



Cite this: *RSC Adv.*, 2018, 8, 5136

Received 7th November 2017
 Accepted 24th January 2018

DOI: 10.1039/c7ra12219e

rsc.li/rsc-advances

Comment on “Incipient plasticity of diamond during nanoindentation” by C. Xu, C. Liu and H. Wang, *RSC Advances*, 2017, 7, 36093

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A recent molecular dynamics simulation study on nanoindentation of diamond carried out by Xu *et al.*¹ has reported observation of the presence of a controversial hexagonal lonsdaleite phase of carbon in the indentation area. In this comment, we question the reported observation and attribute this anomaly to shortcomings of the long range bond order potential (LCBOP) employed in the nanoindentation study.

In 1967, lonsdaleite (a material named in honour of an Irish crystallographer Ms. Kathleen Lonsdale) was first proposed to be a hexagonal lattice structure allotrope of carbon that rivals cubic diamond in hardness.³ Controversy exists concerning the physical existence of lonsdaleite. Recently, evidence suggesting the physical existence of lonsdaleite was obtained from X-ray diffraction data of pyrolytic graphite subjected to laser shock compression at pressures higher than 170 GPa.⁴ This evidence arguing that lonsdaleite is a thermodynamic phase by itself has recently been questioned.⁵ Based on X-ray diffraction patterns,⁶ it is suggested that lonsdaleite is merely a faulted and twinned (stacking disordered) cubic diamond structure. Theoretical *ab initio* results⁷ indicate that the cohesive energy difference per atom between the diamond and lonsdaleite phases is about 51.7 meV.⁷

Absence of a matured theoretical understanding and sufficient data are why the lonsdaleite phase of carbon is generally not considered in the construction of material constitutive models, particularly interatomic potential functions or force-fields needed for molecular dynamics simulations. An interatomic potential function is usually parameterised and fitted for a given set of phases of the material, but none of the currently available potentials captures the mechanical, structural and energetic aspects of all phases of carbon.⁸ It is well known that each potential function has its own characteristic advantages and weaknesses, and whether it is applicable or not to a given problem is governed by a range of factors. Only in rare cases and typically by chance a potential may work to describe a phase for which it was not originally fitted. For instance, the analytical bond order potential (ABOP) of Erhart and Albe has

been found to best describe the most recently identified phase of penta-graphene⁹ whilst the EDIP potential was reported most appropriate for simulating amorphous carbons.¹⁰

Ideally, MD simulation studies of contact loading processes like nanometric cutting or nanoindentation require a potential to be highly transferable as the material undergoes extreme conditions of stress. For an interatomic potential to correctly reproduce changes in the microstructure or predict phase transitions during contact loading, it is necessary (but generally not sufficient) that the potential function correctly reproduces the cohesive energy of the involved phases of the material, particularly because the incipient plasticity in early stages of wear may occur either due to atom-by-atom attrition, diffusion, or bond breaking.

The above considerations motivated us to examine a series of potentials for carbon proposed in the literature, including the LCBOP function² employed in the study of Xu *et al.*,¹ to see how closely they describe the cohesive energy difference between cubic and hexagonal phases of carbon. We performed molecular statics calculations at zero pressure to determine the cohesive energies of the diamond and lonsdaleite phases of carbon. Our results shown in Table 1 highlight that it is only the screening incarnation (REBO + S)¹¹ of the reactive empirical bond-order (REBO) potential^{12,13} predicting energy differences between the diamond and hexagonal phases of carbon that are close to the *ab initio* energy difference.⁷ From this, it can be concluded that the occurrence of lonsdaleite observed in the study of Xu *et al.*¹ may be an artefact of the employed LCBOP potential and is likely to have resulted from the underestimation of the structural energy difference. This renders the significance of the reported transformation process questionable.

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Table 1 Differences in the cohesive energy per atom between diamond and lonsdaleite phases

Name of potential function	Cohesive energy difference between the two phases predicted by the potential (meV per atom)	Cohesive energy difference obtained from <i>ab initio</i> calculation (meV per atom)
Tersoff potential ^{14,15}	0	51.7 (ref. 7)
ABOP potential ¹⁶	0	
REBO + S function ¹¹	41.86	
REBO original formulation ^{12,13}	-0.04	
AIREBO original formulation ¹⁷	155.9	
REAXFF ¹⁸	6117.9	
LCBOP ²	12.48	
EDIP carbon ¹⁹	0	

Conclusions

Based on the discussions, we suggest that the appearance of yellowish atoms (referred as lonsdaleite atoms) in the nano-indentation work of Xu *et al.*¹ are mere artefacts.

Conflicts of interest

There are no conflicts to declare.

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