

Thermal expansion of freestanding graphene: benchmarking semiempirical potentials

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Introduction and background

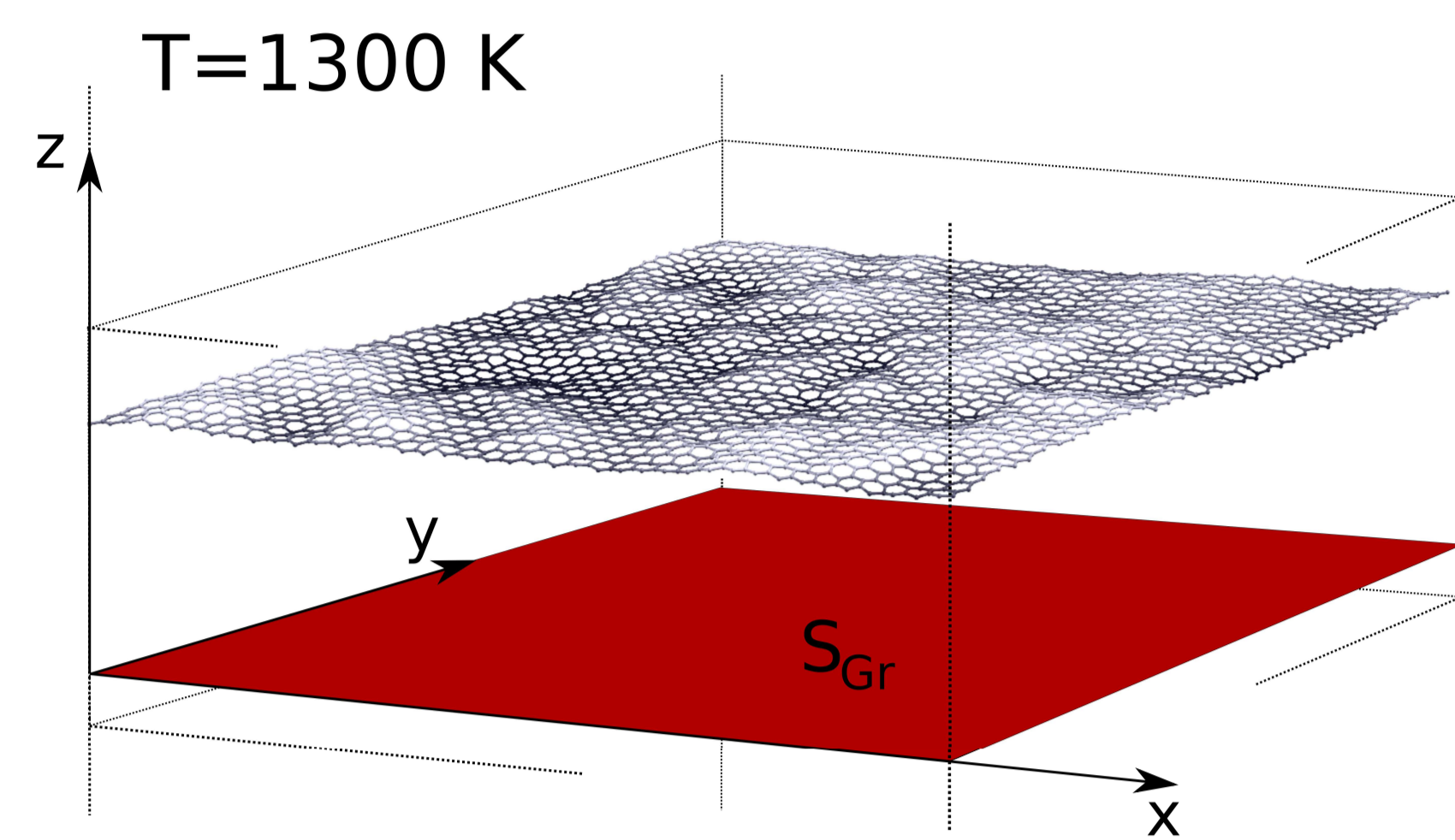
Thermal excitation induces large-scale ripples perpendicular to the graphene layer^[1]. This corrugation decreases the in-plane graphene surface causing a **negative in-plane thermal expansion coefficient** (TEC) $\alpha = (1/a)da/dT$ at low T (with a the in-plane lattice parameter).

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

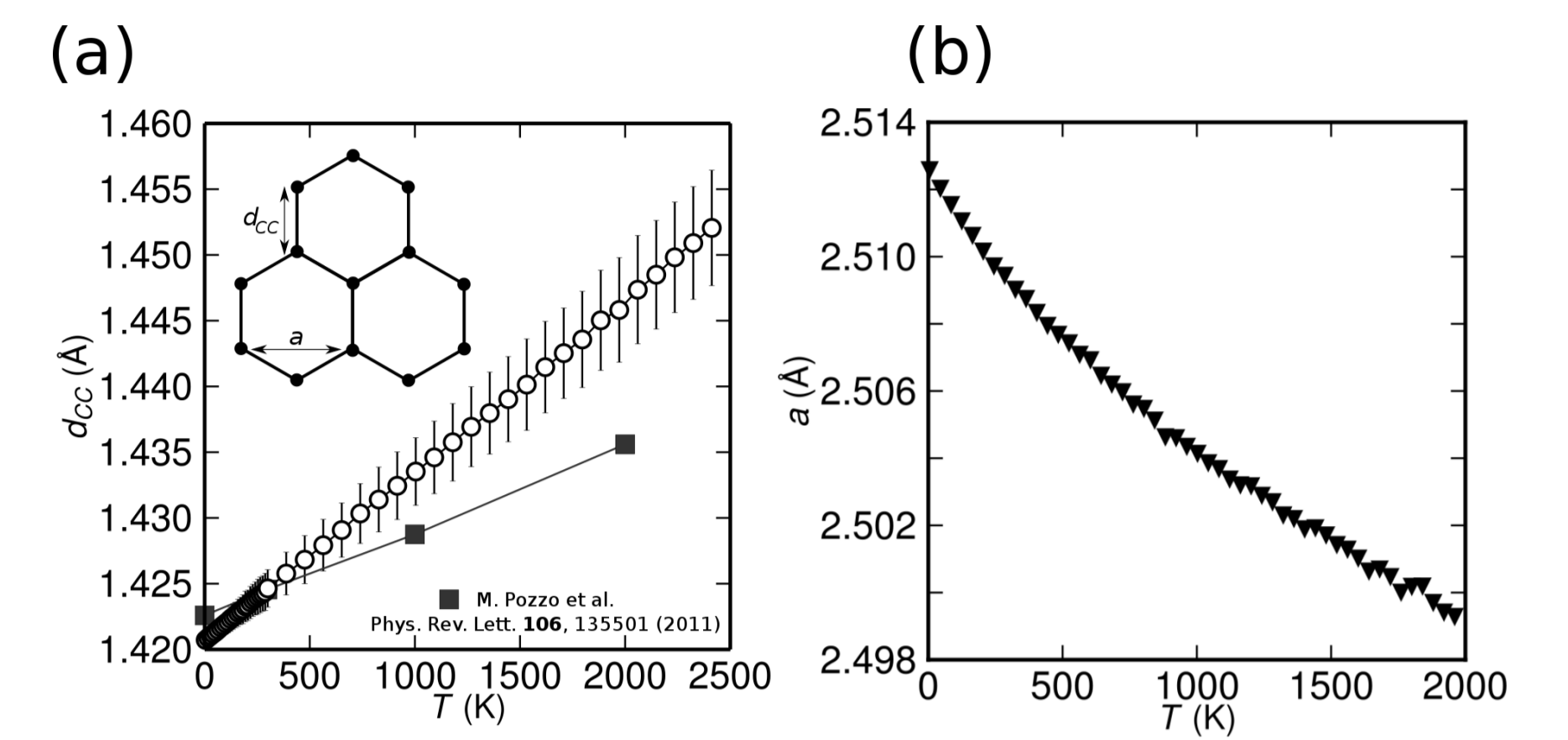
We investigated^[2] thermodynamical properties of freestanding graphene at $P = 0$ as a function of T by Monte Carlo simulations. Atomistic potentials^[3-15] have been used and presented significant discrepancies in a and α .

Thermal properties of graphene: effect of the corrugation

Thermal excitation induces large-scale ripples perpendicular to the graphene layer^[1]



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



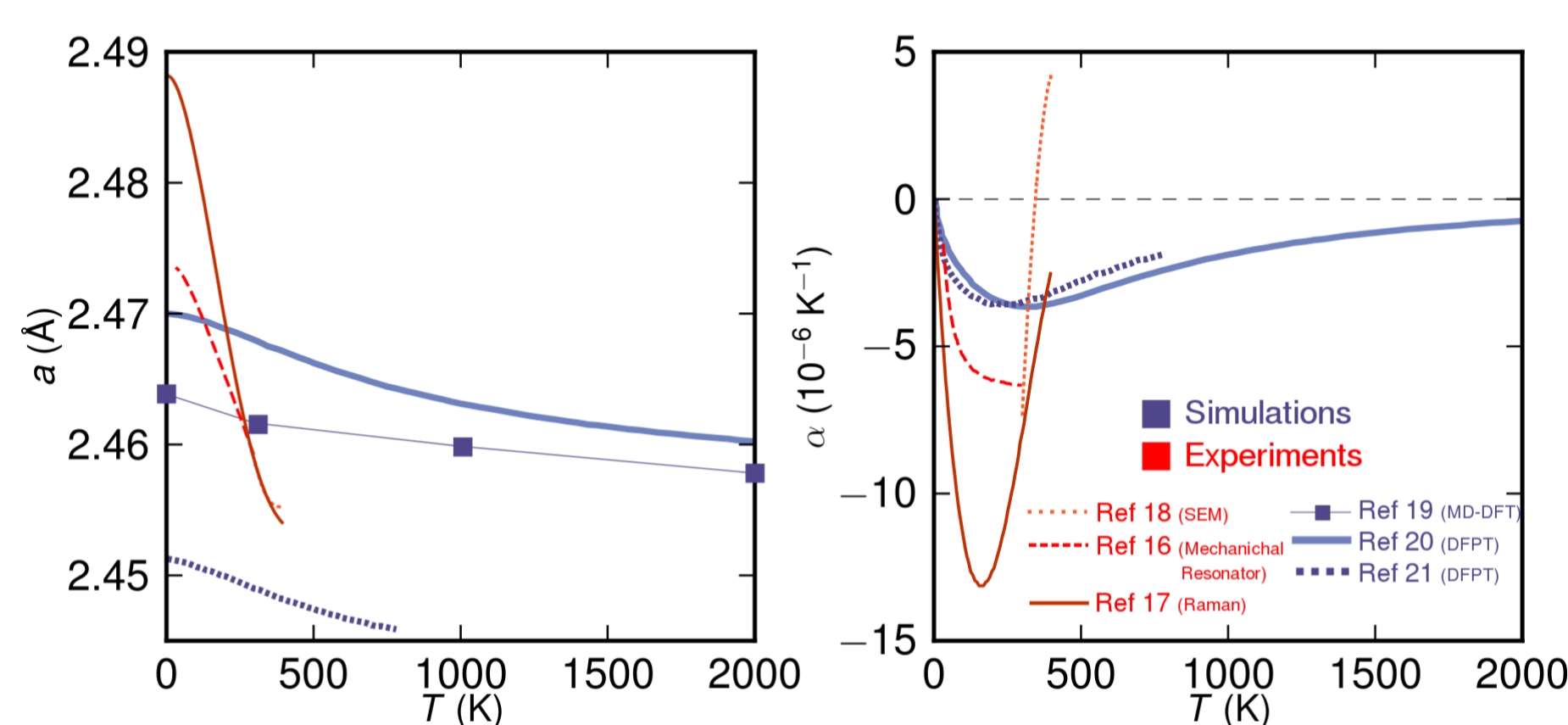
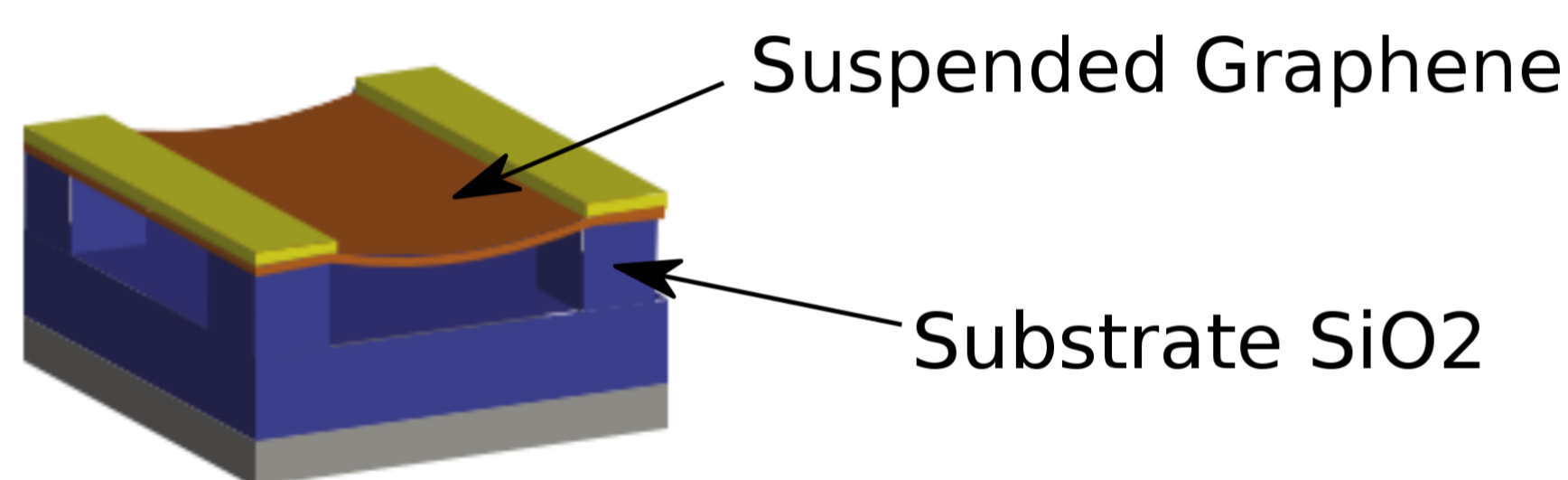
(a) Carbon-carbon bond distances d_{CC} obtained by MC simulations (empty circles) and by molecular dynamics at DFT level^[19] (black squares). (b) In-plane lattice parameter a

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 α negative^[16,17] except^[18] Theoretically,^[19-22] α negative up to 2500 K. **Consensus about a negative sign^[19] of α**



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

Remark: Experimental measurements carried out after removing the biaxial strain of the substrate from DFPT calculations^[20].

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^[3-10,15] and one tight-binding fourth moment approximation^[14] (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**

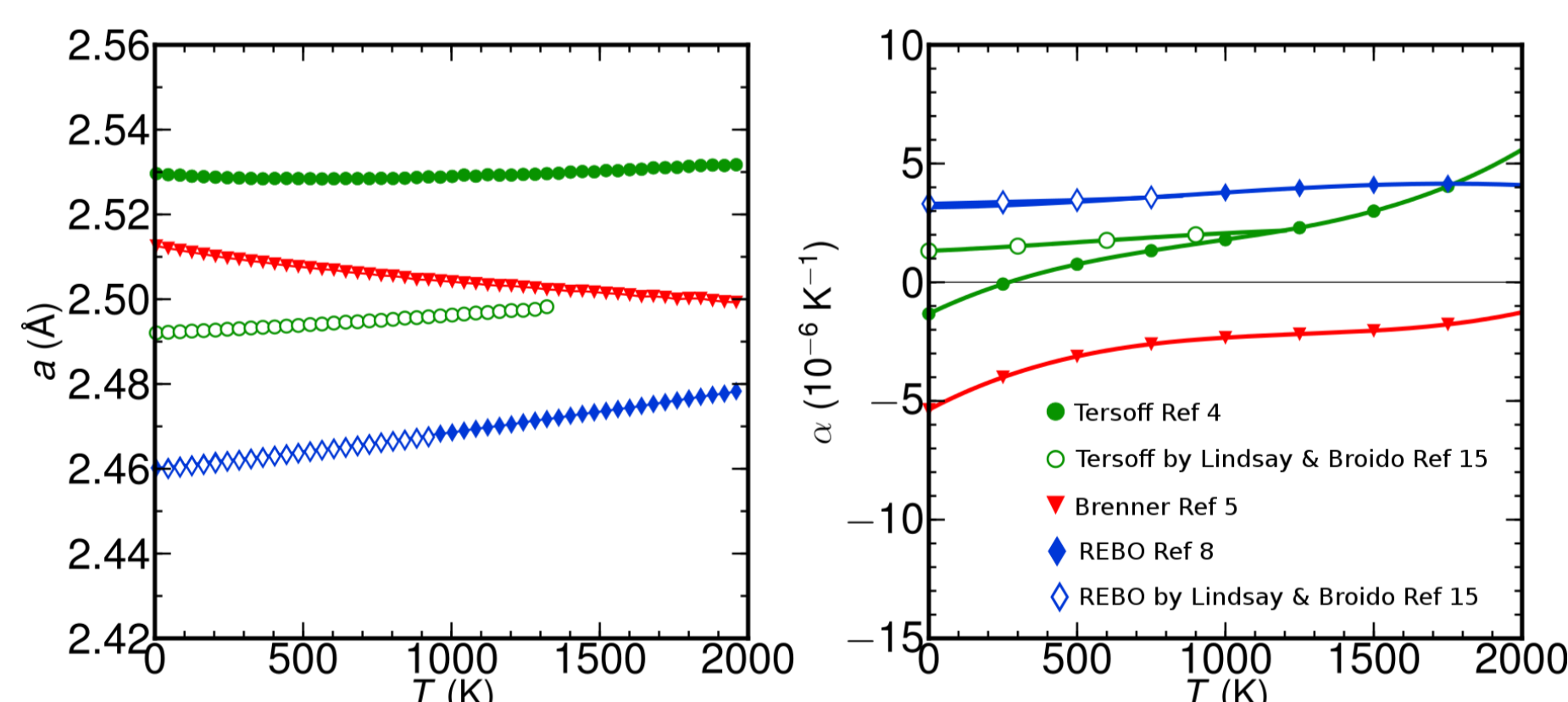
$$G_{ii,\lambda\lambda} = \frac{1}{z - a_1^{\lambda\lambda} - \frac{(b_1^{\lambda\lambda})^2}{z - a_2^{\lambda\lambda} - \frac{(b_2^{\lambda\lambda})^2}{\dots \sum_M(z)}}}$$

and $\mathcal{H} = \epsilon_i + \beta(r_{ij})$ with β 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

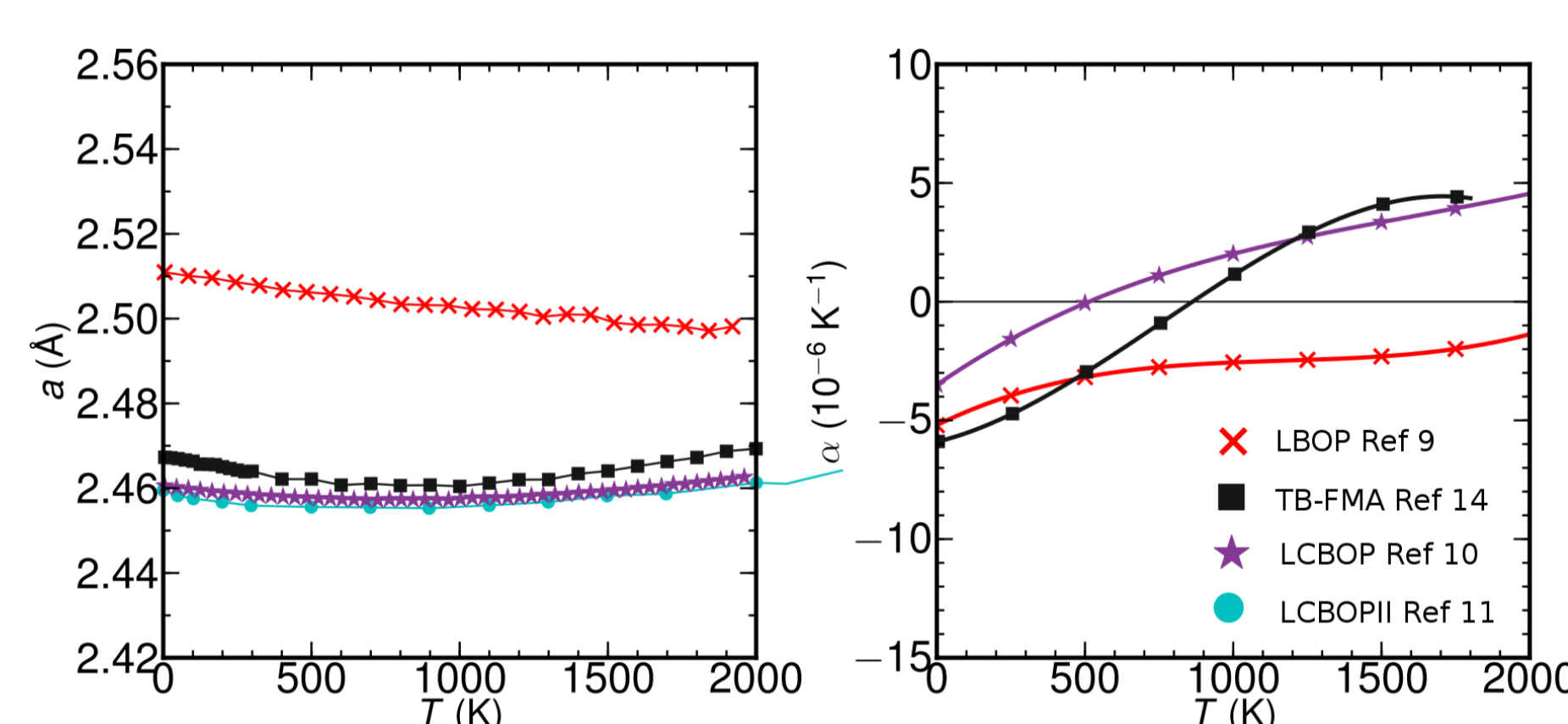
Short-range potentials



Short-range potentials present strong discrepancies

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

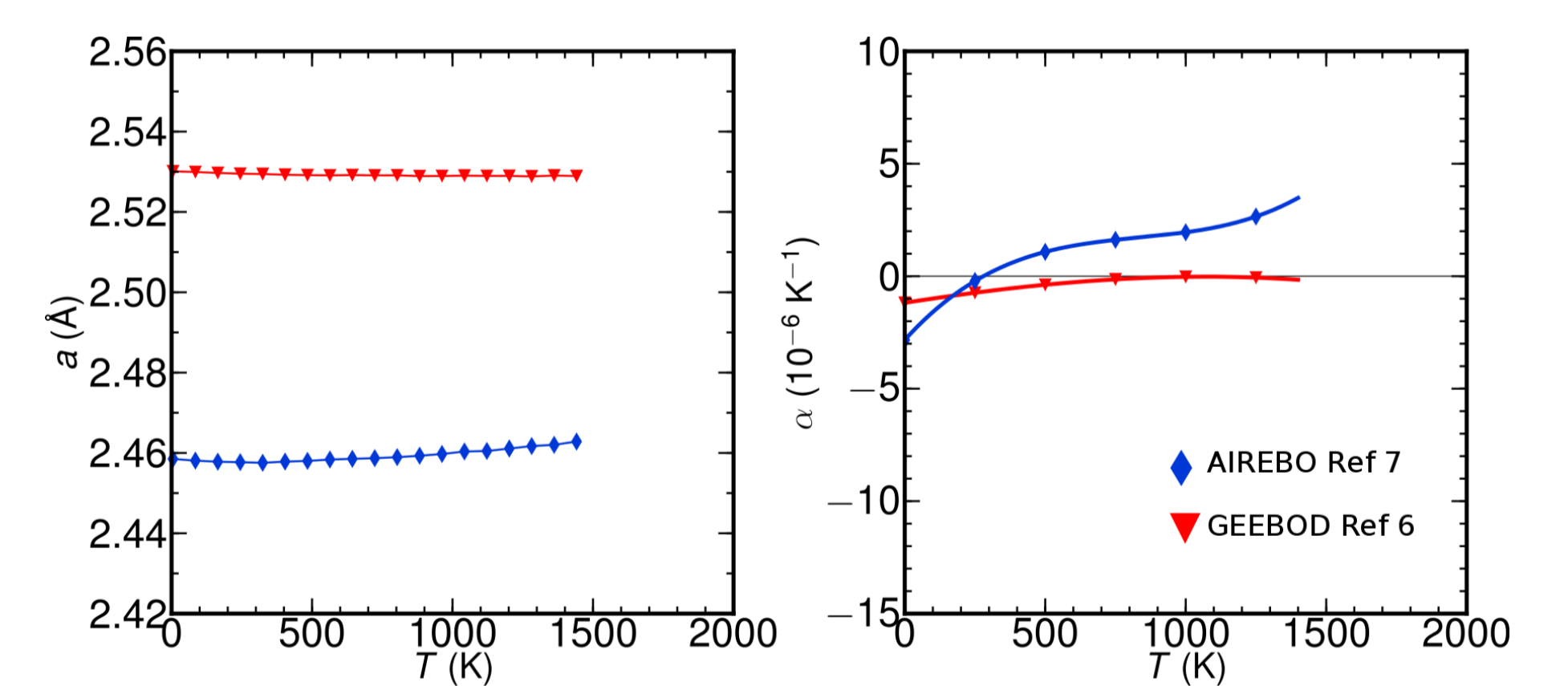
Medium-range potentials



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^[9] a Brenner based potential
- TB-FMA,^[14] LCBOP^[10] and LCBOP^[11] 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^[16,17] and DFT^[19-21]

Long-range potentials



Long-range interactions flatten corrugation

- Long-range potentials^[6,7] 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, α may remain negative, positive, or change sign. Sign change of α was interpreted as a **transition from harmonic behaviour** (soft bending modes, low T) to **anharmonic behaviour^[1]**. **It should be taken with care, because:**

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

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

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