Russian Academy of Sciences
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Anomalous elasticity of graphene

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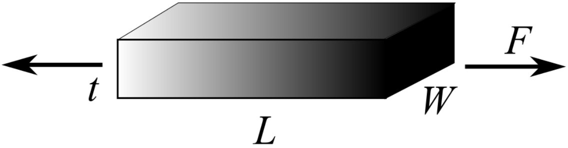
the talk is based on:

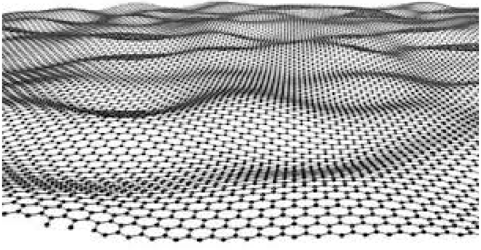
- I.S. Burmistrov, I.V. Gornyi, V.Yu. Kachorovskii, M.I. Katsnelson, A.D. Mirlin, *Quantum elasticity of graphene: Thermal expansion coefficient and specific heat*, Phys. Rev. B 94, 195430 (2016)
- I.S. Burmistrov, I.V. Gornyi, V.Yu. Kachorovskii, M.I. Katsnelson, J.H. Los, A.D. Mirlin, *Stress-controlled Poisson ratio of a crystalline membrane: Application to graphene*, Phys. Rev. B 97, 125402 (2018)
- I.S. Burmistrov, V.Yu. Kachorovskii, I.V. Gornyi, A.D. Mirlin *Differential Poisson's ratio of a crystalline two-dimensional membrane*, Annals of Physics(N.Y.) 396, 119 (2018)
- D.R. Saykin, I.S. Burmistrov, I.V. Gornyi, V.Yu. Kachorovskii, *Absolute Poisson's ratio of a crystalline two-dimensional membrane*, in preparation.



- Hooke's law for bulk materials: $$\frac{F}{Wt} = E\frac{\Delta L}{L}$$
  where E is bulk Young's modulus
- Hooke's law for thin films: $$\sigma = \frac{F}{W} = Y\frac{\Delta L}{L}$$
- Young's modulus $Y = Et$ for monoatomic layers:

	pine wood	aluminium foil	graphene
Y, H/m	1	7	340

Lamé coefficients μ and λ, $Y = 4\mu(\mu+\lambda)/(2\mu+\lambda)$

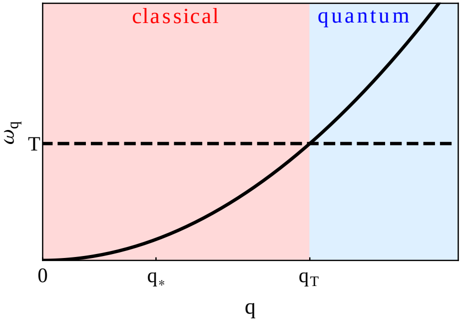


[adopted from Meyer et al. (2007)]

- bending rigidity $\varkappa \sim Yt^2$
- for graphene $\varkappa \approx 1$ eV

graphene density $\rho \approx 7 \cdot 10^{-8}$ g/cm^2

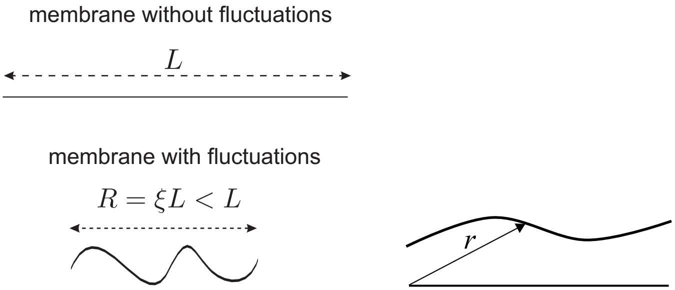
- spectrum of in-plane phonons: $\omega_q^{(t)} = q\sqrt{\mu/\rho}$, $\omega_q^{(l)} = q\sqrt{(2\mu+\lambda)/\rho}$,
- spectrum of flexural phonons: $\omega_q = q^2\sqrt{\varkappa/\rho}$



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

- for room-temperature graphene: $q_T \approx 1$ Å^{-1}, $g \approx 0.05$, $T_{uv} \approx 500$ K

Introduction: instability of 2D membrane



- parametrization of the membrane surface: $\boldsymbol{r} = \xi x \boldsymbol{e}_x + \xi y \boldsymbol{e}_y + \boldsymbol{u} + h \boldsymbol{e}_z$
- membrane surface: $L^2 = \text{const}$
- stretching factor: $\xi^2 \approx 1 - \langle (\nabla h)^2 \rangle / 2$
- instability of 2D membrane at finite temperature:

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

[Peierls (1934), Landau (1937)]

- imaginary time Lagrangian ($\alpha, \beta = x, y$):

$$\mathcal{L}[\boldsymbol{r}] = \rho(\partial_\tau \boldsymbol{r})^2 + \frac{\varkappa}{2}(\triangle \boldsymbol{r})^2 + \frac{\mu}{4}\Big(\partial_\alpha \boldsymbol{r} \partial_\beta \boldsymbol{r} - \delta_{\alpha\beta}\Big)^2 + \frac{\lambda}{8}\Big(\partial_\alpha \boldsymbol{r} \partial_\alpha \boldsymbol{r} - 2\Big)^2$$

- interaction of phonons is important for $q < q_*$

$$\langle \boldsymbol{r}^2 \rangle \sim \int\limits_{q > q_*} \frac{d^2\boldsymbol{q}}{(2\pi)^2} \frac{T}{\varkappa q^4} \sim \frac{T}{\varkappa q_*^2} \sim \frac{\varkappa}{Y} \sim t^2$$

- renormalized bending rigidity

$$\varkappa(q) = \varkappa\big(q_*/q\big)^\eta, \qquad q \ll q_* = \sqrt{g} q_T = \sqrt{\mu T}/\varkappa$$

for graphene: $q_*^{-1} \approx 1$ Å (for 1 mm thick paper sheet $q_*^{-1} \approx 10^6$ m)

- numerics: $\eta = 0.6 \div 0.8$

- for a review, see

[Nelson, Piran, Weinberg, Statistical mechanics of membranes and surfaces (2004)]

- stretching factor

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

- flat phase ($\xi^2 > 0$ at $T < T_{\text{cr}} = 4\pi\eta\varkappa$

- crumpled phase ($\xi^2 = 0$) at $T \geqslant T_{\text{cr}}$

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

- equation of state:

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

- negative thermal expansion coefficient:

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

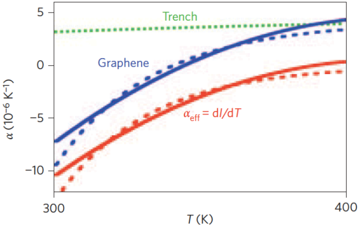
- constant α_T down to zero T contradicts to the 3d law of thermodynamics since:

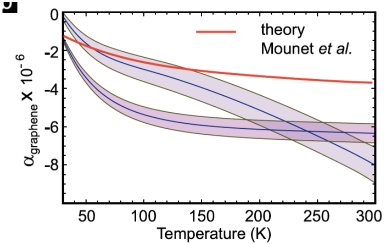
$$\alpha_T = -\left(\frac{\partial s}{\partial \sigma}\right)_T$$

  where s is entropy per unit area

negative thermal expansion coefficient is due to the crumpling transition

Introduction: negative thermal expansion coefficient in graphene





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

- spectrum of in-plane phonons:

$$\omega_q^{(t)} = q\sqrt{(\mu+\sigma)/\rho}, \qquad \omega_q^{(l)} = q\sqrt{(2\mu+\lambda+\sigma)/\rho}$$

- spectrum of flexural phonons:

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

strong modification of flexural phonon spectrum at $q \ll q_\sigma = \sqrt{\sigma/\varkappa}$

- anomalous Hooke's law

$$B\varepsilon = \sigma + \frac{\sigma_*}{\alpha}\left(\frac{\sigma}{\sigma_*}\right)^{\alpha}, \qquad \alpha = \frac{\eta}{2-\eta}$$

where $\varepsilon = \xi^2 - 1 + T/T_{\mathrm{cr}}$, $B = \mu + \lambda$, $\sigma_* \propto \mu T/\varkappa$ $(q_\sigma = q_*)$.

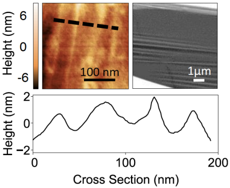
[Guitter, David, Leibler, Peliti (1988,1989); Aronovitz, Golubović, Lubensky (1989)]

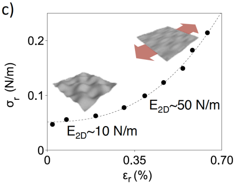
Introduction: anomalous Hooke's law in graphene

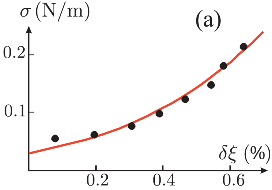
- anomalous Hooke's law

$$B\varepsilon = \sigma + \frac{\sigma_*}{\alpha}\left(\frac{\sigma}{\sigma_*}\right)^{\alpha}, \qquad \alpha = \frac{\eta}{2-\eta}$$

- experiment vs theory ($\alpha = 0.1$); for graphene $\sigma_* \approx 0.1$ N/m







[Nicholl et al. (2015);Kachorovskii, Gornyi, Mirlin (2017)]

- N.B.: the exponent η is affected by disorder, $\eta \to \eta/4$.

- definition:

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

  where $\varepsilon_{||}$ - longitudinal stretching, $\varepsilon_\perp$ - transverse deformation

- classical value for D-dimensional isotropic solid body

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

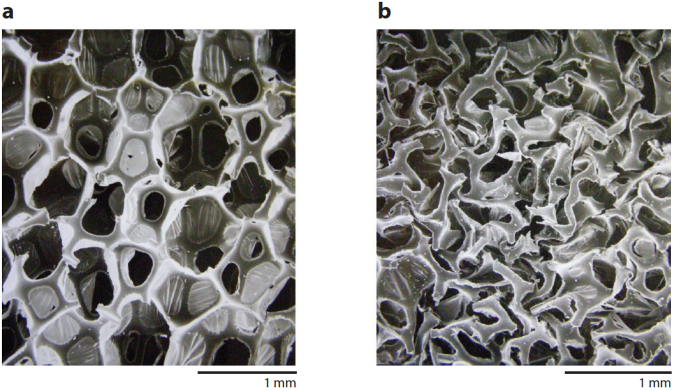
- thermodynamic stability:

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

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

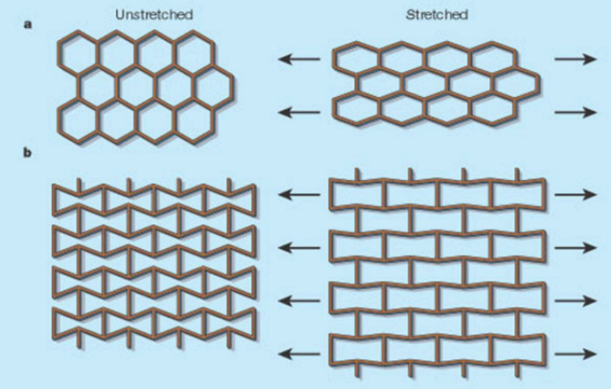
- polyurethane foam with reentrant structure: $\nu = -0.7$

[Lakes, Science (1987)]



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

- positive vs negative Poisson's ratio:



[adopted from Lakes, Nature (2001)]

[Le Doussal, Radzihovsky (1992)]

- self-consistent screening approximation (approximate treatment of phonon's interaction at $q \ll q_*$)

- SCSA prediction for the bending rigidity exponent:

$$\eta_{SCSA} = \frac{4}{d_c + \sqrt{d_c^2 - 2d_c + 16}}$$

where $d_c = D - 2$ is the number of flexural phonon modes.
$\eta_{SCSA} \approx 0.8$ for $d_c = 1$.

- SCSA prediction for the Poisson's ratio: it is independent of d_c at $\sigma \to 0$:

$$\nu_{SCSA} = -\frac{1}{3}$$

No small parameter for SCSA at finite d_c!

- exponent of bending rigidity for $d_c = 1$

$$\eta = 0.6, 0.7, 0.85$$

[Gompper, Kroll (1991); Bowick et al. (1996); Los et al. (2009)]

- the Poisson's ratio for $d_c = 1$ at $\sigma \to 0$:

$$\nu = -0.15, -0.32, -0.37$$

[Zhang et al. (1996); Falcioni et al. (1997); Bowick et al. (2001)]

- strong dependence of ν on the boundary conditions

- how does to reconcile constant negative thermal expansion coefficient and the 3d law of thermodynamics?
- what is the value of the Poisson's ratio at $\sigma \ll \sigma_*$?
- is the superuniversal result within SCSA is correct?
- how the Poisson's ratio depends on the boundary conditions (BC)?

- quantum fluctuations of phonons at $q_T < q < q_{uv}$

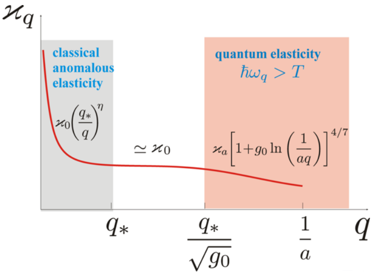
$$-\frac{d\varkappa}{d\ln q} = \frac{4}{7}g\varkappa, \qquad -\frac{dg}{d\ln q} = -g^2$$

[Kats,Lebedev (2014); Burmistrov, Gornyi, Kachorovskii, Katsnelson, Mirlin(2016)]

- classical fluctuations of phonons at $q < q_*$

$$-\frac{d\varkappa}{d\ln q} = \eta\varkappa$$

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



- high temperature: $T \gg T_0 = g\varkappa \exp(-2/g)$

$$\alpha_T = -\frac{1}{8\pi\varkappa}\left[\frac{2}{\eta} + \ln\frac{1}{g}\right]$$

[Andres, Guinea, Katsnelson (2012)]

- graphene: $\alpha_{\max} \approx -0.23$ eV^{-1}, $T_0 \sim 10^{-14}$ K
  for comparison: $\alpha_T \approx 0.1$ eV^{-1} (iron)

- low temperatures $T \ll T_0 = g\varkappa \exp(-2/g)$

$$\alpha_T \simeq -\frac{1}{8\pi\varkappa}\frac{\ln\ln(T_{\rm uv}/T)}{[(g/2)\ln(T_{\rm uv}/T)]^{4/7}}$$

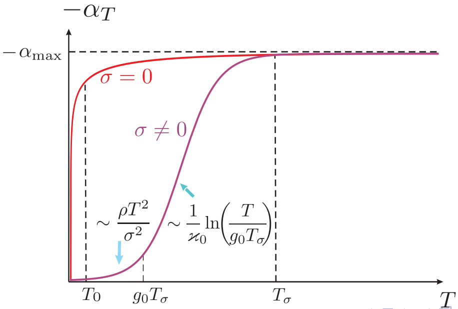
- $\alpha_T \to 0$ at $T \to 0$ in accordance with the 3d law of thermodynamics

- high temperatures: $T \gg T_\sigma \sim \varkappa\sigma/\mu$):

$$\alpha_T \approx -\frac{1}{8\pi\varkappa}\left[\frac{2}{\eta} + \ln\frac{1}{g} - C_1\left(\frac{T_\sigma}{T}\right)^{\eta/(2-\eta)}\right]$$

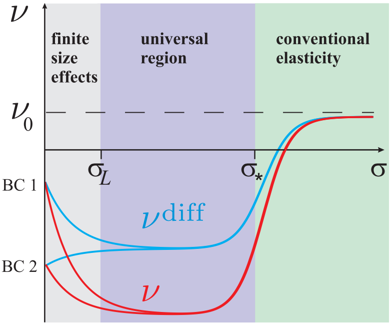
- intermediate temperatures: $gT_\sigma \ll T_\sigma$: $\quad \alpha_T \approx -\frac{1}{8\pi\varkappa}\ln\frac{T}{gT_\sigma}$

- low temperatures $T \ll gT_\sigma$: $\quad \alpha_T \approx -\frac{3\zeta(3)\rho}{2\pi\sigma^2}T^2$



- differential Poisson's ratio, $\sigma_x = \sigma + \delta\sigma,\ \sigma_y = \sigma$: $\quad \nu_{\rm diff} = -\delta\varepsilon_y/\delta\varepsilon_x$

- absolute Poisson's ratio, $\sigma_x = \sigma, \sigma_y = 0$: $\quad \nu = -\varepsilon_y/\varepsilon_x$



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

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

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

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

- for graphene $\sigma_* \approx 1$ N/m and $\nu_{\rm cl} \approx 0.1$

- the bending rigidity exponent

$$\eta = \frac{2}{d_c} + \frac{73 - 68\zeta(3)}{27 d_c^2} + O\left(\frac{1}{d_c^3}\right)$$

- universal differential Poisson's ratio at $\sigma_L \ll \sigma \ll \sigma_* = \sqrt{d_c \mu T}/\varkappa$

$$\nu_{\text{diff}} = -\frac{1}{3} + \frac{0.016}{d_c} + O\left(\frac{1}{d_c^2}\right)$$

- universal absolute Poisson's ratio at $\sigma_L \ll \sigma \ll \sigma_*$

$$\nu = -1 + \frac{2}{d_c} - \frac{1.57}{d_c^2} + O\left(\frac{1}{d_c^3}\right)$$

- non-universal Poisson's ratio at $\sigma \ll \sigma_L$:

$$\nu = \begin{cases} -0.135 + O(1/d_c), & \text{for periodic BC} \\ -0.075 + O(1/d_c), & \text{for free BC} \\ -0.735 + O(1/d_c), & \text{for zero BC} \end{cases}$$

N.B. strong thermodynamic fluctuations of tension $\sqrt{\langle(\Delta\sigma)^2\rangle} \sim \sigma_L/\sqrt{d_c}$ at $\sigma \ll \sigma_L$

Conclusions:

- thermal expansion coefficient is negative upto extremely low T
- thermal expansion coefficient is zero at $T = 0$
- distinction between absolute and differential Poisson's ratios for $\sigma \ll \sigma_*$
- Poisson ratio is a function of tension σ and system size L; the limits $L \to \infty$ and $\sigma \to 0$ do not commute
- in the limit $L \to \infty$ differential and absolute Poisson's ratios acquire universal values which are depend on d_c
- in the limit $\sigma \ll \sigma_L$ Poisson's ratio depends on boundary conditions