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Thermomechanical and Interfacial Properties of Graphene Membranes

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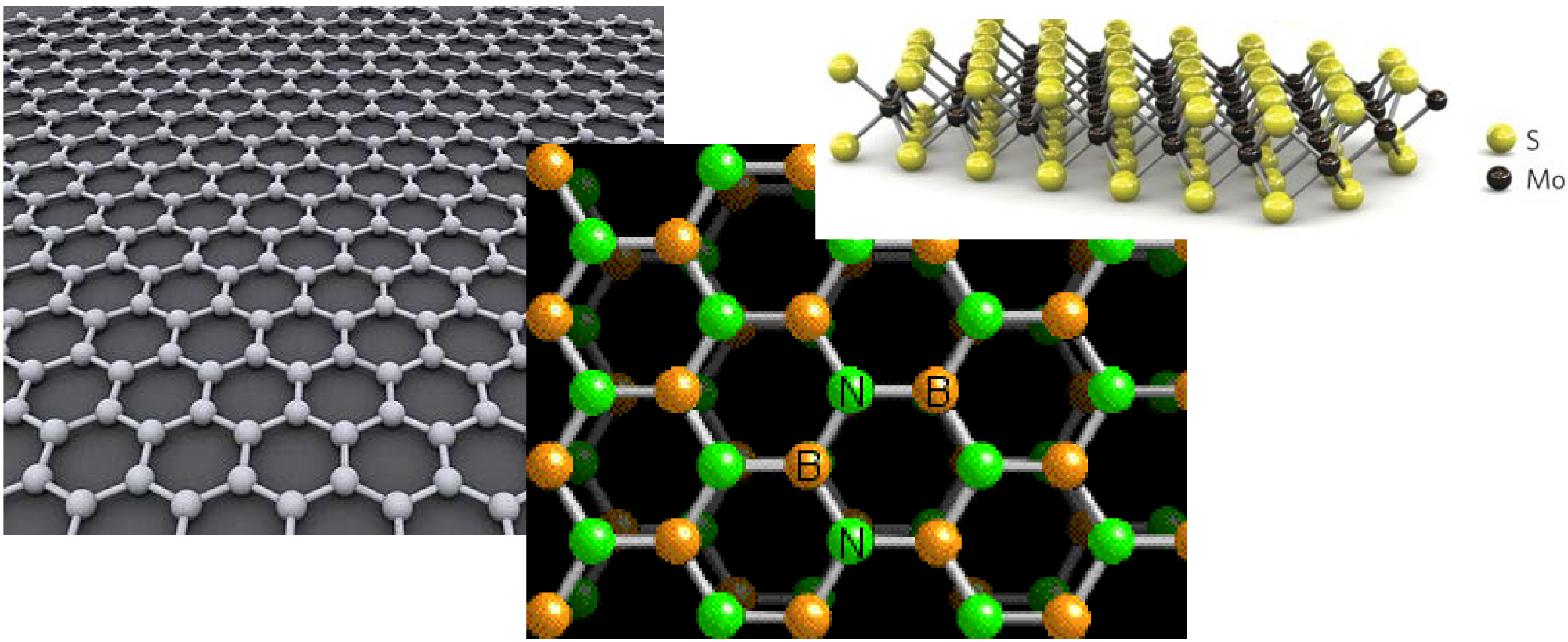
Membrane Materials or Structures

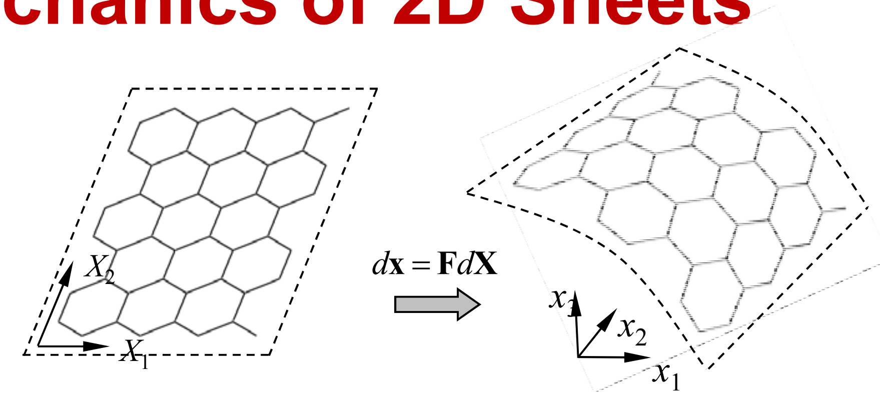
- Mechanical (solid) membranes: no bending rigidity
- Bio-membranes (lipid bilayers, fluid membranes, etc.)
- 2D crystal monolayers: graphene, h-BN, MoS_2, etc.



Nonlinear Continuum Mechanics of 2D Sheets

2D-to-3D deformation gradient:

$$F_{iJ} = \frac{\partial x_i}{\partial X_J}$$



In-plane deformation: 2D Green-Lagrange strain tensor

$$E_{JK} = \frac{1}{2}\left(F_{iJ}F_{iK} - \delta_{JK}\right) \Rightarrow \varepsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial w}{\partial x_\alpha}\frac{\partial w}{\partial x_\beta}\right)$$

Bending: 2D curvature tensor (strain gradient)

$$\mathrm{K}_{IJ} = n_i \frac{\partial F_{iI}}{\partial X_J} = n_i \frac{\partial^2 x_i}{\partial X_I \partial X_J} \Rightarrow \kappa_{\alpha\beta} = \frac{\partial^2 w}{\partial x_\alpha \partial x_\beta}$$

Strain energy: $U = \int_A \Phi(\mathbf{E}, \mathbf{K}) dA$

Temperature effect?

Lu and Huang, Int. J. Applied Mechanics 1, 443-467 (2009).

Small deformation at T = 0 K (Statics)

Linear elastic strain energy: $\Phi(\boldsymbol{\varepsilon}, \boldsymbol{\kappa}) = \Phi_{\varepsilon}(\boldsymbol{\varepsilon}) + \Phi_{\kappa}(\boldsymbol{\kappa})$

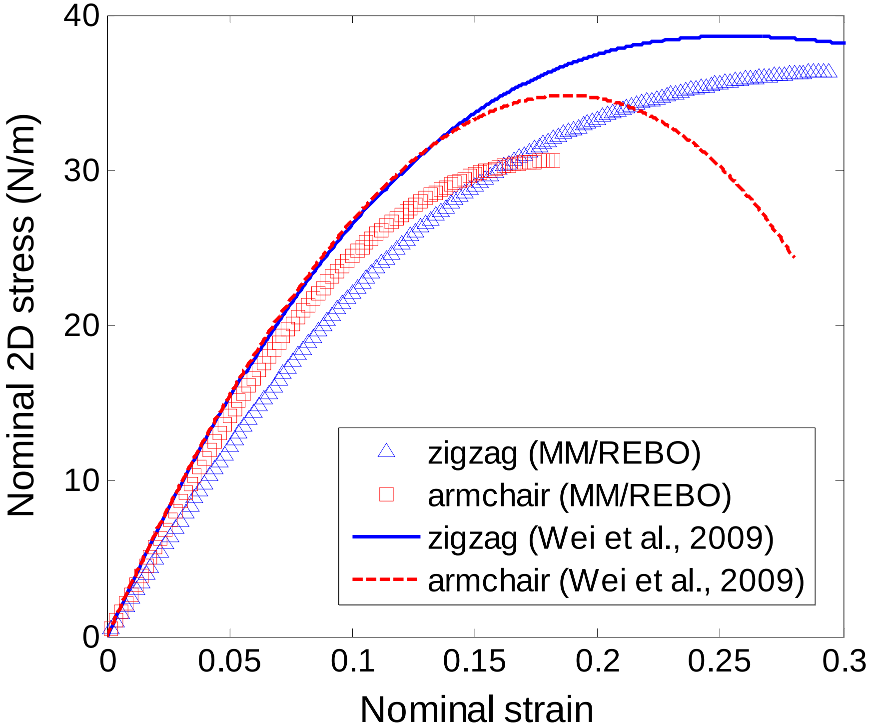
In-plane stretching: $$\Phi_{\varepsilon} = \frac{E}{2(1+\nu)}\left(\varepsilon_{\alpha\beta}\varepsilon_{\alpha\beta} + \frac{\nu}{1-\nu}\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}\right)$$

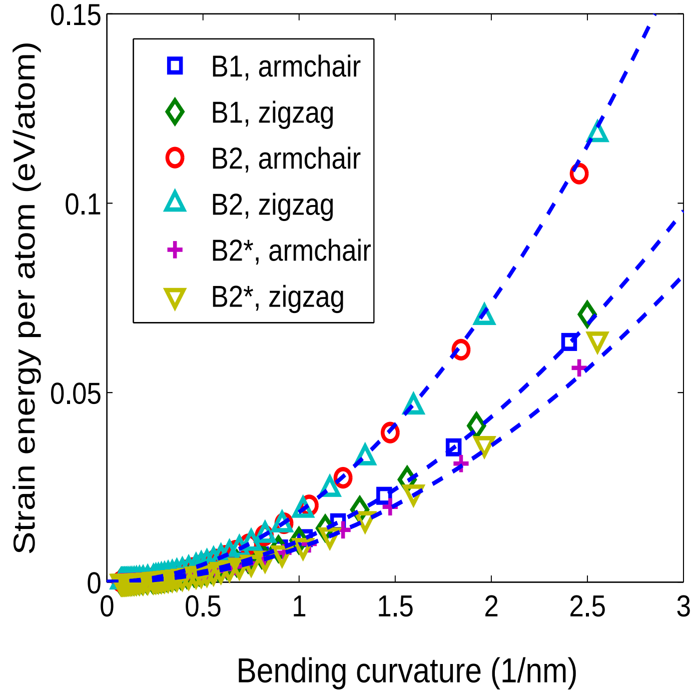
Bending: $$\Phi_{\kappa} = \frac{1}{2}D(\kappa_1 + \kappa_2)^2 - D_G\kappa_1\kappa_2$$

Moderately nonlinear kinematics: $$\varepsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} + \frac{\partial w}{\partial x_{\alpha}}\frac{\partial w}{\partial x_{\beta}}\right)$$

The basic elastic properties (E, ν, D, and D_G) can be determined by DFT or molecular mechanics (statics) calculations. *They are NOT directly related to each other!*

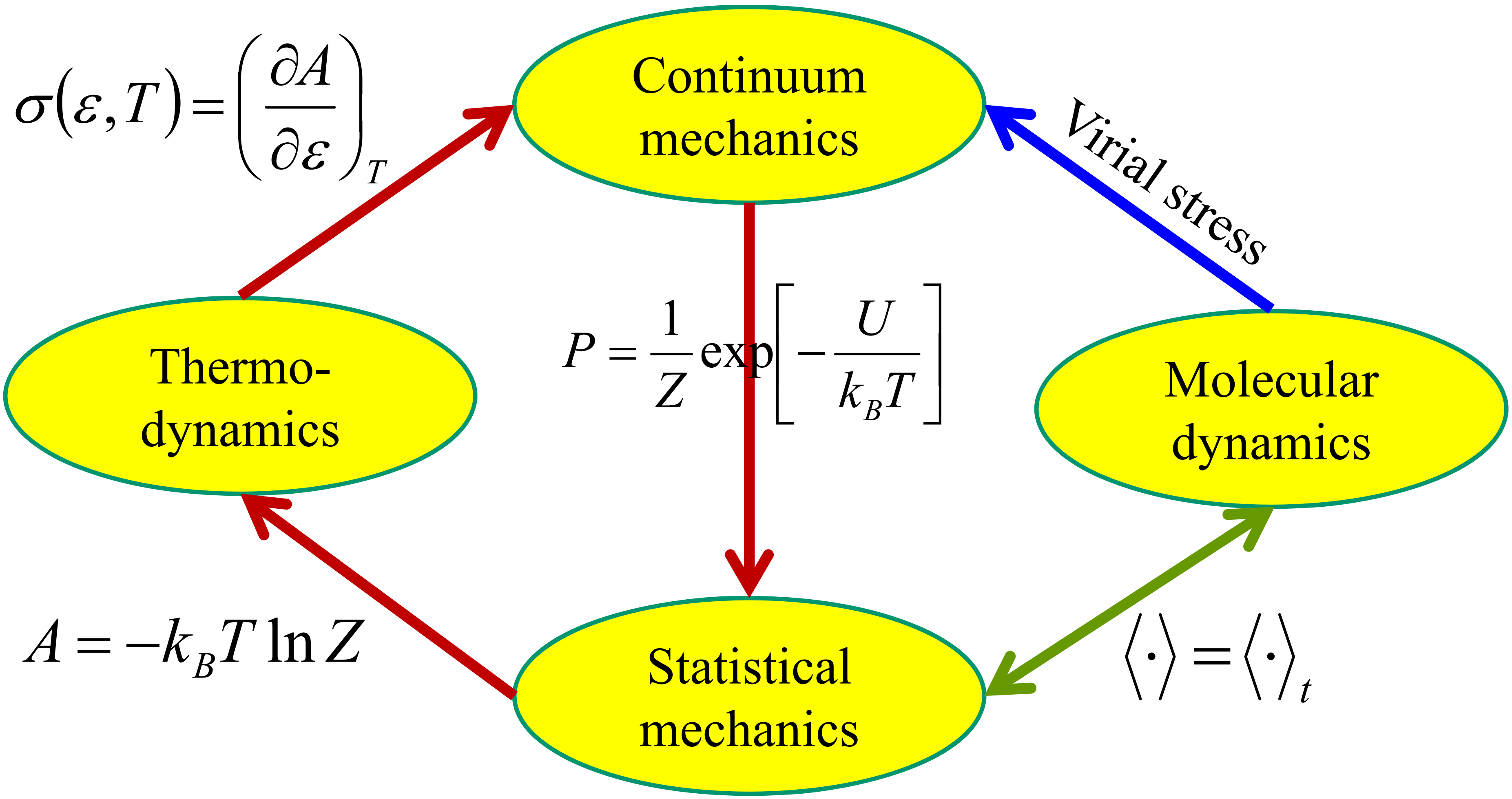
Elastic properties of graphene at T = 0 K





Method	E (N/m)	v	E/(1-v)	D (eV)
DFT	345	0.149	406	1.5
MM (REBO-2)	243	0.397	403	1.4
MM (AIREBO)	277	0.366	437	1.0

T > 0 K: a hybrid approach



Harmonic analysis of thermal fluctuation

$$w(\mathbf{r}) = \sum_k \hat{w}(\mathbf{q}_k) e^{i\mathbf{q}_k \cdot \mathbf{r}} \qquad U_b = \frac{DL_0^2}{2} \sum_k q_k^4 \left[\hat{w}_{\mathrm{Re}}^2(\mathbf{q}_k) + \hat{w}_{\mathrm{Im}}^2(\mathbf{q}_k) \right]$$

$$Z_b = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left(-\frac{U_b}{k_B T} \right) d\hat{w}_{\mathrm{Re}}(\mathbf{q}_1) d\hat{w}_{\mathrm{Im}}(\mathbf{q}_1) \cdots = \prod_{k(\mathbf{q}_k \cdot \mathbf{e}_y \geq 0)} \left(\frac{\pi k_B T}{DL_0^2 q_k^4} \right)$$

$$\left\langle \left| \hat{w}(\mathbf{q}_k) \right|^2 \right\rangle = \frac{1}{Z_b} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left| \hat{w}(\mathbf{q}_k) \right|^2 \exp\left(-\frac{U_b}{k_B T} \right) d\hat{w}_{\mathrm{Re}}(\mathbf{q}_1) d\hat{w}_{\mathrm{Im}}(\mathbf{q}_1) \cdots = \frac{k_B T}{DL_0^2 q_k^4}$$

$$\left\langle h^2 \right\rangle = \sum_k \left\langle \left| \hat{w}(\mathbf{q}_k) \right|^2 \right\rangle = \frac{k_B T}{DL_0^2} \sum_k q_k^{-4}$$

$$\bar{h} = \sqrt{\left\langle h^2 \right\rangle} = L_0 \sqrt{\frac{\gamma_n k_B T}{16\pi^4 D}}$$

Basically a linear plate model, independent of in-plane stiffness or Gaussian curvature.

Effect of pre-tension (still harmonic)

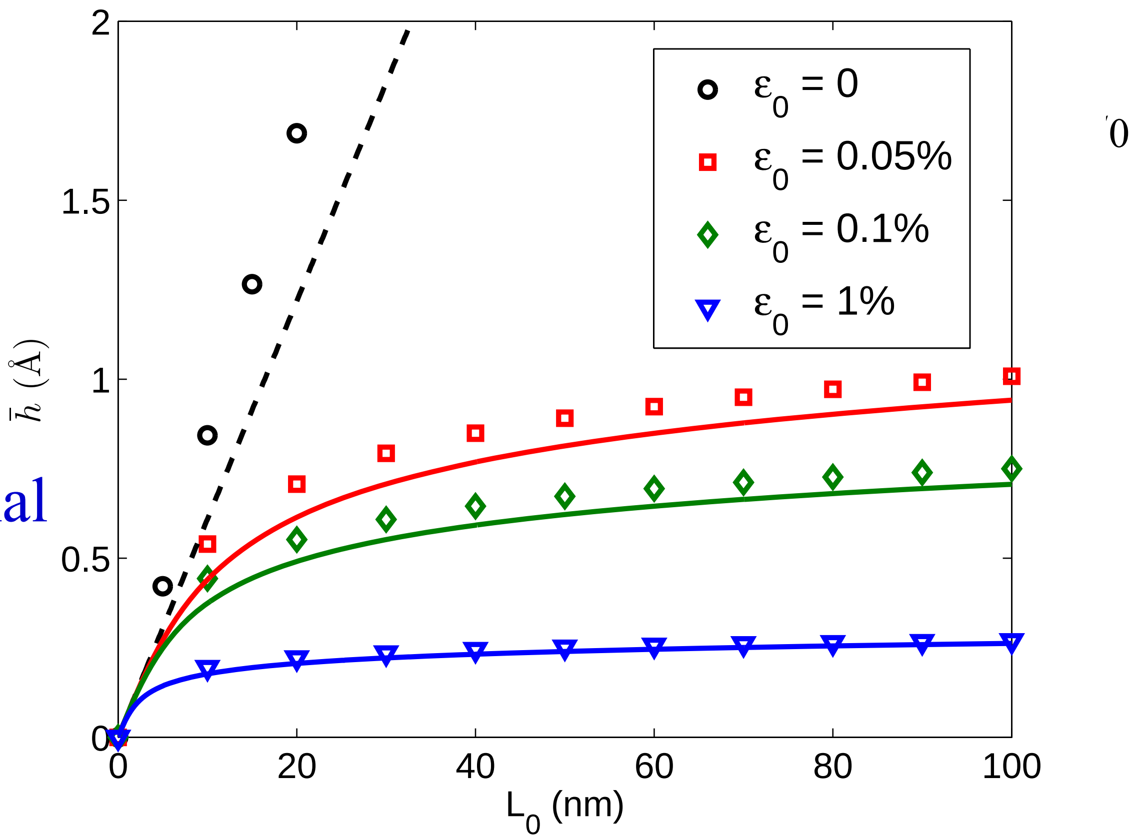
$$U = U_b + U_s = E^* \varepsilon_0^2 L_0^2 + L_0^2 \sum_{k(\mathbf{q}_k \cdot \mathbf{e}_y \geq 0)} \left(Dq_k^4 + E^* \varepsilon_0 q_k^2\right)\left(\hat{w}_{\mathrm{Re}}^2(\mathbf{q}_k) + \hat{w}_{\mathrm{Im}}^2(\mathbf{q}_k)\right)$$

$$\langle h^2 \rangle = \frac{k_B T}{D L_0^2} \sum_k q_k^{-4} \left(1 + \frac{E^* \varepsilon_0}{D q_k^2}\right)^{-1}$$

$$\approx \frac{k_B T}{4\pi E^* \varepsilon_0} \ln\left(1 + \frac{E^* \varepsilon_0 L_0^2}{4\pi^2 D}\right)$$

A small pre-tension can considerably suppress thermal fluctuation, resulting in a different scaling behavior.

$$l = \sqrt{\frac{D}{E^* \varepsilon_0}} = \frac{\mathbf{0.024nm}}{\sqrt{\varepsilon_0}}$$



Gao and Huang, JMPS, in press.

Nonlinear thermoelasticity

Partition function:

$$Z(\varepsilon_0, T) = \exp\left(-\frac{E^* \varepsilon_0^2 L_0^2}{k_B T}\right) \prod_{k(\mathbf{q}_k \cdot \mathbf{e}_y \geq 0)} \left[\left(1 + \frac{E^* \varepsilon_0}{D q_k^2}\right)^{-1} \left(\frac{\pi k_B T}{D L_0^2 q_k^4}\right) \right]$$

Helmholtz free energy: $A(\varepsilon_0, T) = -k_B T \ln Z(\varepsilon_0, T)$

Stress: $$\sigma(\varepsilon_0, T) = \frac{1}{2L_0^2}\left(\frac{\partial A}{\partial \varepsilon_0}\right)_T = E^* \varepsilon_0 + \tilde{\sigma}(\varepsilon_0, T)$$

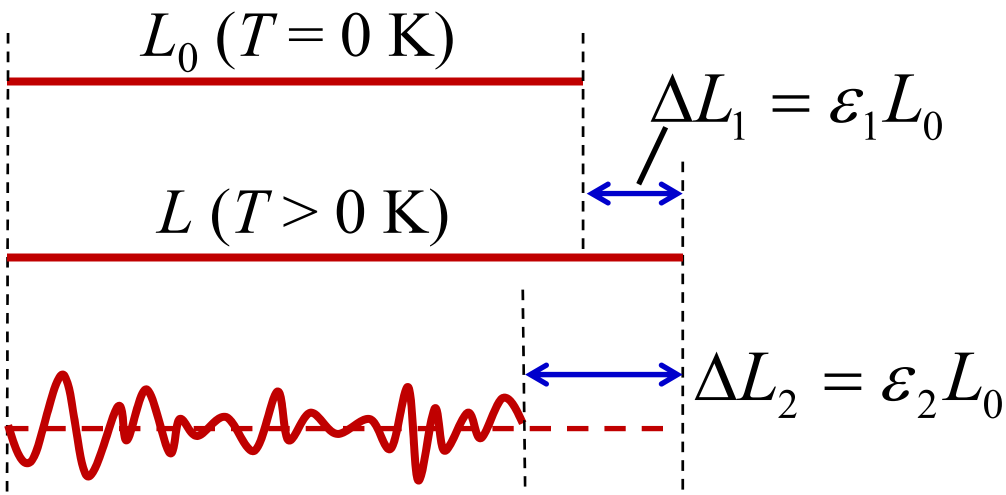
→ Fluctuation induced tension

Tangent modulus: $$\tilde{E}^* = \frac{\partial \sigma}{\partial \varepsilon_0} \approx E^* - \frac{E^* k_B T}{16 \pi D}\left(\frac{4\pi^2 D}{E^* L_0^2} + \varepsilon_0\right)^{-1}$$

→ Thermal softening and strain stiffening; size dependent?

Gao and Huang, JMPS, in press.

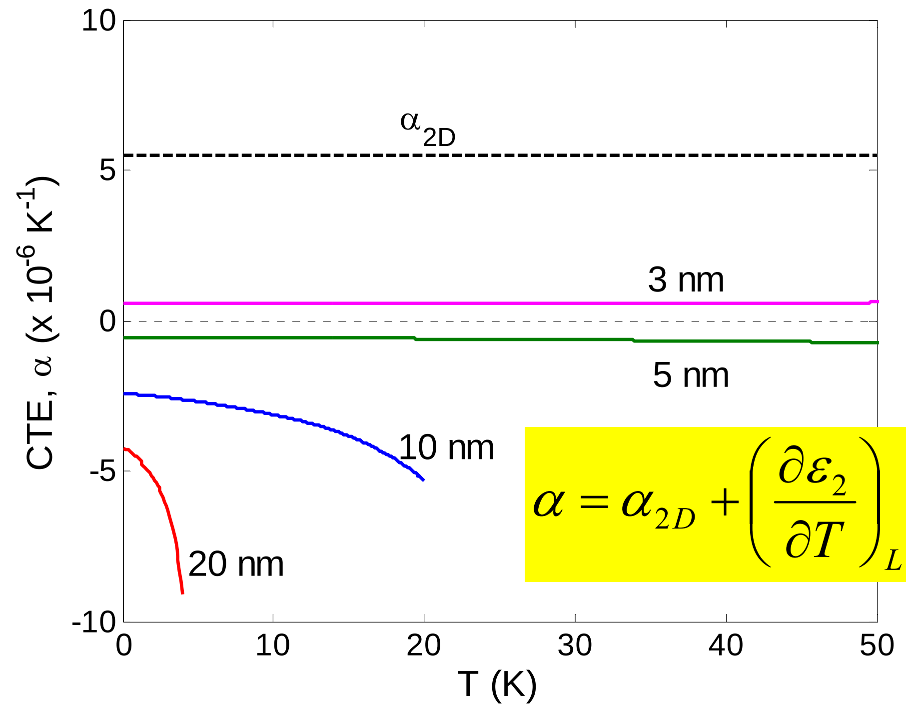
Thermal expansion



$$\varepsilon_1 = \alpha_{2D} T > 0$$

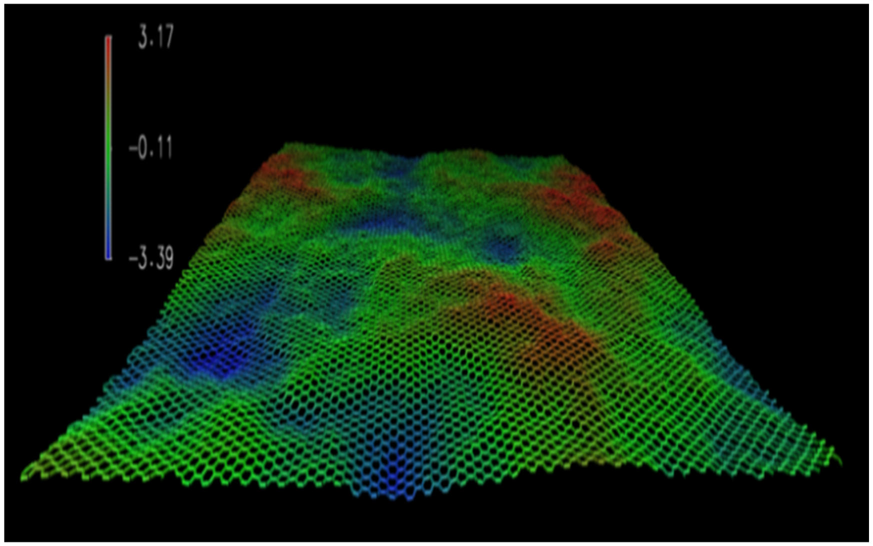
$$\varepsilon_2(T, L_0) < 0$$

- Anharmonic in-plane oscillations result in a positive thermal expansion, nearly independent of temperature (up to 1000 K).
- Out-of-plane fluctuation leads to in-plane contraction (negative thermal expansion) – anharmonic effects TBD



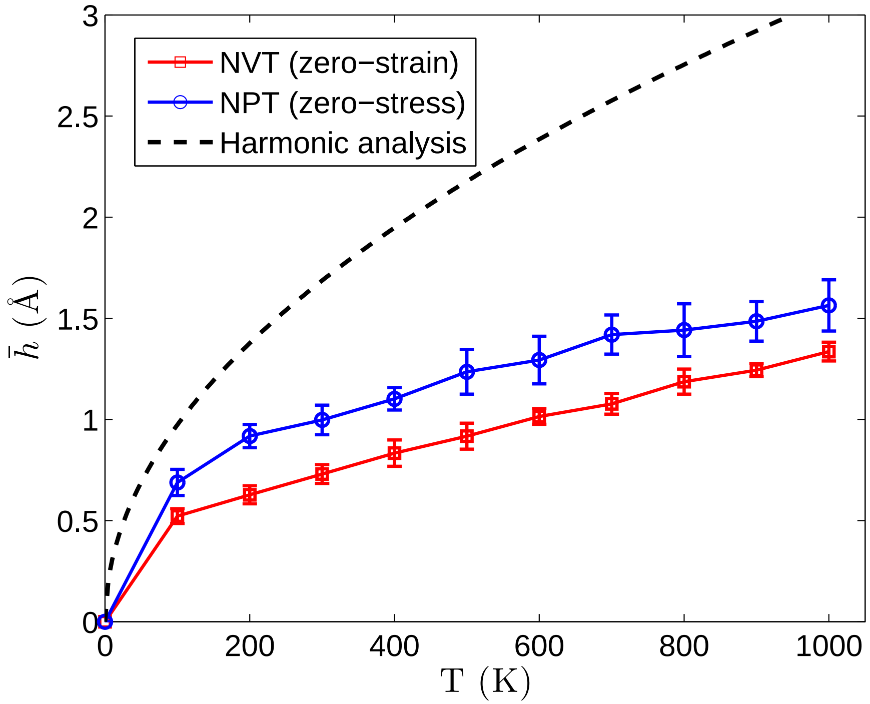
MD Simulations (T > 0 K)

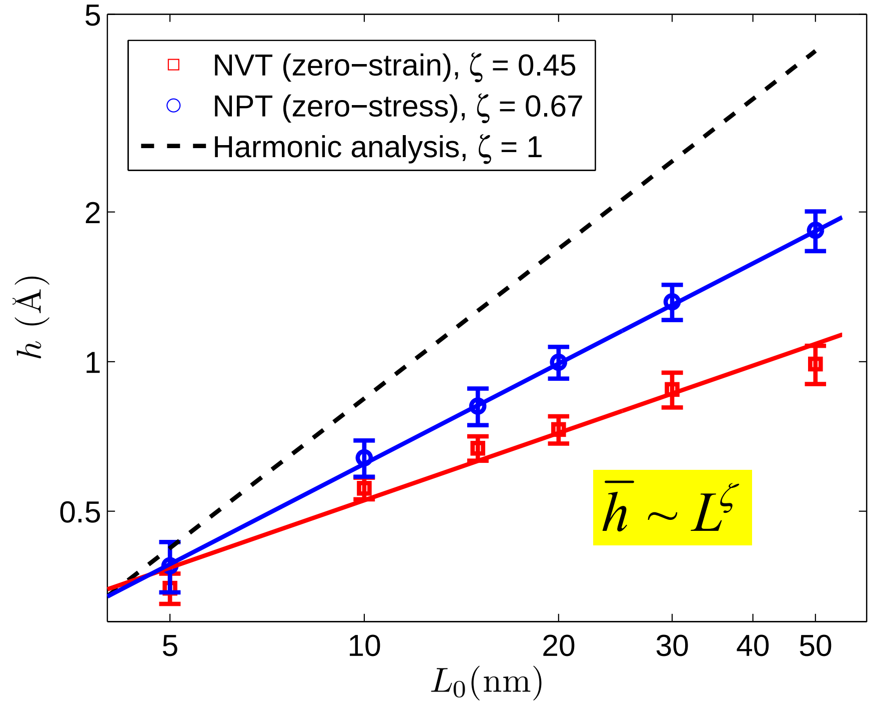
- Free-standing graphene in NPT ensemble (zero stress)
- Constrained graphene in NVT ensemble (zero strain)
- Biaxially strained graphene in NVT ensemble



- ➢ Thermal rippling
- ➢ Thermal expansion/contraction
- ➢ Thermal stress
- ➢ Temperature dependent mechanical properties

Thermal Rippling



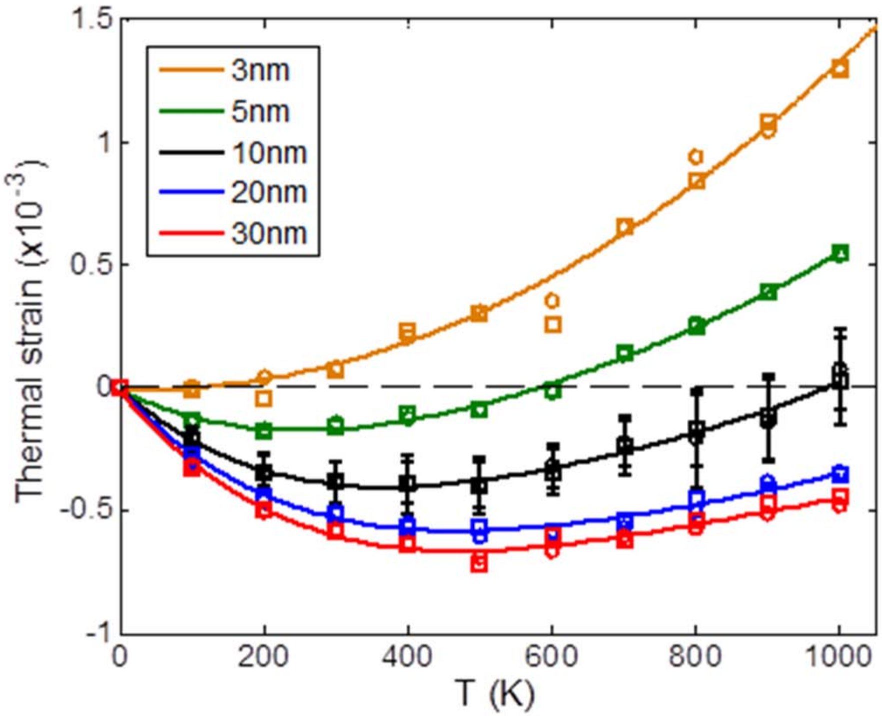


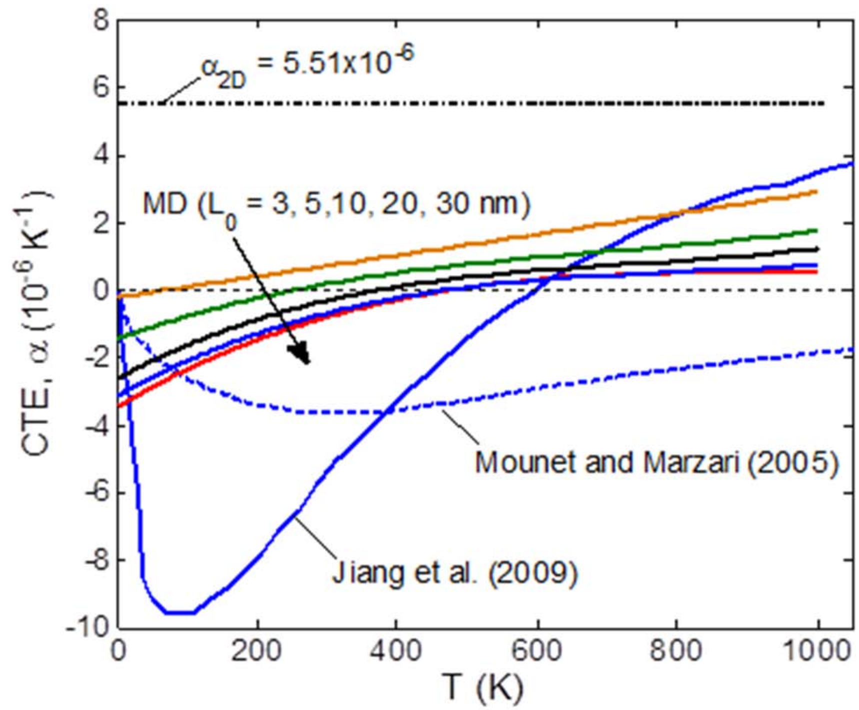
Harmonic approximation: $\bar{h} = \sqrt{\langle h^2 \rangle} = L_0 \sqrt{\frac{\gamma_n k_B T}{16\pi^4 D}}$

- Significant anharmonic effects due to coupling between bending and stretching ($\zeta < 1$), similar to biomembranes!

Gao and Huang, JMPS, in press.

NPT: Thermal Expansion/Contraction

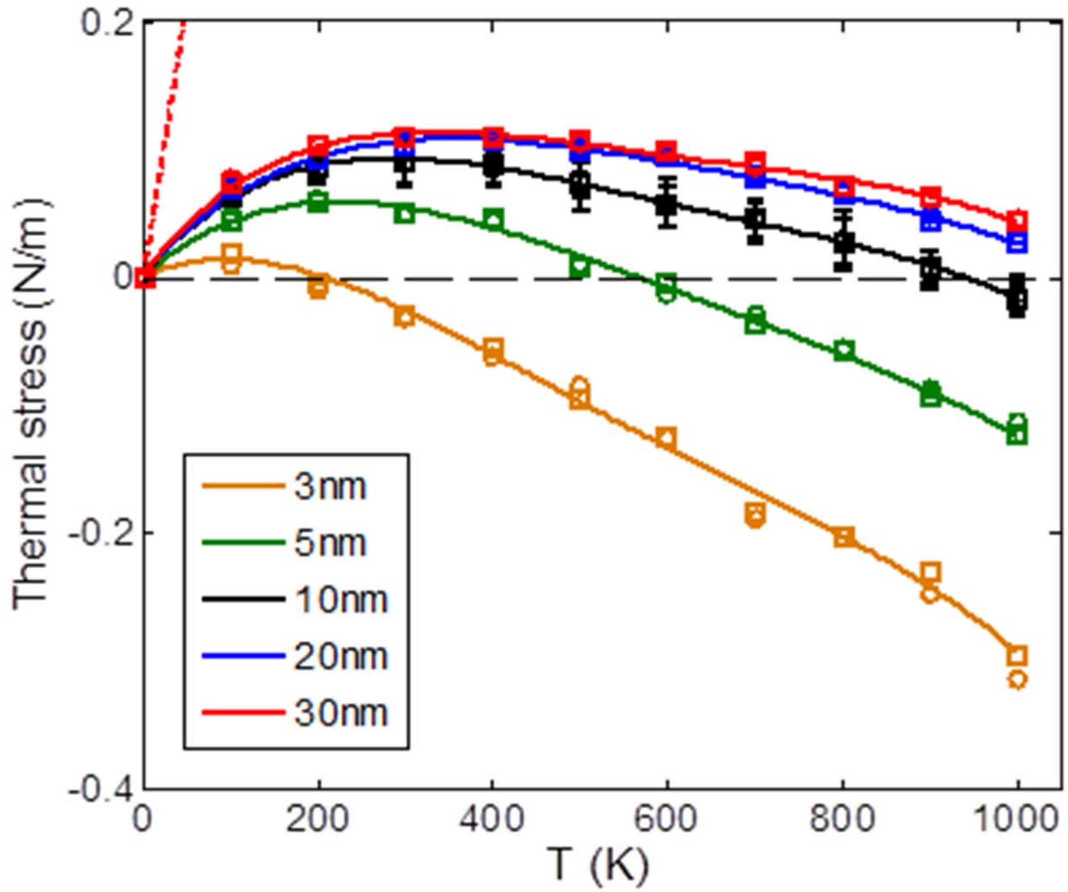




- Negative thermal expansion at low T, and positive at high T.
- Thermal expansion/contraction is size dependent!
- By suppressing out-of-plane fluctuations, 2D simulations predict a constant positive CTE (size-independent).

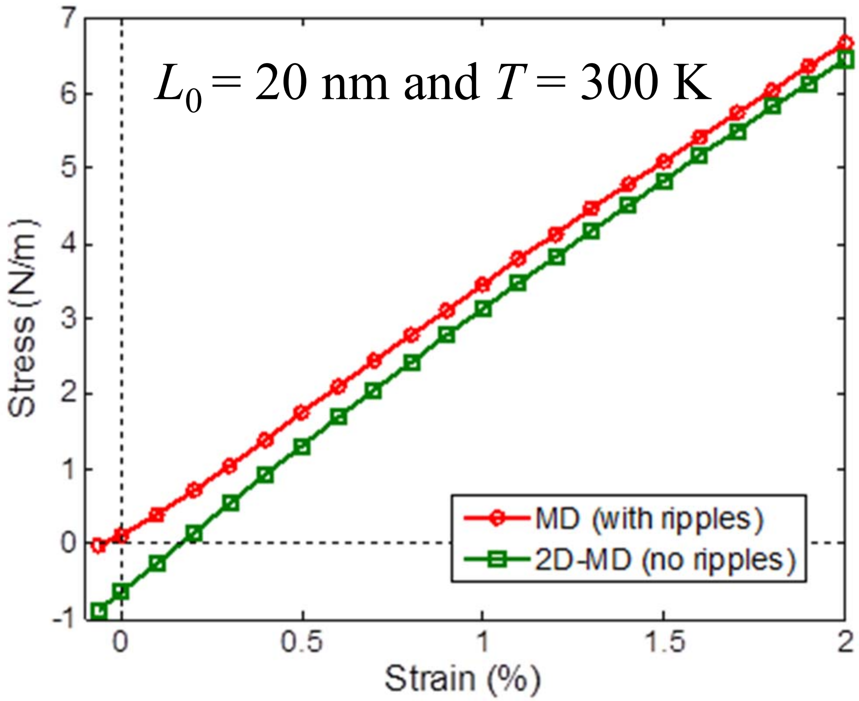
Gao and Huang, JMPS, in press.

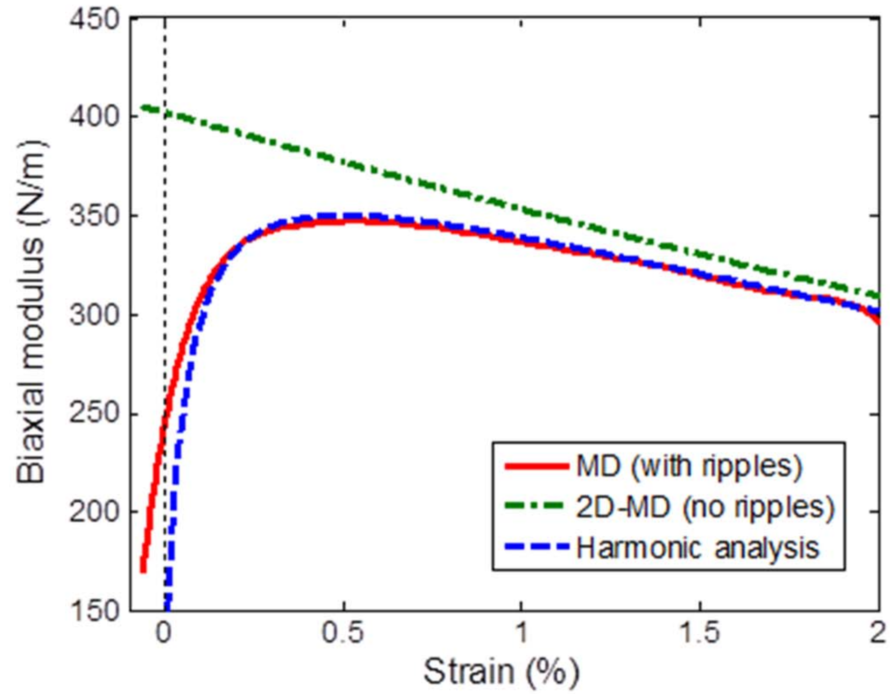
NVT: Thermal Stress at Zero Strain

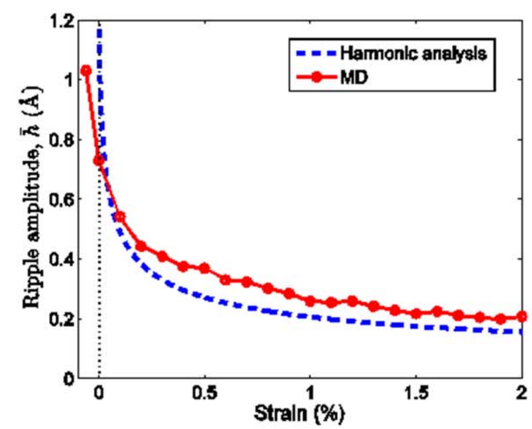


- As expected, negative thermal expansion leads to tensile stress at low T, and the opposite is true at high T.
- However, thermal rippling differs under NPT and NVT.

NVT: biaxially strained graphene







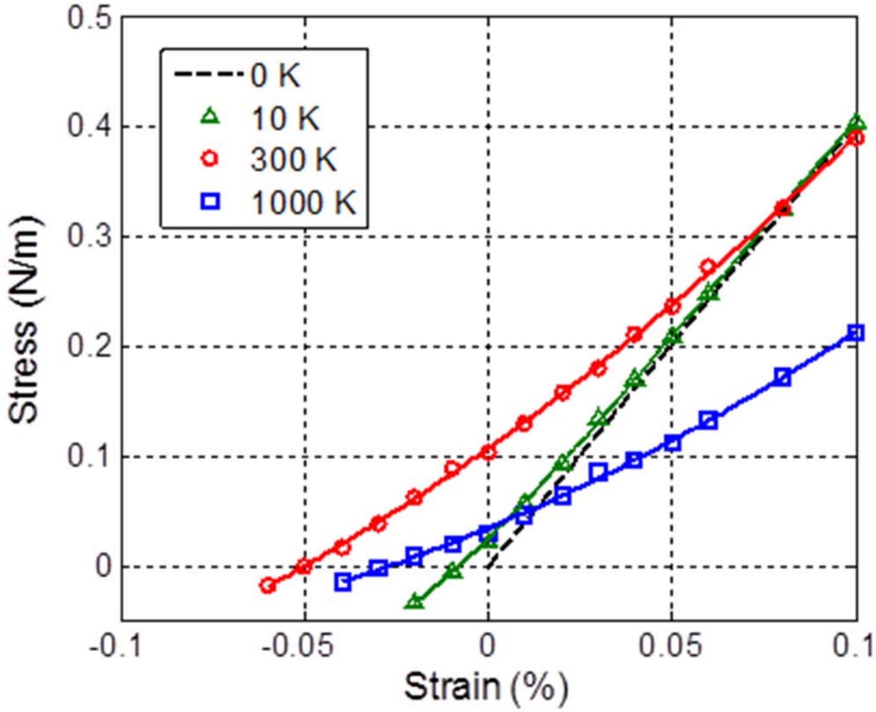
Nonlinear elasticity due to two effects:

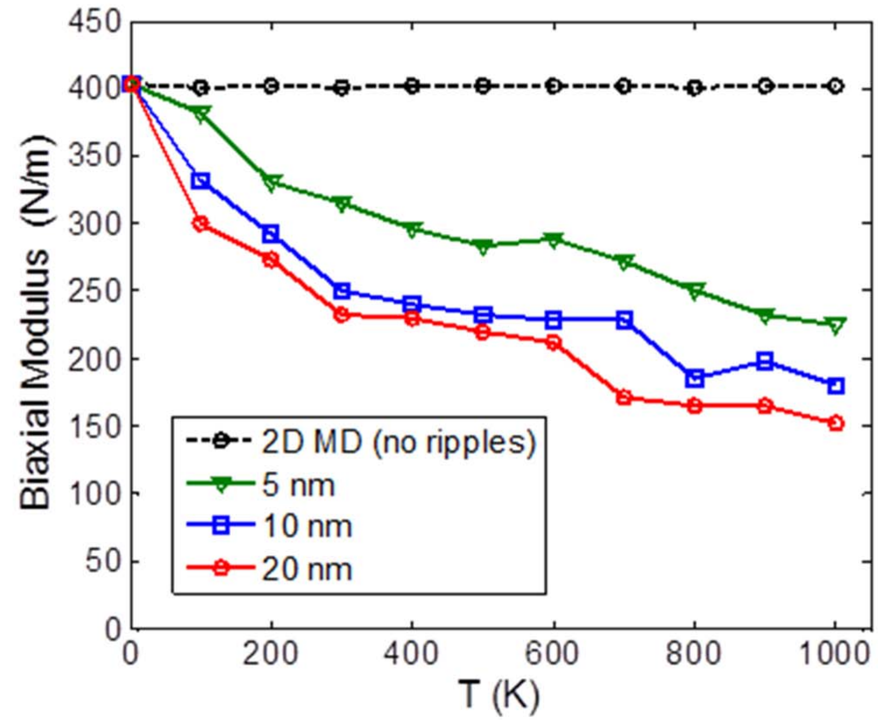
(1) intrinsic strain softening (large strain behavior);

(2) strain stiffening due to thermal rippling (small strain behavior)

Gao and Huang, JMPS, in press.

Biaxial modulus at zero strain

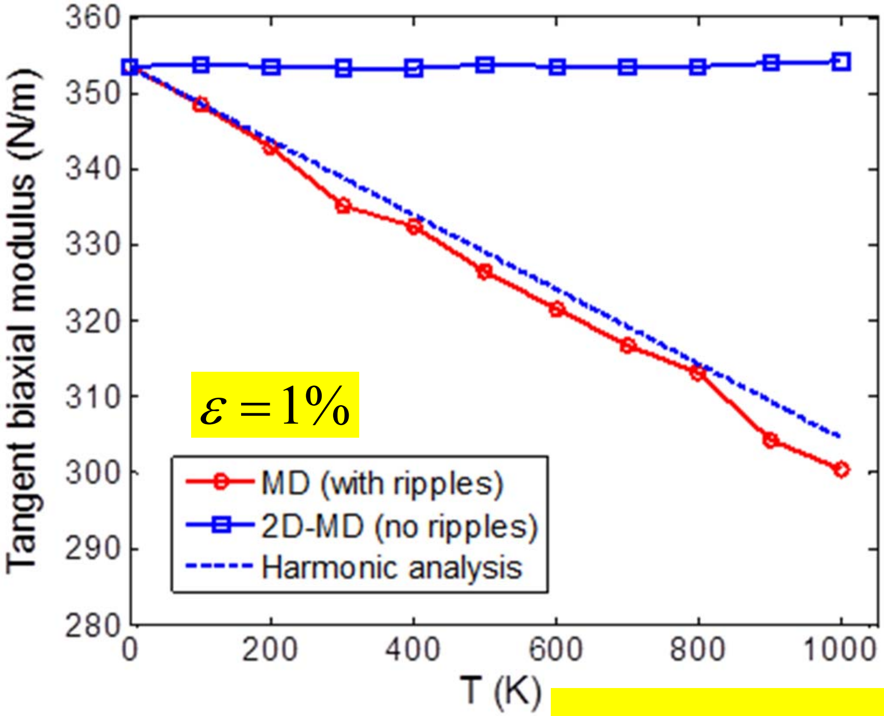


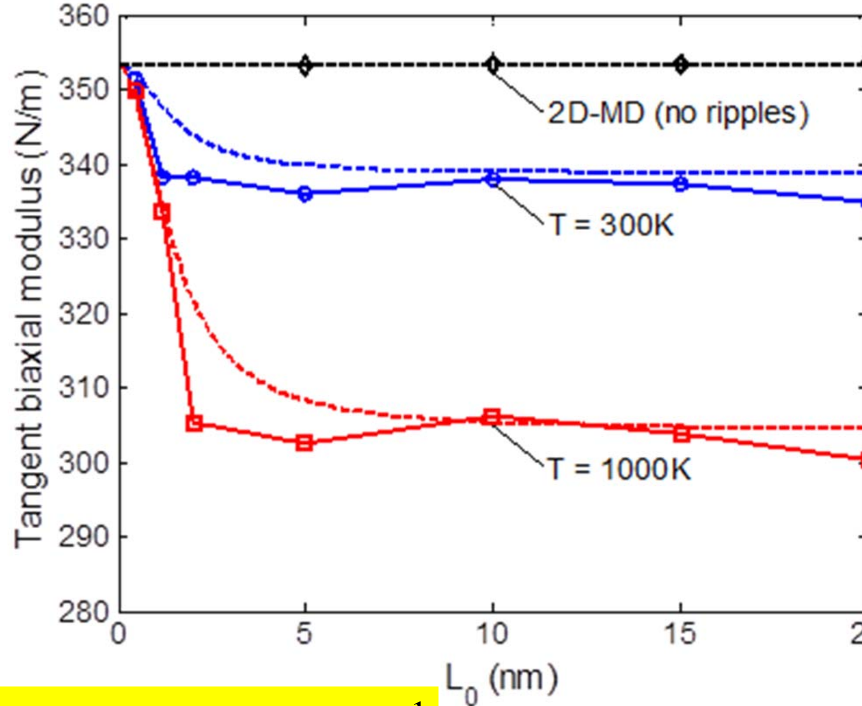


Due to the effect of thermal rippling, the elastic modulus becomes both temperature and size-dependent at zero strain; this effect however is largely beyond harmonic.

Gao and Huang, JMPS, in press.

Biaxial modulus at 1% strain





$$\tilde{E}^* \approx E^* - \frac{E^* k_B T}{16\pi D}\left(\frac{4\pi^2 D}{E^* L_0^2} + \varepsilon_0\right)^{-1}$$

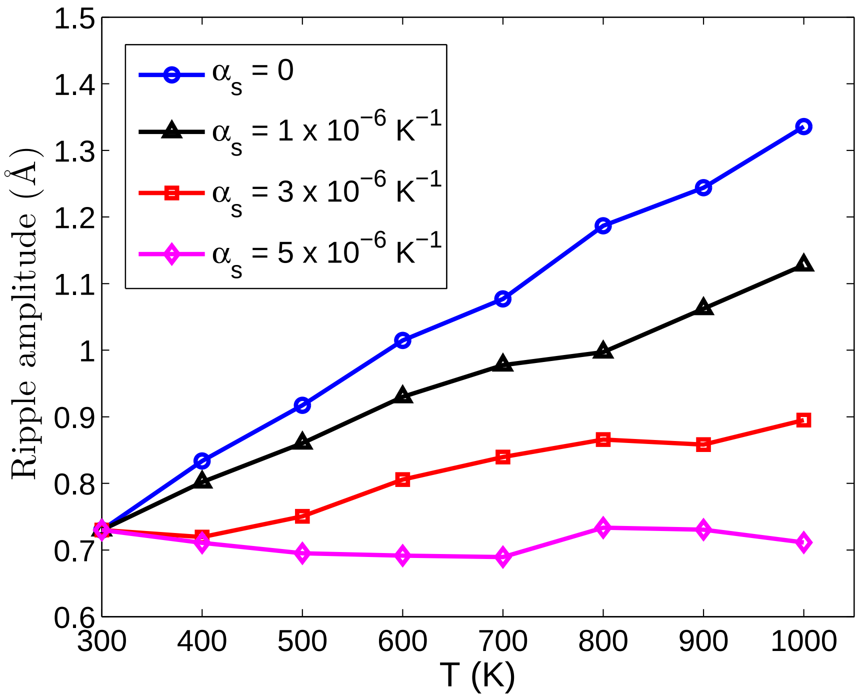
- The effect of thermal rippling reduces as the strain increases;
- The tangent elastic modulus decreases linearly with temperature (almost harmonic), and becomes size independent for relatively large membranes.

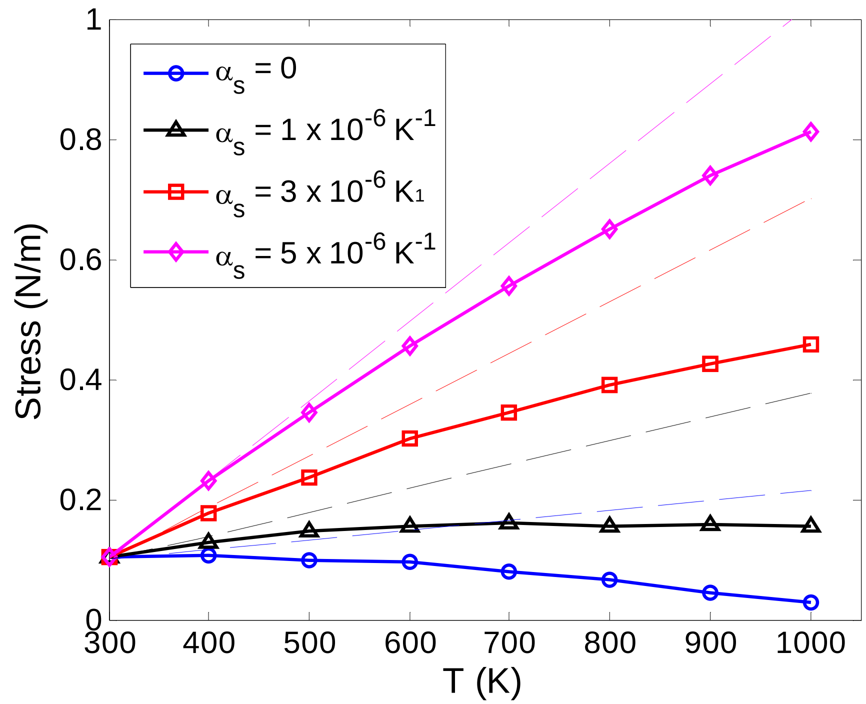
Gao and Huang, JMPS, in press.

Graphene on substrate

$$\varepsilon = \alpha_s (T - T_0)$$

- Assume that the in-plane dimension of graphene follows thermal expansion of the substrate (full strain transfer).

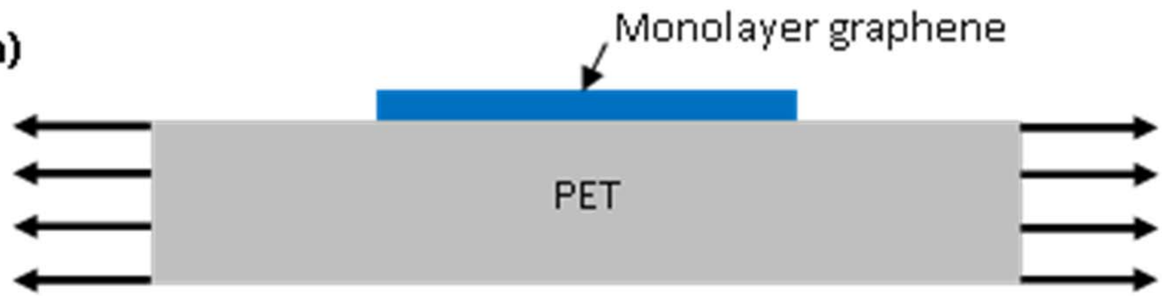




Gao and Huang, JMPS, in press.

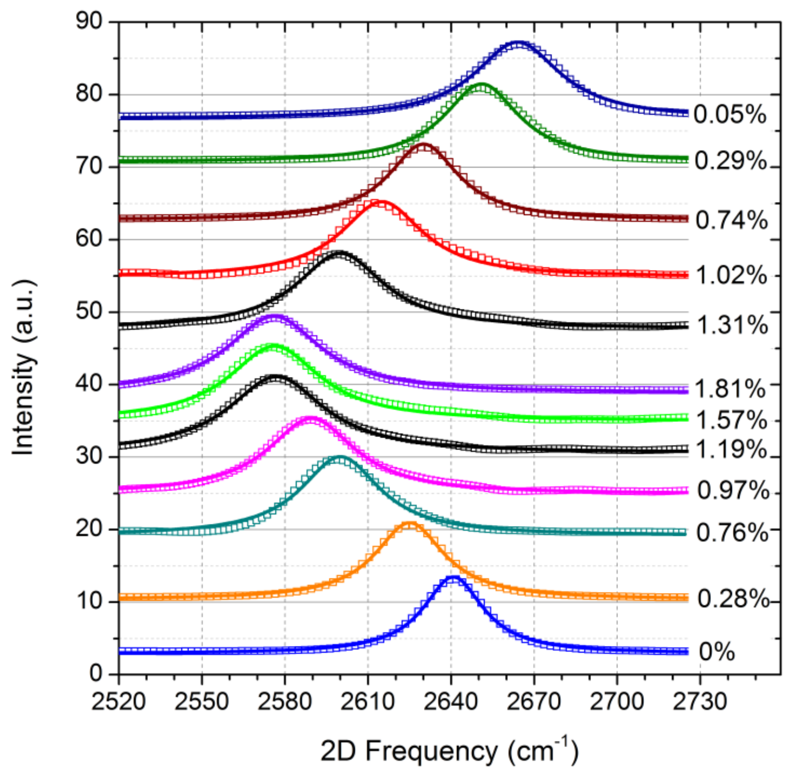
Interfacial strain transfer

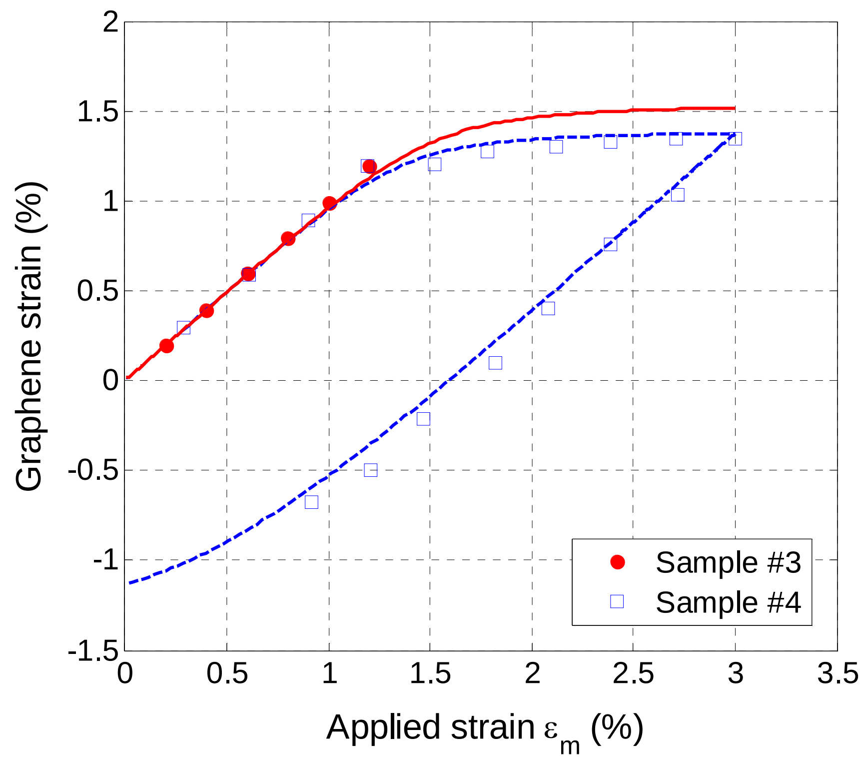
(a)



$$\varepsilon_p = \frac{\tau_c L}{2E_{2D}}$$

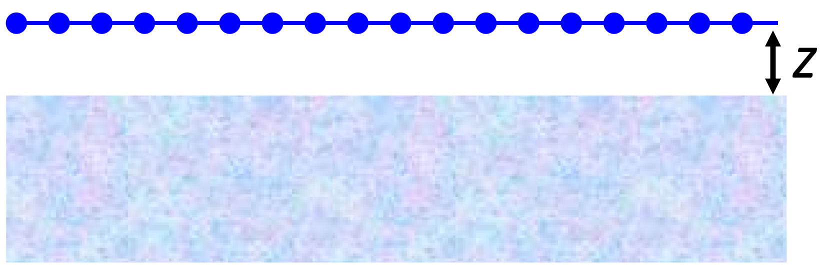
$$\tau_c \sim 0.5\ \mathbf{MPa}$$





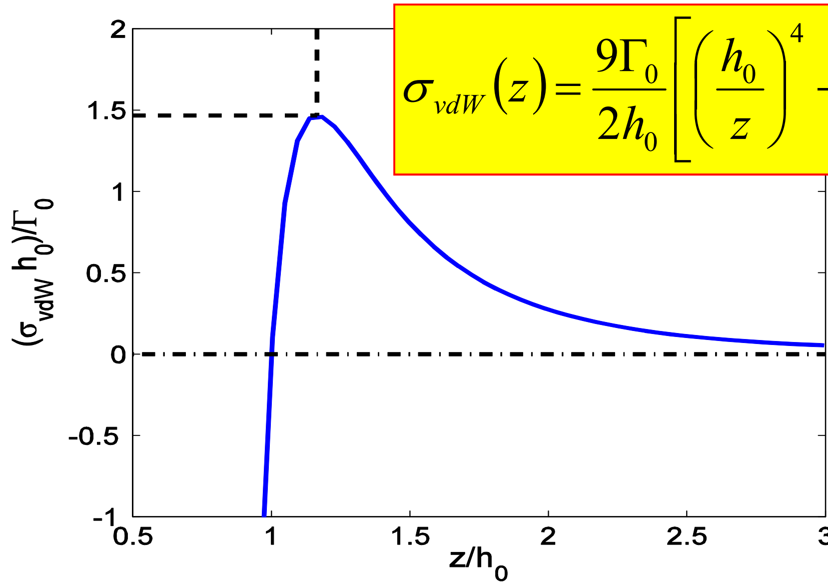
Jiang, Huang, and Zhu, Adv. Funct. Mater., 2014.

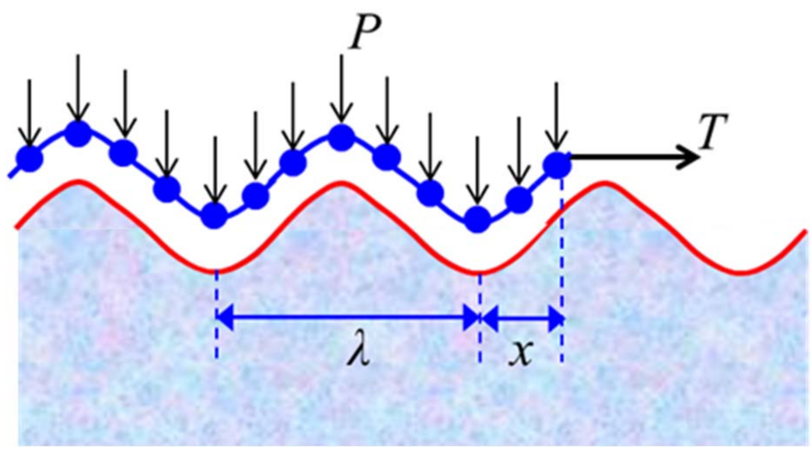
Interfacial properties: Adhesion and Friction



$$U_{vdW}(z) = -\Gamma_0 \left[\frac{3}{2}\left(\frac{h_0}{z}\right)^3 - \frac{1}{2}\left(\frac{h_0}{z}\right)^9 \right]$$

$$\sigma_{vdW}(z) = \frac{9\Gamma_0}{2h_0}\left[\left(\frac{h_0}{z}\right)^4 - \left(\frac{h_0}{z}\right)^{10} \right]$$



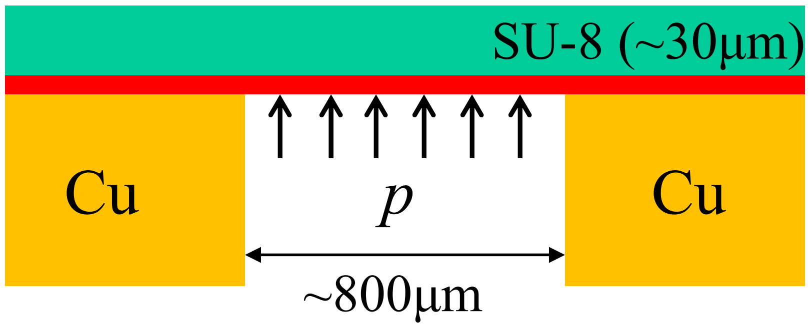


$$\tau_{\max} \approx \left[f_0\left(\frac{\lambda}{h_0}\right) + \mu\left(\frac{\lambda}{h_0}\right)\frac{p h_0}{\Gamma_0} \right] \frac{\Gamma_0 \delta_s}{h_0^2}$$

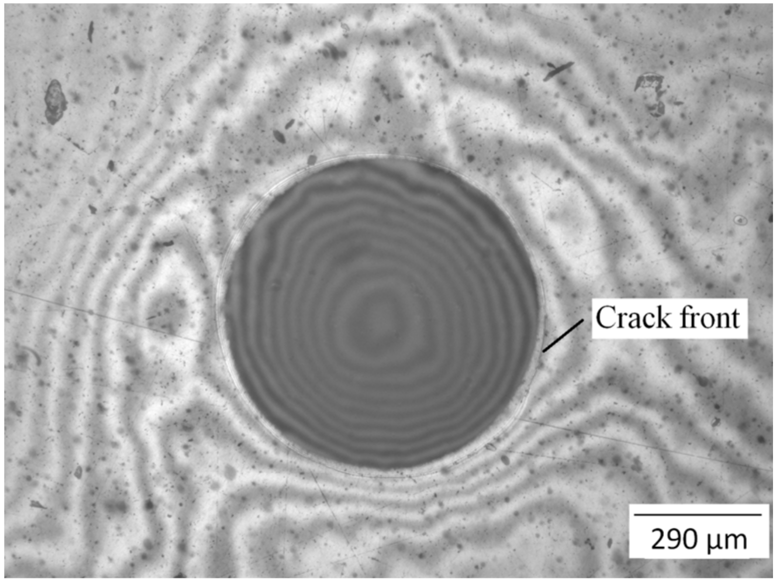
- Zero friction on a perfectly flat surface (assuming vdW).
- Friction strength depends on surface roughness and adhesion.
- Temperature effect?

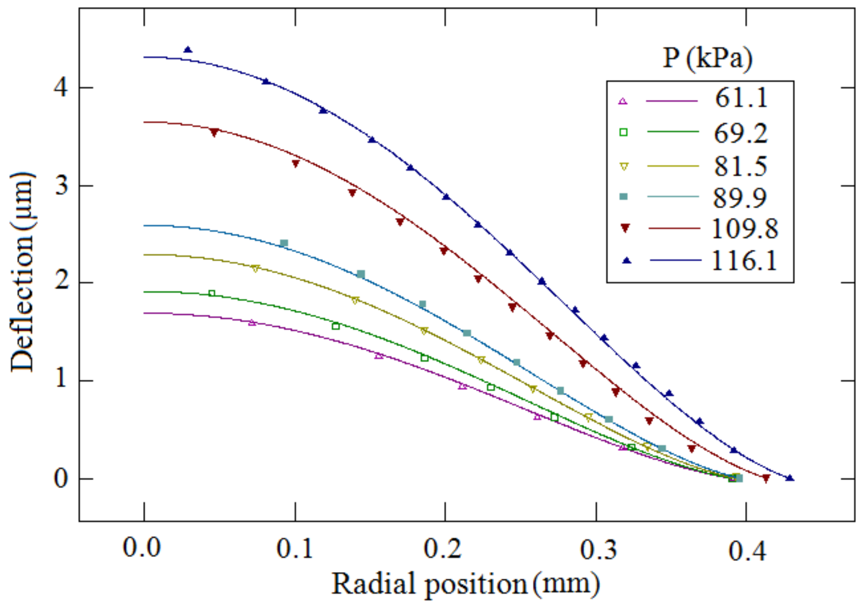
Aitken and Huang, J. Appl. Phys. 107, 123531 (2010).

A blister test



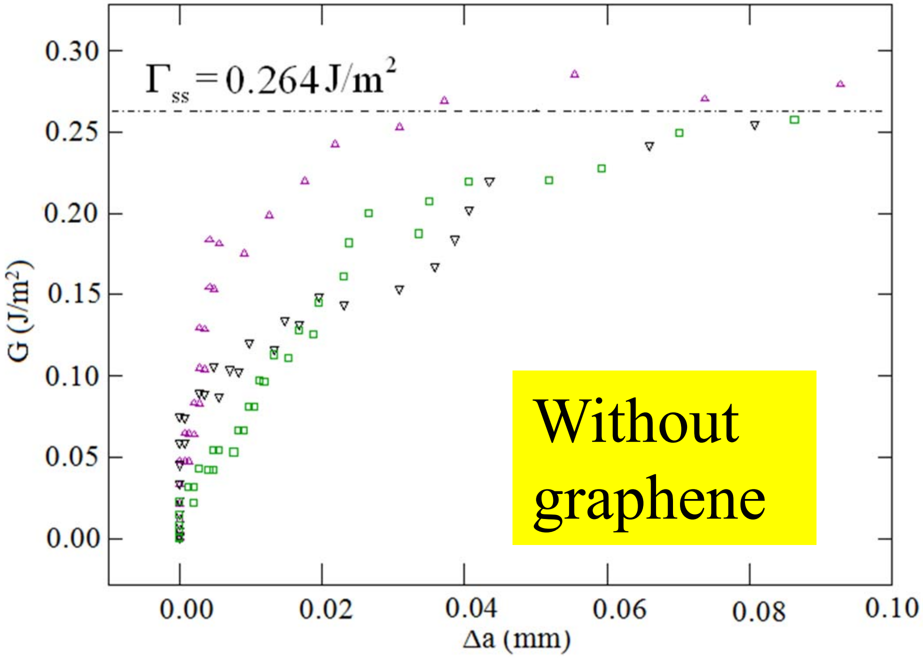
- CVD grown graphene was transferred to a copper substrate.
- The graphene/photoresist composite film was pressurized with deionized water.
- Deflection profiles were measured by a full field interference method.
- Energy release rate was calculated as a function of delamination growth to obtain fracture resistance curves.
- The delamination path was confirmed by Raman spectroscopy.

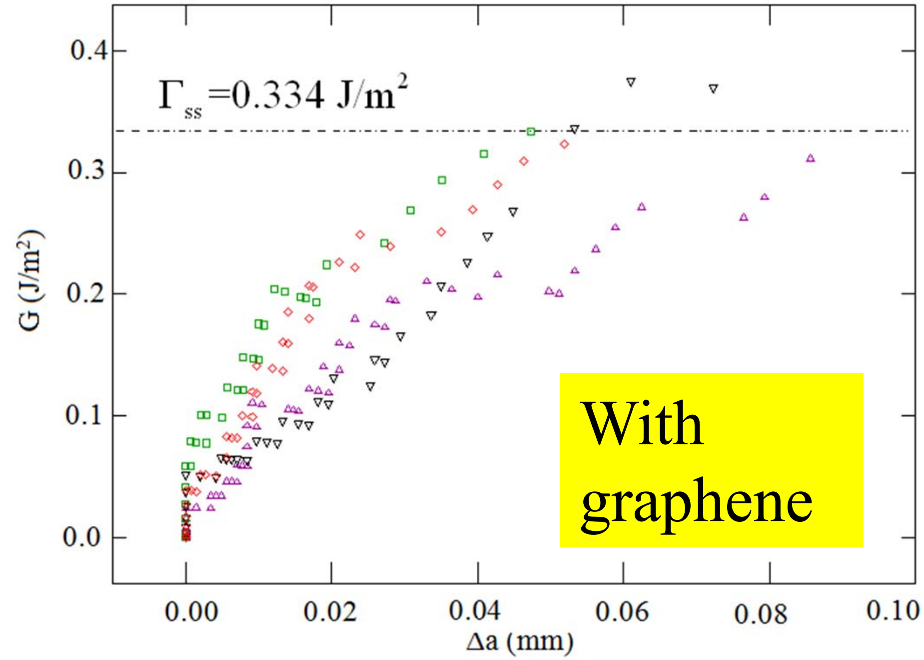




Cao et al., Carbon 2014.

Delamination Resistance Curves



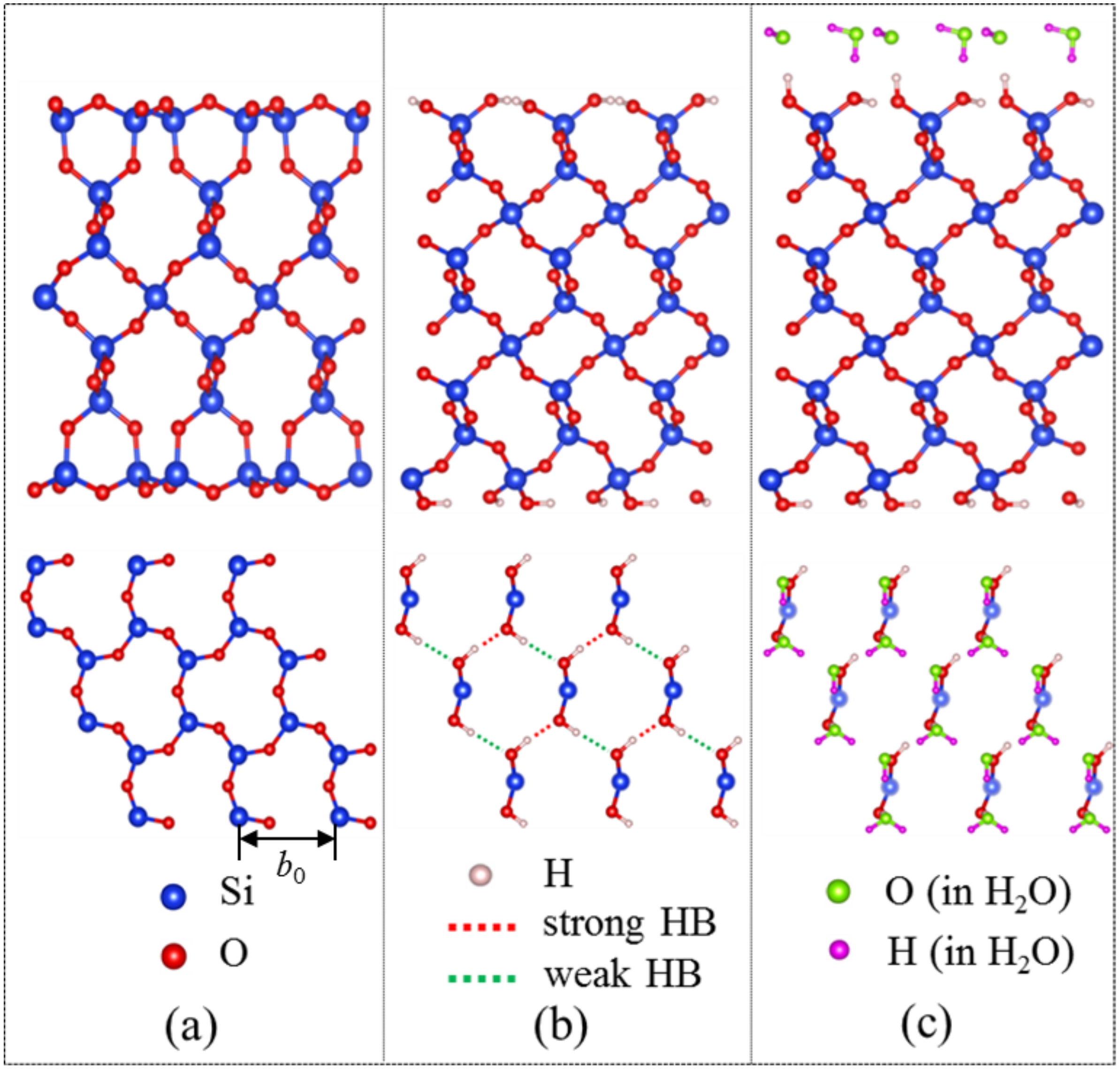


Compare to other measurements:

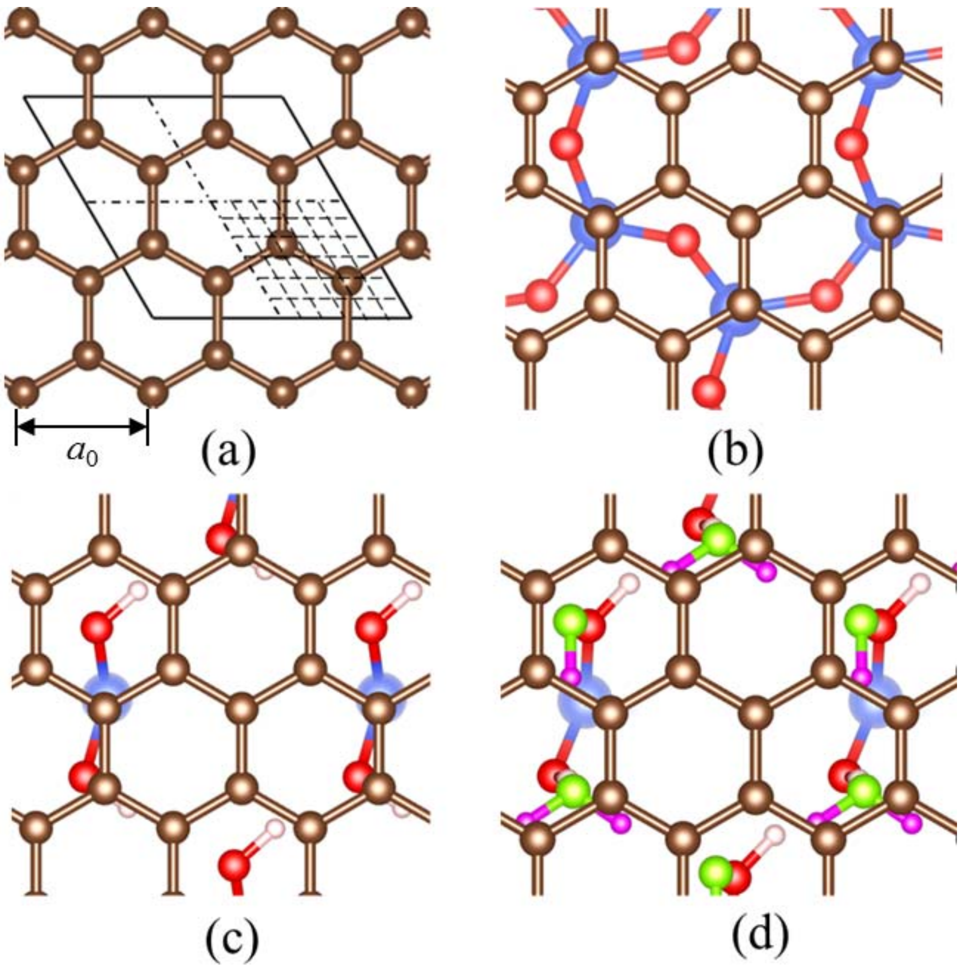
- Graphene/SiO_2: 0.2-0.45 J/m^2 (Scott Bunch)
- Graphene/Cu film: 0.72 J/m^2 (Yoon et al.)

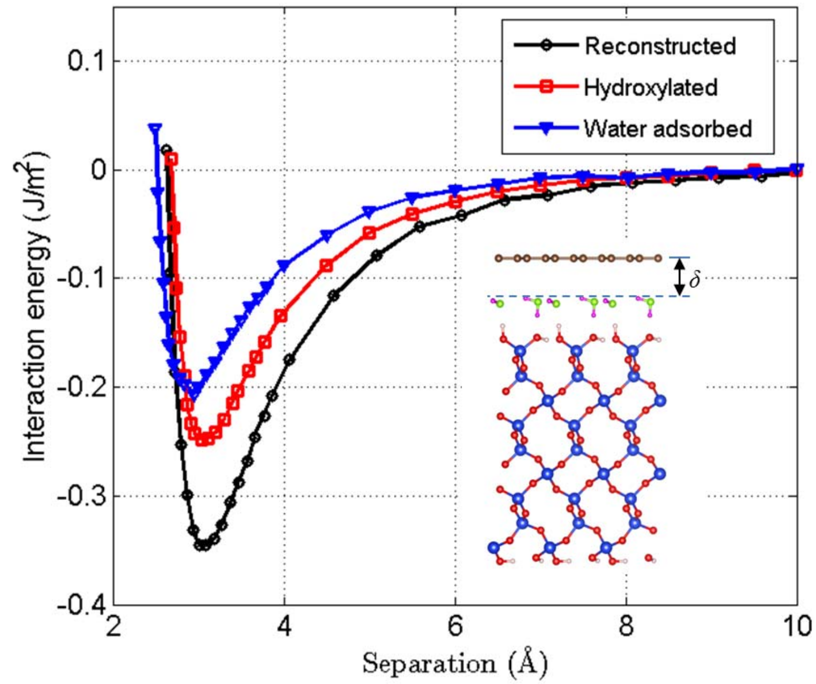
Cao et al., Carbon 2014.

Graphene/SiO_2: effect of surface structures



Graphene/SiO_2: vdW-DFT

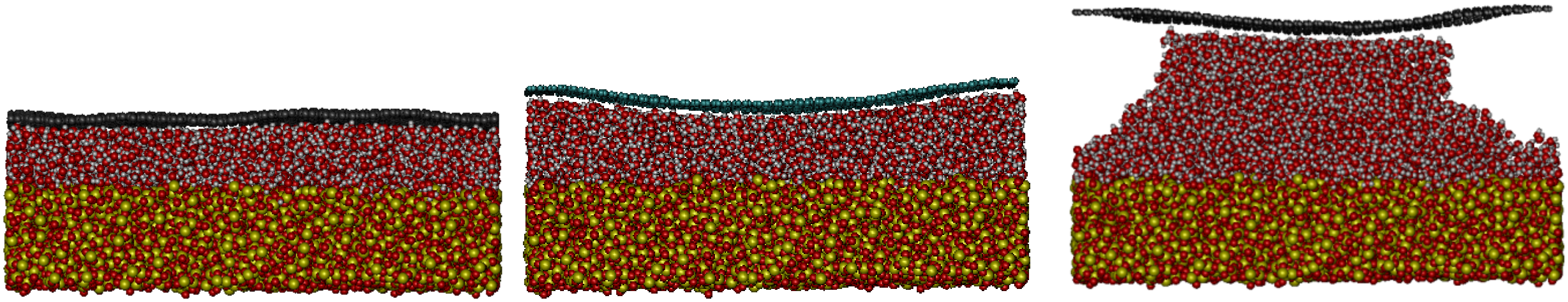


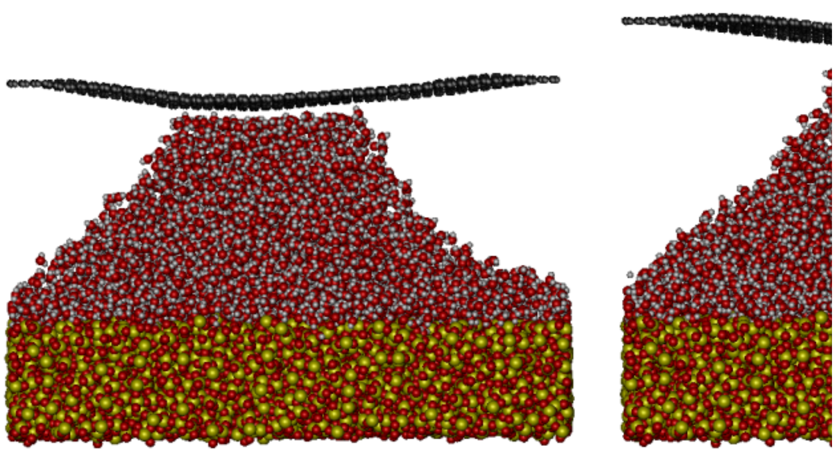


The vdW adhesion energy is reduced by surface hydroxylation and further reduced by adsorption of water molecules.

Gao et al., submitted.

Graphene/SiO_2: capillary forces?





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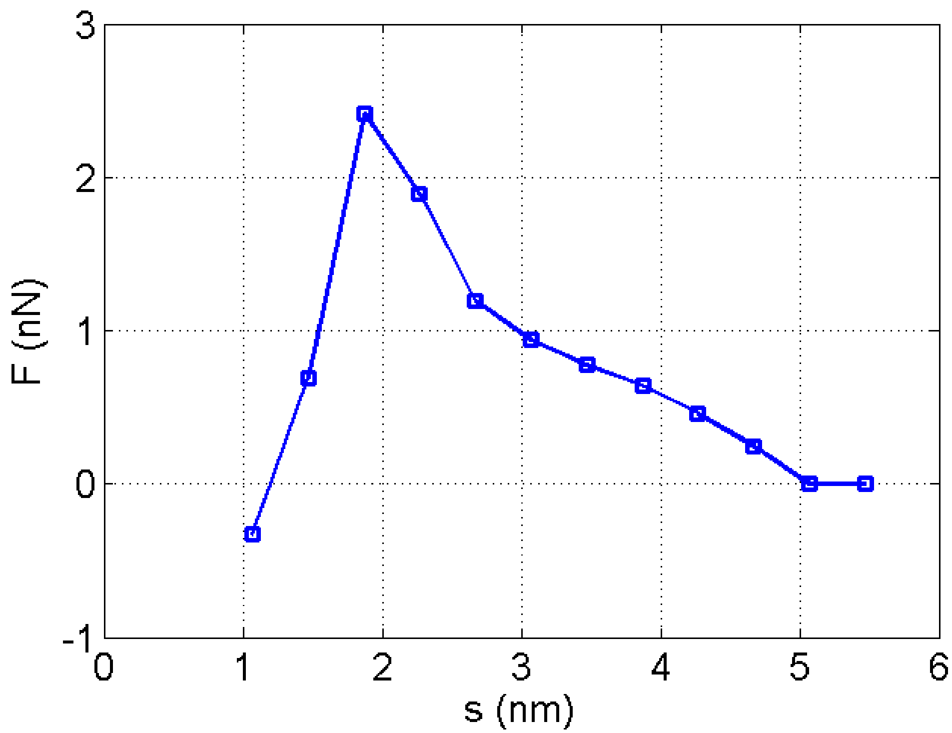

Summary

- A statistical mechanics approach is employed to study thermal rippling and thermoelasticity of graphene membranes; the current analysis is limited by harmonic analysis.
- MD simulations show significant anharmonic effects at zero stress or zero strain, but nearly harmonic behavior when the membrane is subjected to pre-tension.
- Graphene on substrate: strain transfer (shear) and adhesion have been measured, but the underlying mechanisms (vdW or capillary) require further studies.