

# Thermal expansion of freestanding graphene: benchmarking semiempirical potentials

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## Introduction and background

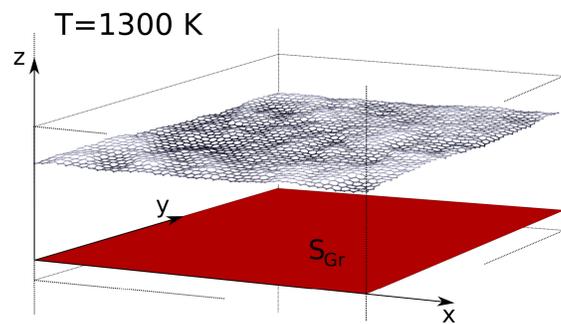
Thermal excitation induces large-scale ripples perpendicular to the graphene layer<sup>[1]</sup>. This corrugation decreases the in-plane graphene surface causing a **negative in-plane thermal expansion coefficient** (TEC)  $\alpha = (1/a)da/dT$  at low  $T$  (with  $a$  the in-plane lattice parameter).

At higher  $T$ , the possibility that  $\alpha$  becomes positive indicates an increase in  $a$  with  $T$  and associated microscopic mechanisms of structural deformation both remain unclear.

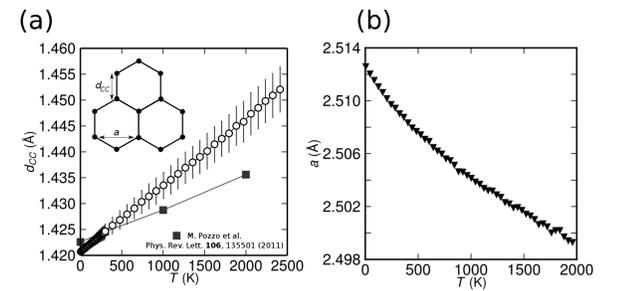
We investigated<sup>[2]</sup> thermodynamical properties of freestanding graphene at  $P = 0$  as a function of  $T$  by Monte Carlo simulations. Atomistic potentials<sup>[3-15]</sup> have been used and presented significant discrepancies in  $a$  and  $\alpha$ .

## Thermal properties of graphene: effect of the corrugation

Thermal excitation induces large-scale ripples perpendicular to the graphene layer<sup>[1]</sup>



Carbon-carbon bond distances,  $d_{CC} \nearrow$  when  $T \nearrow$  (usual behaviour of classical solids). In-plane lattice parameter  $a \searrow$  when  $T \nearrow$ <sup>[2,19]</sup>



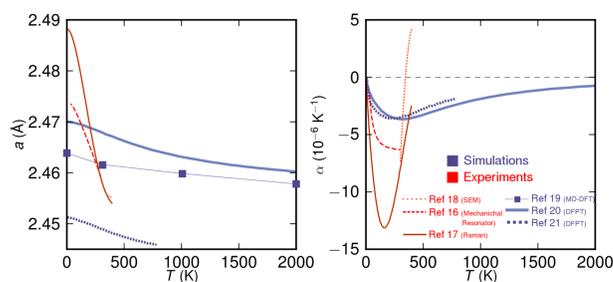
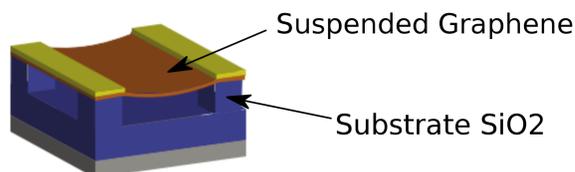
(a) Carbon-carbon bond distances  $d_{CC}$  obtained by MC simulations (empty circles) and by molecular dynamics at DFT level<sup>[19]</sup> (black squares). (b) In-plane lattice parameter  $a$

## Goals

- Study structural observables at finite temperature.
- Assess different Bond-order Potentials (BOPs) by NPT Monte Carlo simulations for pristine graphene
- Compare BOPs with experimental and theoretical results

## Comparison between experimental and theoretical results

Experimentally  $\alpha$  negative<sup>[16,17]</sup> except<sup>[18]</sup> Theoretically,<sup>[19-22]</sup>  $\alpha$  negative up to 2500 K. **Consensus about a negative sign<sup>[19]</sup> of  $\alpha$**



- Dispersion between experimental and theoretical results
- In-plane lattice parameter shows a **monotonic decrease**
- Experimental TECs are **negative** in agreement with DFT except in<sup>[18]</sup>

**Remark:** Experimental measurements carried out after removing the biaxial strain of the substrate from DFPT calculations<sup>[20]</sup>.

## Bond-order potentials

Suitable to highly coordinated material, BOPs contain a built-in correlation between coordination and bond strength:

$$E = \sum_i \sum_{j>i} V_R(r_{ij}) - \frac{\bar{B}_{ij}}{b_{ij}^{\sigma-\pi} + b_{ij}^{\pi-\pi} + 2b_{ij}^{\sigma-\pi}} V_A(r_{ij})$$

$V_R(r_{ij})$ ,  $V_A(r_{ij})$ : Interatomic repulsive and attractive pair functions, respectively

$\bar{B}_{ij}$ : Bond-order, depends on the local coordination and bond angles

The performances of different BOPs<sup>[3-10,15]</sup> and one tight-binding fourth moment approximation<sup>[14]</sup> (TB-FMA) for pristine graphene:

Potential	Year	Nature	Range	Reference
Stillinger-Weber	1985	Empirical	short	[3]
Tersoff	1989	BOP	short	[4]
Brenner	1990	BOP	short	[5]
REBO	2002	BOP	short	[8]
Tersoff-LB	2010	BOP	short	[15]
REBO-LB	2010	BOP	short	[15]
LBOP	2002	BOP	medium	[9]
LCBOP	2003	BOP	medium	[10]
GEEBOD	1999	BOP	long	[6]
AIREBO	2000	BOP	long	[7]
TB-FMA	2009	TB	medium	[14]

## Tight-binding

In tight-binding model, total energy depends on **band structure** and a **repulsive part**

$$E_{tot} = \sum_{i,j=1; i \neq j}^N \int_{-\infty}^{E_F} E n_i(E) dE + E_{rep}(r_{ij})$$

with an orthogonal basis of orbital the LDOS  $n_{i,\lambda}$  reads

$$n_{i,\lambda} = \sum_n c_{i,\lambda}^* c_{i,\lambda} \langle \phi_{i,\lambda} | \delta(E - E_n) | \phi_{i,\lambda} \rangle = -\frac{2}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \langle \phi_{i,\lambda} | (z - \mathcal{H})^{-1} | \phi_{i,\lambda} \rangle$$

Resolvent approximated by continued fraction with the **four first moments calculated exactly**

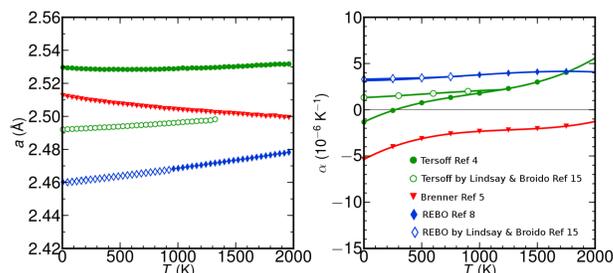
$$G_{ii,\lambda\lambda} = \frac{1}{z - a_1^{\lambda\lambda} - \frac{(b_1^{\lambda\lambda})^2}{z - a_2^{\lambda\lambda} - \frac{(b_2^{\lambda\lambda})^2}{\dots \sum_M(z)}}}$$

and  $\mathcal{H} = \epsilon_i + \beta(r_{ij})$  with  $\beta$  the Slater-Koster hopping integrals. **Moments are given by:**

$$a_1^{\lambda\lambda} = \langle i\lambda | \mathcal{H} | i\lambda \rangle; b_1^{\lambda\lambda} = \sum_{j \neq i} \langle i\lambda | \mathcal{H} | j\mu \rangle \langle j\mu | \mathcal{H} | i\lambda \rangle; \dots$$

## Results

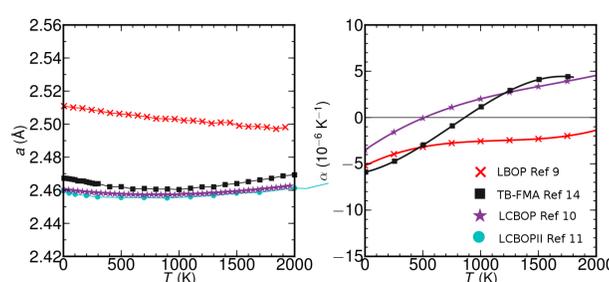
### Short-range potentials



### Short-range potentials present strong discrepancies

- Brenner potential<sup>[5]</sup> shows a contraction in  $a$  and a sign change of  $\alpha(T)$  in agreement with DFT<sup>[19-21]</sup> but overestimates  $a$
- Other potentials<sup>[4,8]</sup> including the reparametrized Tersoff potential for graphene<sup>[15]</sup> presents an **increase of  $a$**

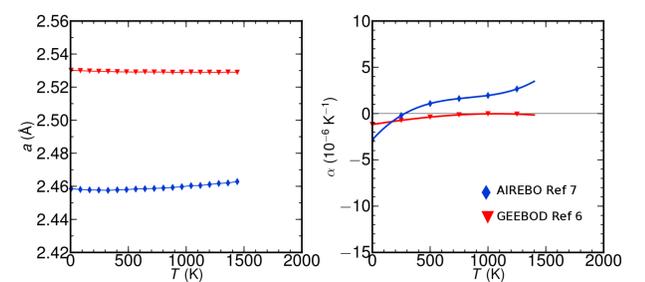
### Medium-range potentials



### Medium-range potentials show non-monotonic behaviors

- Medium-range potentials exhibit a non-monotonic behavior in  $a$  and a sign change of  $\alpha(T)$  except for LBOP<sup>[9]</sup> a Brenner based potential
- TB-FMA,<sup>[14]</sup> LCBOP<sup>[10]</sup> and LCBOP<sup>[11]</sup> exhibit an increase in  $a$  near 700 K although these potentials are quantitatively close to DFT results
- The sign of  $\alpha(T)$  is not consistent with experiments<sup>[16,17]</sup> and DFT<sup>[19-21]</sup>

### Long-range potentials



### Long-range interactions flatten corrugation

- Long-range potentials<sup>[6,7]</sup> exhibit discrepancies with **monotonic or non-monotonic behaviours** in  $a$
- Out-of-plane deformations are energetically penalized, resulting in a **lower value of corrugation**

## Conclusion

In a large temperature range,  $\alpha$  may remain negative, positive, or change sign. Sign change of  $\alpha$  was interpreted as a **transition from harmonic behaviour** (soft bending modes, low  $T$ ) to **anharmonic behaviour<sup>[1]</sup>**. **It should be taken with care, because:**

Lindsay and Broido reparametrized potentials<sup>[15]</sup> from graphite phonon dispersion give  $\alpha > 0$ . **Therefore, a correct harmonic description does not ensure negative  $\alpha$ .**

A recent theoretical work based on elasticity theory<sup>[23]</sup> further indicates that **anharmonicities alone can lead to  $\alpha < 0$ .**

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