha}u_{\beta\beta}\right]$$

- Helmholtz free energy

$$\mathcal{F} = -T \ln \int D[h, \boldsymbol{u}] e^{-F/T},$$

$$F = L^2(\lambda+\mu)\frac{(\xi^2-1)^2}{2} + (\lambda+\mu)\frac{\xi^2-1}{2}\int d^2\boldsymbol{x}[\partial_\alpha h \partial_\alpha h + \partial_\alpha u_\beta \partial_\alpha u_\beta] + \int d^2\boldsymbol{x}\Big[\frac{\varkappa}{2}(\Delta h)^2 + \mu u_{\alpha\beta}u_{\beta\alpha} + \frac{\lambda}{2}u_{\alpha\alpha}u_{\beta\beta}\Big]$$

- tension

$$\sigma = \frac{1}{L^2}\frac{\partial \mathcal{F}}{\partial \xi^2}$$

- Gibbs free energy

$$\Phi = \mathcal{F} - \sigma(\xi^2-1), \qquad \xi^2 - 1 = -\frac{\partial \Phi}{\partial \sigma}$$

- Hooke's law in the absence of fluctuations ($u_x = u_y = h = 0$)

$$\sigma = (\lambda+\mu)(\xi^2-1)$$

- Lagrangian for a membrane

$$\mathcal{L} = \frac{1}{2}\rho \int d^2x \left[\left(\frac{\partial h}{\partial t}\right)^2 + \left(\frac{\partial \boldsymbol{u}}{\partial t}\right)^2 \right] - F,$$

$$F = L^2(\lambda+\mu)\frac{(\xi^2-1)^2}{2} + (\lambda+\mu)\frac{\xi^2-1}{2}\int d^2\boldsymbol{x}[\partial_\alpha h \partial_\alpha h + \partial_\alpha u_\beta \partial_\alpha u_\beta]$$
$$+ \int d^2\boldsymbol{x}\Big[\frac{\varkappa}{2}(\Delta h)^2 + \mu u_{\alpha\beta}u_{\beta\alpha} + \frac{\lambda}{2}u_{\alpha\alpha}u_{\beta\beta}\Big]$$

where ρ is the mass density of a membrane

NB $\varkappa(\Delta h)^2 \sim Y(\nabla h)^4$ or $\varkappa/Y \sim \langle h^2\rangle \sim T/(\varkappa L^2)$ hence $L_*^2 \sim \varkappa^2/(YT)$

- Fourier transform to momentum and frequency space

$$h(\boldsymbol{x},t) = \int \frac{d^2\boldsymbol{q}d\omega}{(2\pi)^3} h(\boldsymbol{q},\omega) e^{i\boldsymbol{q}\boldsymbol{x}-i\omega t}, \quad u_\alpha(\boldsymbol{x},t) = \int \frac{d^2\boldsymbol{q}d\omega}{(2\pi)^3} u_\alpha(\boldsymbol{q},\omega) e^{i\boldsymbol{q}\boldsymbol{x}-i\omega t}$$

- quadratic part of the Lagrangian

$$\mathcal{L}^{(2)} = \frac{1}{2}\int \frac{d^2\boldsymbol{q}d\omega}{(2\pi)^3}\Big[h(\boldsymbol{q},\omega)(\rho\omega^2 - \varkappa q^4)h(-\boldsymbol{q},-\omega) + u_\alpha(\boldsymbol{q},\omega)M_{\alpha\beta}u_\beta(-\boldsymbol{q},-\omega)$$

$$M_{\alpha\beta} = [(\rho\omega^2 - \varkappa q^4 - \mu\xi^2 q^2 - (\lambda+\mu)(\xi^2-1)q^2)]\delta_{\alpha\beta} - (\lambda+\mu)\xi^2 q_\alpha q_\beta$$

- spectrum of in-plane transverse and longitudinal phonons (at $q \to 0$)

$$\det M = 0 \quad \Longrightarrow \quad \omega_q^{(l)} = q\sqrt{[\sigma_0 + (2\mu+\lambda)\xi^2]/\rho},$$

$$\omega_q^{(t)} = q\sqrt{[\sigma_0 + \mu\xi^2]/\rho}$$

where $\sigma_0 = (\lambda+\mu)(\xi^2-1)$.

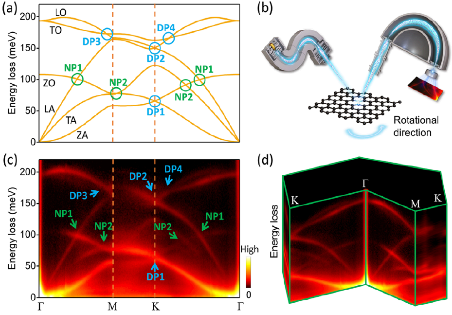
- spectrum of flexural phonons

$$\omega_q^{(f)} = \sqrt{[q^2(\lambda+\mu)(\xi^2-1) + q^4\varkappa]/\rho}$$

- out-of-plane (flexural) phonons with spectrum

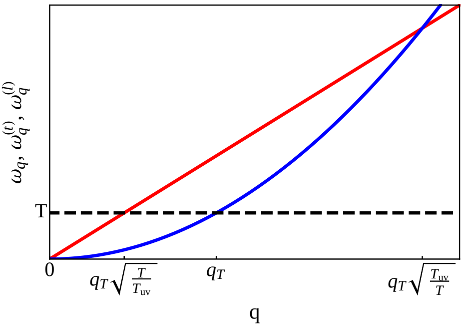
$$\omega_q^{(f)} = q^2 \sqrt{\varkappa_0/\rho},$$

where $\varkappa_0$ is bending rigidity



measurements of the phonon spectrum in graphene by means of high-resolution electron energy-loss spectroscopy

a figure adopted from Jiade Li et al., Phys. Rev. Lett. (2023)



- temperature momentum: $\hbar\omega_q \sim T \Longrightarrow q_T = \frac{\rho^{1/4}T^{1/2}}{\hbar^{1/2}\varkappa^{1/4}}$
- ultra-violet energy scale: $T_{uv} \approx g\varkappa$, $g = \frac{\hbar\mu}{\rho^{1/2}\varkappa^{3/2}}$

- for graphene: $q_T \approx 0.1\ \mathrm{nm}^{-1}$, $g \approx 0.05$, $T_{uv} \approx 500$ K

- stretching of 2D membrane at finite temperature in the absence of tension

$$0 = \frac{1}{L^2}\frac{\partial \mathcal{F}}{\partial \xi^2} \quad \Longrightarrow \quad \xi^2 = 1 - \frac{1}{2}\langle (\nabla h)^2 + (\nabla \boldsymbol{u})^2 \rangle$$

$$\xi^2 = 1 - T\int \frac{d^2\boldsymbol{q}}{(2\pi)^2}\frac{q^2}{2\varkappa q^4} = 1 - \frac{T}{4\pi\varkappa}\ln\frac{L}{a}$$

- $\xi^2 = 0$ at any $T > 0$ in the thermodynamic limit $L \to \infty$.

[Peierls (1934), Landau (1937)]

- 2D crystal is unstable in harmonic approximation. But phonons do interact

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NB for graphene $\varkappa \approx 1.1$ eV, so for $L \sim 1$ μm reduction of ξ^2 is 2% at room temperature!

NB PROBLEM: to estimate the contribution from $(\nabla \boldsymbol{u})^2$ term into ξ^2.

Interaction: the role of phonon-phonon interaction -I

- renormalization in the absence of tension, $\sigma = 0$,

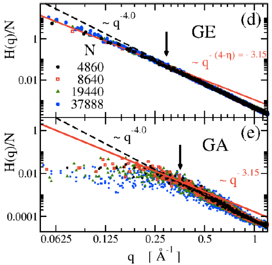
- bending rigidity

$$\varkappa(q) \simeq \varkappa \begin{cases} 1, & q \gg q_* \\ (q_*/q)^\eta, & q \ll q_* \end{cases}$$

- Young's modulus ($Y = \frac{4\mu(\mu+\lambda)}{(2\mu+\lambda)}$)

$$Y(q) \simeq Y \begin{cases} 1, & q \gg q_* \\ (q/q_*)^{2-2\eta}, & q \ll q_* \end{cases}$$

[Nelson,Peliti (1987); Aronovitz,Lubensky (1988)]



Costamagna, Neek-Amal, Los, Peeters (2012)

$H(q) \sim \frac{T}{\varkappa(q) q^4}$

- Ginzburg length

$$q_*^{-1} \sim \frac{\varkappa}{\sqrt{YT}}$$

numerical computations give $\eta \approx 0.795 \pm 0.01$

[Tröster (2013)]

NB for graphene $\varkappa_0 \approx 1.1$ eV, $Y \approx 340$ N/m, and $q_*^{-1} \approx 1$ nm at room temperature

- stretching of 2D membrane at finite temperature in the absence of tension

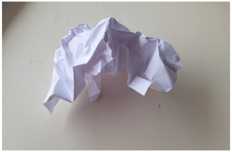
$$0 = \frac{1}{L^2}\frac{\partial \mathcal{F}}{\partial \xi^2} \quad \Longrightarrow \quad \xi^2 = 1 - \frac{1}{2}\langle (\nabla h)^2 + (\nabla \boldsymbol{u})^2 \rangle$$

$$\xi^2 = 1 - T \int\limits_{q<q_*} \frac{d^2\boldsymbol{q}}{(2\pi)^2}\frac{q^2}{2\varkappa(q)q^4} = 1 - \frac{T}{4\pi\eta\varkappa}$$

- crumpling transition at $T_{\rm cr}{=}4\pi\eta\varkappa$ ($\xi^2{=}0$ at $T{\geqslant}T_{\rm cr}$)

[Paczuski, Kardar, Nelson (1988); David, Guitter (1988)]

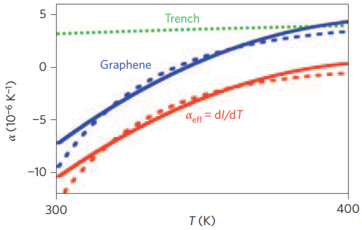
flat phase
$T < T_{\rm cr}$

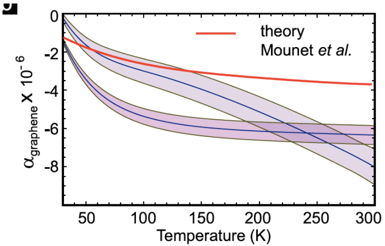


crumpled phase
$T > T_{\rm cr}$

- negative thermal expansion coefficient (at $T < T_{cr}$)

$$\alpha_T = \frac{\partial \xi^2}{\partial T} = -\frac{1}{4\pi\eta\varkappa}$$





[adopted from Bao et al. (2009); Singh et al. (2010)]

NB constant negative thermal expansion coefficient violates the 3d law of the thermodynamics!?

- the effect of tension σ on the phonon spectrum (in harmonic approximation) for in-plane phonons

$$\omega_q^{(\mathrm{t})} = q\sqrt{(\mu+\sigma)/\rho}, \qquad \omega_q^{(\mathrm{l})} = q\sqrt{(\lambda+\mu+\sigma)/\rho},$$

and for flexural phonons

$$\omega_q^{(\mathrm{f})} = \sqrt{(\varkappa q^4 + \sigma q^2)/\rho} = \begin{cases} q^2\sqrt{\varkappa/\rho}, & q \gg q_\sigma^{(0)}, \\ q\sqrt{\sigma/\rho}, & q \ll q_\sigma^{(0)}, \end{cases}$$

where $q_\sigma^{(0)} = \sqrt{\sigma/\varkappa}$

- tension stops the renormalization of bending rigidity and Young's modulus

$$\varkappa(q) \simeq \varkappa \begin{cases} 1, & q_* \ll q, \\ (q_*/q)^\eta, & q_\sigma \ll q \ll q_*, \\ (q_*/q_\sigma)^\eta, & q \ll q_\sigma, \end{cases} \quad Y(q) \simeq Y \begin{cases} 1, & q_* \ll q, \\ (q/q_*)^{2-2\eta}, & q_\sigma \ll q \ll q_*, \\ (q_\sigma/q_*)^{2-2\eta}, & q \ll q_\sigma, \end{cases}$$

where $q_\sigma = q_*(\sigma/\sigma_*)^{1/(2-\eta)}$ and $\sigma_* = \varkappa q_*^2 \sim TY/\varkappa$

- stretching of 2D membrane at finite temperature in the presence of tension

$$\sigma = \frac{1}{L^2}\frac{\partial \mathcal{F}}{\partial \xi^2} \quad \Longrightarrow \quad \frac{\sigma}{B} = \xi^2 - 1 + \frac{1}{2}\langle (\nabla h)^2 + (\nabla \boldsymbol{u})^2 \rangle$$

$$\frac{\sigma}{B} = \xi^2 - 1 + \frac{T}{2}\int\limits_{q<q_*} \frac{d^2\boldsymbol{q}}{(2\pi)^2}\frac{q^2}{\varkappa(q)q^4 + \sigma q^2} = \xi^2 - 1 + \frac{T}{8\pi\varkappa}\int\limits_0^1 \frac{du}{u^{1-\eta/2} + \sigma/\sigma_*}$$

$$= \xi^2 - 1 + \frac{T}{8\pi\varkappa}\Phi_\eta\left(\frac{\sigma}{\sigma_*}\right), \qquad \Phi_\eta(z) = \frac{1}{z}\,{}_2F_1\left(1, \frac{2}{2-\eta}, \frac{4-\eta}{2-\eta}; -\frac{1}{z}\right)$$

where $B = \lambda + \mu$.

- asymptotics

$$\Phi_\eta(z) = \begin{cases} 2/\eta - c_\eta z^{\eta/(2-\eta)}, & z \ll 1, \\ 1/z, & z \gg 1. \end{cases}$$

where $c_\eta = -\Gamma[(4-\eta)/(2-\eta)]\Gamma[\eta/(\eta-2)] \simeq 6.05$.

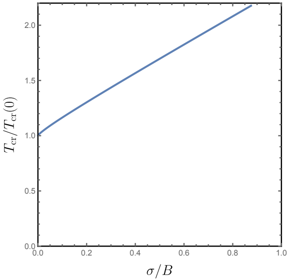
NB the external tension σ in the denominator of the integral fixed by the Ward identity

- equation of state and crumpling transition

$$\xi^2 = 1 + \frac{\sigma}{B} - \frac{T}{8\pi\varkappa}\Phi_\eta\left(\frac{\varkappa\sigma}{TY}\right) \quad \Longrightarrow \quad T_{\rm cr} = 8\pi\varkappa\frac{1+\sigma/B}{\Phi_\eta(\varkappa\sigma/T_{\rm cr}Y)}$$

- crumpling transition in the presence of tension

$$T_{\rm cr}(\sigma = 0) = 4\pi\eta\varkappa \qquad\qquad T_{\rm cr}(\sigma\to\infty) \sim \frac{\varkappa\sigma}{\sqrt{BY}}$$

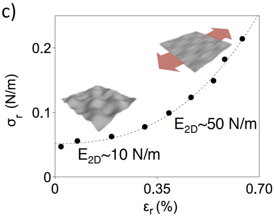


- equation of state

$$\xi^2 = 1 + \frac{\sigma}{B} - \frac{T}{8\pi\varkappa}\Phi_\eta\left(\frac{\varkappa\sigma}{TY}\right)$$

- anomalous Hooke's law (at $\sigma \ll TY/\varkappa$)

$$\xi^2 - \xi^2(T,\sigma{=}0) = \frac{c_\eta T}{8\pi\varkappa}\left(\frac{\varkappa\sigma}{TY}\right)^{\eta/(2-\eta)}$$



[Nicholl et al. (2015) (Bolotin's group)]

NB standard Hooke's law with renormalized bulk modulus $\varepsilon \sim \sigma/B(q_\sigma) \sim \sigma^{\eta/2-\eta}$

- equation of state

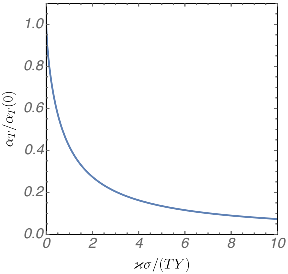
$$\xi^2 = 1 + \frac{\sigma}{B} - \frac{T}{8\pi\varkappa}\Phi_\eta\left(\frac{\varkappa\sigma}{TY}\right)$$

- negative expansion coefficient

$$\alpha_T = \frac{\partial \xi^2}{\partial T} = -\frac{1}{8\pi\varkappa}\Psi_\eta\left(\frac{\varkappa\sigma}{TY}\right), \qquad \Psi_\eta(z) = \Phi_\eta(z) - z\Phi'_\eta(z),$$

$$\Psi_\eta(z) = \begin{cases} 2/\eta - c'_\eta z^{\eta/(2-\eta)}, & z \ll 1, \\ 2/z, & z \gg 1. \end{cases}$$

where $c'_\eta = 2(1-\eta)c_\eta/(2-\eta)$.



- equation of state

$$\xi^2 = 1 + \frac{\sigma}{B} - \frac{T}{8\pi\varkappa}\Phi_\eta\left(\frac{\varkappa\sigma}{TY}\right)$$

- compressibility coefficient

$$\chi = \frac{\partial\xi^2}{\partial\sigma} = \frac{1}{B} - \frac{1}{8\pi Y}\Phi'_\eta\left(\frac{\varkappa\sigma}{TY}\right)$$

$$\Psi'_\eta(z) = \begin{cases} -c''_\eta z^{-2/(2-\eta)}, & z \ll 1, \\ -2/z^2, & z \gg 1. \end{cases}$$

where $c''_\eta = \eta c_\eta/(2-\eta)$.

NB $\chi > 0$ for all σ; $\chi \to \infty$ at $\sigma \to 0$.

NB wrong approach

$$\sigma \simeq B(\xi^2 - 1) + \frac{TB}{8\pi\varkappa}\Phi_\eta\left(\frac{\varkappa B(\xi^2-1)}{TY}\right)$$

$\chi < 0$ at $\sigma \to 0$ (thermodynamic instability)

- definition:

$$\nu = -\frac{\varepsilon_\perp}{\varepsilon_l}$$

where ε_l - longitudinal stretching, $\varepsilon_\perp$ - transverse deformation

- classical value

$$\nu_{\text{cl}} = \frac{\lambda}{2\mu + (D-1)\lambda}$$

where μ and λ are Lamé coefficients

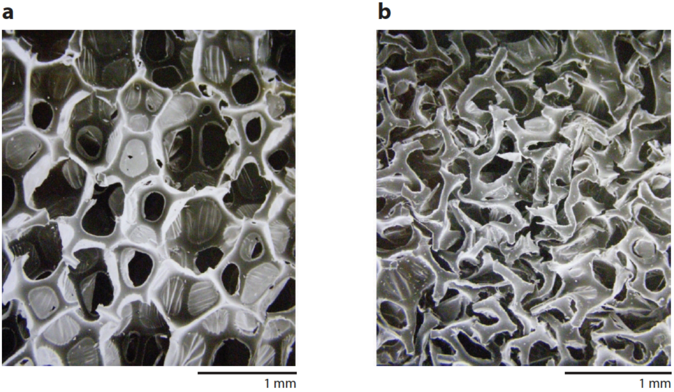
- thermodynamic stability:

$$-1 < \nu < 1/(D-1)$$

- for example, $\nu = 0.33$ for aliminum

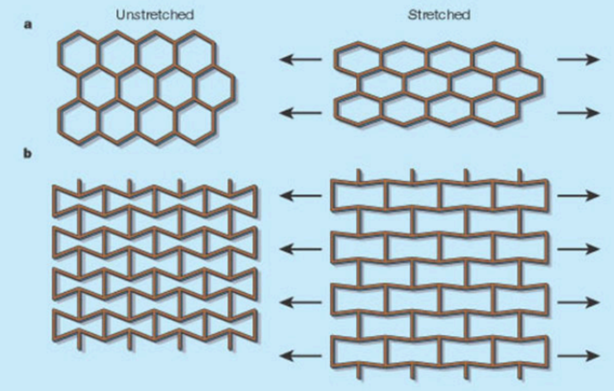
- polyurethane foam with reentrant structure: $\nu = -0.7$

[Lakes, Science (1987)]



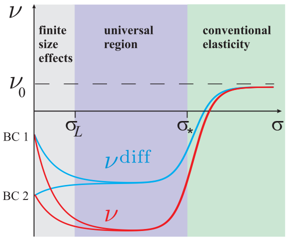
[adopted from Lakes, Annu. Rev. Mater. Res. (2017)]

◦ positive vs negative Poisson's ratio:



[adopted from Lakes, Nature (2001)]

- differential Poisson's ratio, $\sigma_x = \sigma + \delta\sigma$, $\sigma_y = \sigma$: $\nu_{\text{diff}} = -\delta\varepsilon_y/\delta\varepsilon_x$
- absolute Poisson's ratio, $\sigma_x = \sigma, \sigma_y = 0$: $\nu = -\varepsilon_y/\varepsilon_x$



$$\nu = \nu_{\text{diff}} = \nu_{\text{cl}} = \frac{\lambda}{2\mu + \lambda}, \ \sigma \gg \sigma_*$$

$$\nu \neq \nu_{\text{diff}}, \quad \sigma_L \ll \sigma \ll \sigma_*$$

$$\nu = \nu_{\text{diff}}, \quad \sigma \ll \sigma_L$$

$$\sigma_L = \sigma_*(q_* L)^{\eta-2} \text{ for } q_* L \gg 1$$

- for graphene $\sigma_* = \varkappa q_*^2 = YT/\varkappa \approx 1$ N/m and $\nu_{\text{cl}} \approx 0.1$

NB EXERCISE: using Hooke's law to derive the classical expression for the Poisson's ratio: $\nu_{\text{cl}} = \lambda/(2\mu + \lambda)$

Conclusions:

- 2D flexible crystalline materials have interesting unusual physical properties:
  - anomalous Hooke's law
  - negative thermal expansion
  - negative Poisson's ratio
- Future reading:
  - I.S.Burmistrov, I.V. Gornyi, V.Yu. Kachorovskii, M.I. Katsnelson, A.D. Mirlin, "Quantum elasticity of graphene: Thermal expansion coefficient and specific heat", Phys. Rev. B 94, 195430 (2016)
  - I.S. Burmistrov, I.V. Gornyi, V.Yu. Kachorovskii, M.I. Katsnelson, J.H. Los, A. D. Mirlin, "Stress-controlled Poisson ratio of a crystalline membrane: Application to graphene", Phys. Rev. B 97, 125402 (2018)
  - D.R. Saykin, V.Yu. Kachorovskii, and I.S. Burmistrov, "Phase diagram of a flexible two-dimensional material", Phys. Rev. Research 2, 043099 (2020)
  - I.S. Burmistrov, V. Yu. Kachorovskii, M. J. Klug, J. Schmalian, "Emergent continuous symmetry in anisotropic flexible two-dimensional materials", Phys. Rev. Lett. 128, 096101 (2022)

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