

Comment on "Structure, Dynamics, and Electronic Properties of Diamondlike Amorphous Carbon"

Recently Wang and Ho [1] presented a model of diamondlike amorphous carbon. We received the coordinates from one of the authors, and analyzed them with a more complete theory, and find that their coordinates are missing important features of the sp^3 topology. We believe this to be a consequence of the nontransferability of orthogonal tight binding.

Using *ab initio* local basis density functional (LBDF) methods [2], we performed a steepest descent quench of their coordinates and observed: (1) The initial coordinates were far from equilibrium: the root-mean-square force on the atoms was 1.5 eV/\AA , a large force. (2) The structure *significantly changed topology*; the initial structure contained 42 threefold atoms; the quenched structure had 28 (for coordination radius 2 \AA). This is a major change for a 216 atom cell. (3) For both the relaxed and unrelaxed model, any 2 eV interval containing the Fermi level contained many localized states. This contradicts experiments [3] which yield an exponentially small density of states in the approximately 2.0 eV band gap. (4) We separately found [4] that threefold defects *paired* with substantial π bonding, and this effect led to a clean (state free) gap of more than 2.0 eV. This mechanism was absent in the cell of Ref. [1].

There are important differences between Ref. [1] tight-binding molecular dynamics (TBMD) and LBDF. The Harris [5] version of density functional theory is implemented in the LBDF method. The nonorthogonality of the basis (compact orbitals with range $8.2a_B$) is dealt with: the generalized eigenvalue problem is solved; matrix elements are not fit in LBDF; they are computed; the repulsive interaction is evaluated as per density functional theory; no *ansatz* for the repulsion is required. TBMD assumes orthogonality, ignores three-center integrals, and fits matrix elements and the repulsive interaction.

Transferability is best understood in terms of the carbon phase diagram. Xu *et al.* [6] have reported total energy calculations of many crystalline phases of C. LBDF results are reported in Fig. 1 and are much improved over TBMD for the cubic phases (see Ref. [6], Fig. 2). It is plausible to attribute much of the TBMD-LBDF discrepancy to this difference in transferability. This suggests that it is inadequate to reproduce the graphite and diamond curves on the phase diagram and expect universal transferability. Menon *et al.* [7] have drawn related conclusions. In contrast to Ref. [1], using LBDF on the *a*-C structure of Galli *et al.* [8] produced no topological change.

The present work *only* reflects on sp^3 *a*-C; we have not explored transferability of TBMD in other contexts.

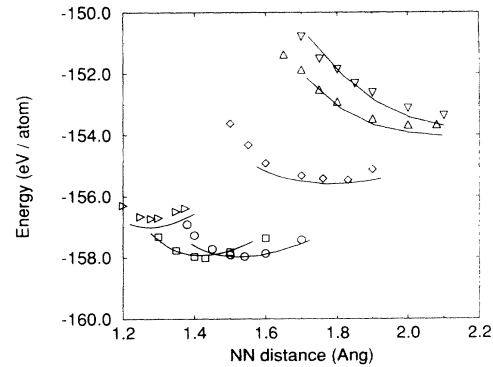


FIG. 1. Cohesive energy vs nearest neighbor distance. Symbols: self-consistent local density approximation (SCLDA) calculations (Ref. [6]); solid lines: LBDF method (Ref. [2]). Squares: graphite; circles: diamond; diamonds: sc; triangles: bcc; inverted triangles: fcc; triangles to right: linear chain. A single constant was added to all the SCLDA data to make the diamond energies identical.

TBMD is a useful and powerful technique, but there are limits to its reliability in an arbitrary bonding environment.

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