Energy scaling law for nanostructured materials

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The equilibrium binding energy is an important factor in the design of materials and devices. However, it presents great computational challenges for materials built up from nanostructures. Here we investigate the binding-energy scaling law from first-principles calculations. We show that the equilibrium binding energy per atom between identical nanostructures can scale up or down with nanostructure size. From the energy scaling law, we predict finite large-size limits of binding energy per atom. We find that there are two competing factors in the determination of the binding energy: Nonadditivities of van der Waals coefficients and center-to-center distance between nanostructures. To uncode the detail, the nonadditivity of the static multipole polarizability is investigated. We find that the higher-order multipole polarizability displays ultra-strong intrinsic nonadditivity, no matter if the dipole polarizability is additive or not.

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I. INTRODUCTION

There is strong interest in nanomaterials, motivated by the development of nanotechnology and by their novel properties arising from quantum confinement. In particular, the discovery of various atomic-level materials has received overwhelming attention for their remarkable properties and wide-ranging applications [1]. A common feature of these materials is the strong adhesive van der Waals (vdW) force due to the instantaneous charge fluctuations. To understand the nature of the vdW force, a variety of experiments ranging from the smallest atomistic to the largest macroscopic scales have been performed recently [2-6]. However, details of many surprising phenomena due to the vdW interaction have not been well understood at the nanoscale [7]. Here we will ask and answer another such question.

The equilibrium binding energy between identical nanostructures is an important property involving microscopically the short-range contribution arising from the density overlap and the long-range vdW interaction. However, due to the large size of nanostructures, it presents great computational challenges. As such, an energy scaling law showing the variation of equilibrium binding energy per atom with system size is highly desired. We here apply an efficient first-principles method, the vdW-DF-cx [8] density functional, to investigate the energy scaling law, aiming to provide novel insights into nanostructures. Figure 1 shows the energy scaling law for a variety of nanomaterials, while Table I shows the energy scaling law for a variety of nanostructures obtained by fitting to our numerical calculations. We find that the binding-energy scaling law is largely due to the competing size effects of the vdW coefficients and sum of the vdW radii of nanostructures determining the intermolecular distance. Our finding is different from previous works [7, 9, 10], in which the vdW coefficients and intermolecular distance are treated independently, allowing one to study the dependence of the vdW interaction upon the power of distance.

II. COMPUTATIONAL METHODS

The binding energy per atom is defined as \( E_b/N \), with \( N \) being the total number of C/B/N atoms in a nanostructure. For nanotubes, \( N \) is the number of atoms per unit length (in Å). All our calculations of binding energies and distances \( d_{cc} \) (center to center) and \( d_{ww} \) (wall to wall) were performed with Quantum ESPRESSO [11], using the vdW-DF-cx [8] nonlocal density functional. We used ultrasoft pseudopotentials with a plane-wave energy cutoff at 680 eV. The binding energy \( E_b \) is taken as the energy difference between relaxed nanostructures in the conventional unit cell and in the empty space, except for nanowires, in which the distance between two nanowires is fixed at 4.21 Å (the relaxed distance between C-NWs with seven atoms), due to the high instability. For fullerenes, we used 2 × 2 × 2 for the \( k \)-mesh. For C-PAHs and BN-PAHs, only the \( \Gamma \)-point is included in the \( k \)-mesh, due to the large size of the cell. For nanotubes, we used 6 × 6 × 17 to 1 × 1 × 17 from (3,3) to (40,40). For nanowires, we used 3 × 3 × 2 for all cases.

The nonlocal correlation part of the vdW-DF-cx is the same as in the original Rutgers-Chalmers [12] vdW-DF,
which was derived from the fluctuation-dissipation theorem [13] of electron gas for the description of the long-range vdW interaction [14]. The method contains both the leading-order and higher-order contributions, the latter of which are important for solids [15–19]. Its exchange part is based on a modified semilocal functional, which aims to improve the short-range description.

The vdW-DF-cx is a useful first-principles method, as supported by Appendices A and B. The experimental geometries of fullerene solids (Appendix A) and their equilibrium binding energies (Table I and Appendix B) are well reproduced, although $C_{60}$ for a fullerene pair is not, as anticipated in Ref. [20]. Like SCAN+rVV10 [21], and with nearly the same binding energy curve, vdW-DF-cx predicts [22] a chemisorption minimum for graphene on Ni(111) at a distance of 2.1 Å from the top nickel plane, in close agreement with experiment. Some of us have previously argued [14, 21] that a vdW functional can be accurate for equilibrium binding energies, even if it is not for asymptotic interactions.

To analyse the energy scaling law revealed from our calculation, we have to make use of the efficient yet accurate spherical-shell model within the single-frequency approximation (SFA) [23–25] to evaluate the vdW coefficients between nanostructures. In the SFA, we assume that (i) only valence electrons in the outermost subshell are polarizable, and (ii) the density is uniform inside the effective radius $R_l$ and zero otherwise. Within the SFA, the model dynamic multipole polarizability takes the simple expression

$$\alpha^\text{SFA}_{li}(iu) = R_l^{2l+1} \frac{\omega^2_{s}}{\omega^2_{s} + u^2} \frac{1 - \rho_l}{1 - \beta_l \rho_l},$$  \hspace{1cm} (1)

where $R_l$ is the effective outer radius of the shell, $\beta_l = \omega^2_{s} \omega^2_{p}/[(\omega^2_{s} + u^2)(\omega^2_{p} + u^2)]$ describes the coupling of the sphere and cavity plasmon oscillations, and $\rho_l = (1 - t_l/R_l)^{2l+1}$ describes the shape of the shell, with $t_l$ being the shell thickness [24–26]. $\omega_s = \omega_p \sqrt{l/(2l + 1)}$ is the average sphere plasmon frequency, $\omega_p$ is the cavity plasmon frequency, and $\omega_p = \sqrt{4\pi n}$ is the average plasmon frequency of the extended electron gas, with $n = N/V_l$ and $V_l$ being the $l$-dependent vdW volume.

Since the geometry effect can be accounted for via $\alpha^\text{SFA}_{li}(0)$, the model is valid for any geometry [23]. For fullerences, $V_l = (4\pi/3)[R^3_l - (R_l - t_l)^3]$. For nanotubes, we take a unit length to study. The volume per unit length is given as $V_l = 2\pi R_0 t_l$, where $R_0$ is the average radius of a nanotube, which can be accurately calculated from first principles methods [27–31], and $t_l$ is the effective thickness of the nanotube. For C-NT, we set $t_l = 3.4$ bohr, as adopted for fullerene molecules [24–26], while for BN-NT, we set $t_l = 2.08$ bohr [29]. For PAH and nanowire, we can make a similar analysis by taking carbon or BN atoms as a unit. It has been shown that this model can yield very accurate vdW coefficients [28–29].

### III. BINDING-ENERGY SCALING LAW FOR NANOSTRUCTURES

#### Ball-to-ball interaction.

Fullerene is an important class of nanomaterials with a variety of applications in physics, chemistry, and materials science. The binding energy between fullerene pairs is a typical example of ball-to-ball interaction [19–23]. We have calculated the binding energies per atom of fullerene solids with the optimized fcc-type geometries (Appendix A). For $C_{60}$, the experimental value was already extrapolated to 0 K, while for others, the experimental values are available only at high temperature ($\sim 850$ K) [34], due to the strong vdW force. We have estimated the thermal energy correction ($\sim 2$ meV/atom) for $C_{70}$ solid, for which the heat capacity data are available [34]. For $C_{76}$, $C_{84}$, and $C_{84}$ [34], we take the same thermal correction per atom as for $C_{70}$. From Table I, we observe that the calculated binding energies are generally within the range of thermally corrected experiments, while the intermolecular distance $d_{cc}$ is between the DFT-LSDA [19] (local spin-density approximation) and experimental value [30] (at room temperature). This suggests that the method used in this work is not only reliable for binding energy, but also for the center-to-center distance. See appendix A for further detailed discussion.

Figure 1(a) shows that the binding energy of fullerenes per atom decreases slowly (only 3 meV/atom from $C_{60}$ to $C_{84}$) with fullerene size, while Table II shows that the large-size limit of binding energy saturates to a constant 24 meV/atom. From Table II, we can see that the center-to-center distance $d_{cc}$ gradually becomes larger and larger from $C_{60}$ to $C_{84}$. With the increase of fullerene size, vdW coefficients per atom pair, in particular the higher-order ones (Table III), dramatically increase, while the sum of the vdW radii of fullerenes characterized by $d_{cc}$ also increases. These two factors have opposite effects on the energy scaling law, leading to the slow variation of the binding energy with system size. It is interesting to note that the wall-to-wall distance $d_{ww}$ of fullerenes gets slightly shrunk from $C_{60}$ to $C_{84}$. This is because the vdW force between fullerenes decreases from $C_{60}$ to $C_{84}$, pulling two fullerenes slightly closer.

#### Plane-to-plane interaction.

Polycyclic aromatic hydrocarbons (C-PAHs) are a large class of conjugated $\pi$-electron systems of great importance in many areas such as environmental chemistry, materials science, and astrochemistry [37]. The energy scaling law between C-PAHs reflects the plane-to-plane vdW interaction [38–40]. Here we focus on the binding energies per atom of C-PAH.
FIG. 1: Binding-energy scaling law (in meV/atom) of fullerenes in fcc solids (Panel (a)), and of pairs of other identical nanoparticles: C-PAHs and BN-PAHs in AA stacking dimers (Panel (b)), C-NTs and BN-NTs in AA stacking solids (Panel (c)), as well as carbon nanowires (C-NWs) and boron-nitride substitutes (BN-NWs) in AA stacking dimers (Panel (d)), with system size. \( N \) on the vertical axis is the total number of C/B/N atoms in a nanostructure. The dotted curve (yellow for carbon and green for BN) is the analytic modeling from Table II.

dimers with the optimized AA stacking. Crucial to this problem is the fact that the center-to-center distance \( d_{cc} \) remains nearly the same for all C-PAH, with a slight decreasing trend similar to \( d_{ww} \) for fullerene pairs, as shown in Table I. This is because from benzene to pentacene, the vdW force increases, pulling two planar molecules slightly closer. Since the vdW coefficients per atom rapidly increase with system size \[41\], due to the nonadditivity arising from \( \pi \)-electron delocalization, while their center-to-center distance \( d_{cc} \) does not change much, the binding energy between C-PAHs scales up rapidly, as shown in Fig. 1(b). A similar energy scaling law is also observed for boron-nitride (BN) substitutes \[42\] for the same reason, as shown in Table I and Fig. 1(b), respectively.

From Table I we see that our energy scaling law predicts the same binding energy 30 meV/atom between two identical long-chain limits of PAH and BN-PAH (AA stacking). Note that this limit is physically different from a bi-layer of infinite two-dimensional sheets.

**Tube-to-tube interaction.** Carbon nanotubes (C-NTs) are perhaps one of the most-widely studied nano-materials, due to their many unusual properties and applications \[43\]. Study of their energy scaling law is of broad interest. A C-NT has cylindrical symmetry. It is characterized by a pair of integer parameters \((n, m)\), with radius given by \((\sqrt{3}a/2\pi)\sqrt{n^2 + m^2 + nm}\), with \(a\) being the bond length. When \(n = m\), it takes the armchair structure, while for \(n \neq m\), it takes the zigzag structure. Their size can be adjusted with \(n\) or \(m\). Here we focus on the binding energies per atom of the optimized close-packed solids of infinitely-long armchair C-NTs. Figure 1 (c) shows the variation of binding energy per atom with...
TABLE I: Variation of binding energies per atom $E_b/N$ (in meV/atom) of fullerenes in fcc solids, and of pairs of other identical nanoparticles: C-PAHs and BN-PAHs, C-NTs and BN-NTs, and carbon and BN nanowires with system size, and center-to-center ($d_{cc}$) and wall-to-wall ($d_{ww}$) distances (Å). We extrapolated experimental binding energies [34] at 850 K to 0 K for fullerenes, except for $C_{60}$, which was already extrapolated to 0 K, by estimating the thermal correction per atom from the thermal heat capacity of $C_{70}$ [34] and then making the same correction per atom from $C_{70}$ to the experimental values for fullerenes $C_{76}$ [35] and $C_{84}$ [34]. Experimental center-to-center distances are from Ref. [36]. All $d_{cc}$ between wires are fixed at 4.21 Å.

| Fullerene    | $N$ | $d_{cc}$ (Å) | $d_{ww}$ (Å) | $E_b^{cal}/N$ (meV/atom) | $d_{cc}^{exp}$ (Å) | $E_b^{exp}/N$ (meV/atom) |
|--------------|-----|--------------|--------------|--------------------------|-------------------|---------------------------|
| $C_{60}$(Ih) | 60  | 9.96        | 3.05         | 35.0                     | 10.02             | 28 $\sim$ 35             |
| $C_{70}$(D$_{5h}$) | 70  | 10.52       | 2.99         | 32.9                     | 10.61             | 26 $\sim$ 32             |
| $C_{76}$(D$_{2d}$) | 76  | 10.92       | 2.92         | 32.2                     | 10.94             | 28 $\sim$ 29             |
| $C_{84}$(D$_{2d}$) | 84  | 11.06       | 2.78         | 31.6                     | 11.36             | 29 $\sim$ 35             |

| C-PAH       |     |             |              |                          |                   |                           |
| Benzene     | 6   | 4.07        | –            | 17.4                     |                   |                           |
| Naphthalene | 10  | 3.95        | –            | 22.4                     |                   |                           |
| Anthracene  | 14  | 3.90        | –            | 25.0                     |                   |                           |
| 2,3-Benzanthracene | 18  | 3.86 | – | 26.8 |                   |                           |
| Pentacene   | 22  | 3.84        | –            | 27.8                     |                   |                           |

| BN-PAH      |     |             |              |                          |                   |                           |
| $B_3N_3H_6$ | 6   | 3.98        | –            | 21.8                     |                   |                           |
| $B_5N_5H_8$ | 10  | 3.90        | –            | 25.2                     |                   |                           |
| $B_7N_7H_{10}$ | 14  | 3.85       | –            | 26.8                     |                   |                           |
| $B_9N_9H_{12}$ | 18  | 3.84  | – | 27.6 |                   |                           |
| $B_{11}N_{13}H_{14}$ | 22  | 3.83 | – | 28.4 |                   |                           |

| C-NT        |     |             |              |                          |                   |                           |
| (3,3)       | 5   | 7.28        | 3.08         | 44.3                     |                   |                           |
| (5,5)       | 8   | 10.01       | 3.14         | 33.2                     |                   |                           |
| (10,10)     | 16  | 16.78       | 3.15         | 23.6                     |                   |                           |
| (20,20)     | 32  | 30.34       | 3.15         | 17.0                     |                   |                           |
| (40,40)     | 64  | 57.47       | 3.15         | 11.9                     |                   |                           |

| BN-NT       |     |             |              |                          |                   |                           |
| (3,3)       | 5   | 7.18        | 2.95         | 43.3                     |                   |                           |
| (5,5)       | 8   | 10.07       | 3.10         | 32.3                     |                   |                           |
| (10,10)     | 16  | 16.97       | 3.11         | 22.9                     |                   |                           |
| (20,20)     | 32  | 30.78       | 3.10         | 16.5                     |                   |                           |
| (40,40)     | 64  | 58.38       | 3.10         | 11.8                     |                   |                           |

| Carbyne $(C_N)$ |     |             |              |                          |                   |                           |
| $C_8$         | 8   | 4.21        | –            | 31.4                     |                   |                           |
| $C_{10}$      | 10  | 4.21        | –            | 27.7                     |                   |                           |
| $C_{12}$      | 12  | 4.21        | –            | 25.6                     |                   |                           |
| $C_{14}$      | 14  | 4.21        | –            | 24.4                     |                   |                           |
| $C_{16}$      | 16  | 4.21        | –            | 23.8                     |                   |                           |

| BN-carbynes $(BN)_{N/2}$ |     |             |              |                          |                   |                           |
| (BN)$_4$      | 8   | 4.21        | –            | 35.4                     |                   |                           |
| (BN)$_6$     | 10  | 4.21        | –            | 31.0                     |                   |                           |
| (BN)$_8$     | 12  | 4.21        | –            | 28.6                     |                   |                           |
| (BN)$_{10}$  | 16  | 4.21        | –            | 25.6                     |                   |                           |

tube size for the AA stacking at the optimized geometry. From Fig. 1(c), we observe that when the size of C-NT increases from (3, 3) to (40, 40), the binding energy per atom drops significantly from 44.3 meV/atom to 11.9 meV/atom. Table I shows that the wall-to-wall distance $d_{ww}$ is nearly a constant with tube size, while the center-to-center distance $d_{cc}$ dramatically increases, a situation similar to fullerene. This largely decreases the vdW force, due to the fact that the nonadditivity of vdW coefficients is unable to cancel that of the vdW radii for C-NT pairs, leading to the decreasing trend of the binding energy with tube size. Clearly, this trend has been followed by BN-NTs as shown in Table I and Fig. 1(c). However, the binding energy for BN-NTs is slightly smaller than that for C-NTs. A possible explanation is that, because C-NTs and BN-NTs take structures similar to those of their bulks (the BN layered materials), the BN atoms in BN-NTs may not all be on the same surface, as they are for C-NTs. This will increase the band gap (5.5 eV) [44] of BN-NT (a situation similar to h-BN [45]) and thus decrease the vdW coefficients between BN-NTs, compared to C-NTs, as shown in Table III. The energy scaling law in Table II predicts the binding energies of 12.8 meV for C-NT, and 12.0 meV for BN-NT with AA stacking in the large size limit, which are rather close to 11.5 meV/atom for graphene (quantum Monte Carlo value) [46] and 9.9 meV/atom of h-BN [47].

Wire-to-wire interaction. Carbyne is a carbon-based nanowire (C-NW) with an infinite chain of sp-$^3$ hybridized carbon atoms, held together by either double or alternating single and triple atomic bonds. It displays unusual properties, such as strong chemical activity and extreme instability in ambient conditions. C-NW and its BN substitute (BN-NW) have attracted great attention.
recently \[2,38,50\], due to a variety of remarkable properties. Here we study the variation of binding energy per atom between two AA-stacked finite-length C-NWs with system size. Due to the instability of C-NW, the binding energy is calculated at a fixed distance between two C-NWs, rather than at the relaxed distance (see Computational Methods for detail). As shown by Fig. 1(d), the binding energy per atom between C-NWs decreases with system size. This is rather similar to those of fullerenes and nanotubes, but with much stronger size-dependence. It is also opposite to the energy scaling law of PAHs. This feature has been inherited by its BN substitute. However, the binding energy between BN-NWs is slightly stronger, due to the additional permanent dipole-dipole interaction between B and N atoms, a similar situation to BN-PAHs. In the large-size limit, the binding energy (16 meV/atom) between C-NWs becomes slightly larger than that (15.2 meV/atom) between BN-NWs, suggesting that crossover arising from the distortion of BN atoms occurs somewhere.

### IV. DISCUSSION

To understand the energy scaling law of nanostructures, knowledge of the vdW coefficients is essential. Due to the direct relevance of the vdW coefficients to the static multipole polarizability, and in view of the relatively large size of the nanostructures, our starting point is the classical conducting solid or hollow sphere model, which is exact for slowly-varying densities. In this model, the static multipole polarizability satisfies \[20\]

\[
\alpha_l(0) = [\alpha_1(0)]^{(2l+1)/3}, \tag{2}
\]

where \(l\) is the order of the polarizability, with \(l = 1\) (dipole), 2 (quadrupole), 3 (octupole), etc. (The dipole polarizability of a fullerene can be estimated \[26\] from \(\alpha_1(0) = [R_N + t/2]^3\), where \(R_N\) is the average radius of the nuclear framework of a fullerene, and \(t\) is the effective thickness of the shell.) Suppose the sphere contains \(N_i\) identical atoms with the static multipole polarizability \(\alpha_l^i(0)\). Now let the volume of the sphere increase from \(V_i\) to \(V_f\) with fixed electron density, so that \(N_f\) will increase to \(N_f\). We seek interpolation relating the multipole polarizabilities at \(N_i\) and \(N_f\), the endpoints of the range over which we know \(\alpha_l(0)\). The dipole polarizability per atom at \(N_f\) can be written as \(\alpha_l^f(0)/N_f = \alpha_l^f(0)/N_f^{1+\delta_l}\). If \(\delta_l = 0\), the dipole polarizability is additive. Otherwise, it is nonadditive \[51\]. Similarly, the higher-order polarizabilities can be written as

\[
\alpha_l^f(0)/N_f = \alpha_l^f(0)/N_f^{1+\delta_l}, \tag{3}
\]

where \(\delta_l\) is a measure of nonadditivity of the multipole polarizability. Substituting Eq. (2) into Eq. (3) and performing some simple algebra, we can express the nonadditivity of the multipole polarizability in terms of that of the dipole polarizability as

\[
\delta_l = [(2l + 1)(1 + \delta_1) - 3]/3 - 1/[3(2l + 1) - 3]\left(\ln N_i/\ln N_f\right). \tag{4}
\]

The last term of Eq. (4) is the size correction to the nonadditivity of the higher-order multipole polarizability. It vanishes for \(l = 1\) (dipole), and in the classical limit \((N_f \to \infty)\). When the dipole polarizability is additive (i.e., \(\delta_1 = 0\)), we can still observe the strong nonadditivity of the higher-order multipole polarizability (i.e., \(\delta_l > 0\)). Therefore, the nonadditivity of the higher-order multipole polarizability is an intrinsic property of a material. For any \(N_i < N < N_f\), we just replace \(N_f\) by \(N\) in Eq. (4). For the smallest possible data set \(N_i = N_f\), our formulas would predict \(\delta_l = 0\). In other words, the multipole polarizability at a single point \(N\) cannot deliver the physical nonadditivity. In order to identify the physical nonadditivity in which the initial value should be taken from an atom \[24\], we need the multipole polarizability at \(N\) or \(N_f\) that is reasonably larger than \(N_i\). The scaling properties for the static multipole polarizabilities of various nanostructures are given by Table III [The dipole polarizabilities \[52\] of nanotubes are taken from Refs. \[27,31\], while the higher-order polarizabilities are estimated from Eq. (2).]

With the scaling properties of the static multipole polarizability, we can study the nonadditivity of the vdW interactions. The vdW coefficients between two identical solid spheres, each having \(N\) atoms, take the simple form \[24,36\]

\[
C_6 = \alpha_1(0)\alpha_1(0)\hbar_6(n), \quad C_8 = \alpha_1(0)\alpha_2(0)\hbar_8(n), \quad \text{and} \quad C_{10} = \alpha_1(0)\alpha_3(0)\hbar_{10,1}(n) + \alpha_2(0)\alpha_2(0)\hbar_{10,2}(n).
\]

Here \(n\) is the average valence electron density of the sphere, and \(\hbar_6,\hbar_8,\hbar_{10,1},\hbar_{10,2}\) are functions of \(n\) determined by the Casimir-Polder formula. Our calculation shows that \(n\) is nearly a constant with system size, so that the nonadditivity of vdW coefficients is essentially determined by the nonadditivity of the static multipole polarizability. According to Eqs. (2)-(4), we can express the nonadditivity of the vdW coefficients as

\[
C_6^i/N_i^2 = C_6^f/N_f^{2+\delta_6}, \quad C_8^i/N_i^2 = C_8^f/N_f^{2+\delta_8}, \quad C_{10}^i/N_i^2 = C_{10}^f/N_f^{2+\delta_{10}}. \tag{5}
\]

If \(\delta_l = 0\) or the dipole polarizability is additive, so is \(C_6\). Similarly, we have

\[
C_6^i/N_i^2 = C_6^f/N_f^{2+\delta_6}, \quad C_8^i/N_i^2 = C_8^f/N_f^{2+\delta_8}, \quad C_{10}^i/N_i^2 = C_{10}^f/N_f^{2+\delta_{10}}. \tag{6}
\]

### TABLE II: Binding-energy scaling law (in meV), \(E_b/N = a + b/N + 1000c[(N_d - d)^2]/N_1 + [e(N_d - d)]^2\)

| System          | \(a\)  | \(b\)  | \(c\)  | \(d\)  |
|-----------------|--------|--------|--------|--------|
| Fullerene pair  | 24.55  | 0.00025| 75     |        |
| C-PAH pair      | 30.50  | -0.00002| 22     |        |
| BN-PAH pair     | 30.35  | -0.00001| 22     |        |
| C-NT pair       | 12.80  | 1.70   | 20     |        |
| BN-NT pair      | 12.17  | -0.000018| 20     |        |
| C-NW pair       | 16.115 | 0.0006 | 12     |        |
| BN-NW pair      | 15.20  | 0.0002 | 10     |        |
TABLE III: Scaling properties of the static multipole polarizabilities of fullerenes, C-NTs, and BN-NTs, with armchair (m,m) and zigzag (m,0) structures, and the vdW coefficients between identical pairs. \( N \) is the number of atoms in a nanostructure. For NTs, it represents the number of atoms per unit length (Å). The static dipole polarizability and \( C_6 \) for fullerenes are the \textit{ab initio} values taken from Ref. [53], while the higher-order static polarizabilities and vdW coefficients are calculated in this work. For nanotubes, the static dipole polarizabilities are the \textit{ab initio} values taken from the literature [27-31], while all others are obtained in this work.

|                  | Polarizability scaling | vdW coefficients' scaling |
|------------------|------------------------|---------------------------|
|                  | \( \alpha_1(0)/N^{1.19} \) | \( \alpha_2(0)/N^{1.63} \) |
|                  | \( \alpha_1(0)/N^{1.2} \)  | \( \alpha_3(0)/N^{2.17} \) |
| Carbon nanotubes | Armchair (m,m)          |                           |
|                  | \( \alpha_1(0)/N^{1.71} \) | \( \alpha_2(0)/N^{1.61} \) |
|                  | \( \alpha_1(0)/N^{1.16} \) | \( \alpha_3(0)/N^{2.09} \) |
|                  | \( \alpha_1(0)/N^{1.06} \) | \( \alpha_2(0)/N^{1.09} \) |
| BN-based         | Armchair (m,m)          |                           |
| nanotubes        | \( \alpha_1(0)/N^{1.06} \) | \( \alpha_2(0)/N^{1.33} \) |
|                  | \( \alpha_1(0)/N^{1.06} \) | \( \alpha_3(0)/N^{2.13} \) |
|                  | \( \alpha_1(0)/N^{1.06} \) | \( \alpha_2(0)/N^{1.42} \) |

\( \delta_i \) are given by Eq. (4). (Note that \( \delta_1 + \delta_3 = 2\delta_2 \).) From Eqs. (1)-(6), we can see that the nonadditivity of the vdW coefficients for \( C_6 \), \( C_8 \) \& \( C_{10} \) largely arises from that of the multipole polarizability. If \( C_6 \) is additive, \( C_8 \) \& \( C_{10} \) are still nonadditive, because, even if \( \delta_1 = 0 \), \( \delta_2 \) \& \( \delta_3 \) are not zero. This finding suggests that the nonadditivity of higher-order vdW coefficients essentially originates from the intrinsic nonadditivity of the multipole polarizability. The scaling properties for the vdW coefficients between nanostructures are also listed in Table III.

With knowledge of the nonadditivity of vdW coefficients, we can now explain the energy scaling law for fullerenes as follows. Let us consider the interaction between two identical classical solid spheres that are close enough [6]. Each sphere has a radius of \( R = [\alpha_1(0)]^{1/3} \). The vdW coefficients are

\[
C_6 \sim \alpha_1(0)\alpha_1(0) \sim R^6 \sim N^{2(1+\delta_1)},
\]

\[
C_8 \sim \alpha_1(0)\alpha_2(0) \sim R^8 \sim N^{8(1+\delta_1)/3},
\]

\[
C_{10} \sim \alpha_1(0)\alpha_3(0) \sim R^{10} \sim N^{10(1+\delta_1)/3}.
\]

This yields

\[
C_{2j}/(2R)^{2j} \sim R^6.
\]

When the spheres are close to each other, all energy terms of the vdW series are independent of \( R \) or system size. This nonadditivity cancellation is valid for both solid spheres and hollow spheres with a cavity, because our analysis for solid spheres is also valid for hollow spheres. To demonstrate this cancellation, we have calculated the energy series \( C_6/d^6 \), \( C_8/d^8 \) and \( C_{10}/d^{10} \) for fullerene solids, with \( d = d_{cc} \) given in Table I. Our calculation shows that both the leading-order and higher-order energy terms are nearly size-independent. However, it was found [51] that this series diverges when two identical classical conducting spheres touch, but this spurious divergence can be removed without changing the asymptotic series. Nevertheless, the binding energy per atom \( (|C_{2j}|/(2R)^{2j})/N \) is decreasing with \( N \), as shown by Fig. 1(a).

The physics behind the energy scaling law is now clear. The behavior observed in Fig 1(a)-1(d) is a consequence of a competition between the nonaddativities in the vdW coefficients and in the vdW radii, which are saturated to the bulk values. For ball-ball interactions, there is large cancellation between \( C_{2j} \) and \( (2R)^{2j} \), leading to a rather slow variation of the binding energy per atom with system size. For plane-plane interactions, the nonadditivity of vdW coefficients is dominant, because the parallel distance \( d_{cc} \) is nearly a constant, leading to significant increase in binding energy. For tube-tube interactions, the nonadditivity of vdW coefficients becomes relatively less important due to the much larger size of tubes, compared to that of fullerenes, leading to a faster variation of the binding energy per atom with system size than that between fullerenes. There is a difference between BN atoms in BN-PAH and BN-NT. The reason is that BN atoms of BN-PAH can form \( \pi \)-electron delocalization, as in C-PAH. However, as in bulk h-BN, BN atoms of BN-NT can not, because both BN-NT and bulk h-BN have large gaps [13]. This difference in bonding explains why the binding energy of BN-PAH is greater than that of C-PAHs, but the binding energy for BN-NTs is slightly smaller than that for C-NTs. From BN-NW to h-BN bulk material, we can see that the energy gap evolves from a small value (nanowire) to a larger value 5.5 eV (BN-NT), to a even larger value 5.9 eV (h-BN), suggesting the deformation of B atoms from the surface of N atoms and thus a change in energy scaling law from nanowires to nanotubes. Due to the \( \pi \)-electron delocal-
ization, the difference in binding energy scaling between C-PAH and BN-PAH is the same as that between C-NW and BN-NW: BN-based PAHs and BN-based nanowires show faster energy variation with system size than C-based counterparts. The binding energy per atom of the nanowire dimers may decrease with increasing length due to dilution of the effect of covalent bonding between C atoms at the ends of the dimer.

V. CONCLUSION

The binding energy determines the stability of nanostructures and is therefore very important in the study of nanostructures. However, it has presented computational challenges. In this work, we have studied the binding energy law of nanostructures based on a first-principles method. We find that there is a binding-energy scaling law between identical nanostructures. From the law, we can predict the binding energy at any structure size. We illustrate this finding with fullerenes, PAHs, nanotubes, and nanowires. Apart from fullerenes, we chose AA stacking in our study. From the energy scaling law, we predict finite large-size limits, which are expected. To understand the energy-scaling law, we have studied the vdW coefficients using the accurate hollow-sphere model within the SFA. We find that the energy scaling law is determined by two competing factors: Nonadditivities of the vdW coefficients and the center-to-center distance. This leads us to conclude that the energy-scaling law in part originates from the nonadditivity of the static multipole polarizability of nanostructures.

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APPENDICES

Appendix A: vdW-DF-cx characterization of Fullerenes

Here we will show that the vdW-DF-cx functional predicts the geometries of fullerene solids in agreement with what is known experimentally about them. Other evidence for the accuracy of vdW-DF-cx is presented in Appendix B and in Refs. [22, 59, 55–61].

Figure A1 shows the atom structure of C_{60} and the high-symmetry axis (dark gray line) going out of a pair of hexagonal facets; C_{60} also has a secondary axis (light gray line) going through a pair of pentagonal facets. The initial coordinates of C_{60}, C_{70}, C_{76}, and C_{80} fullerenes are taken from the supplemental material of Ref. [52]. C_{60} and C_{70} have I_h and D_5h symmetry, respectively. Since C_{76} and C_{80} have isomers, here we focus on C_{70} and C_{80} with D_2 symmetry.
Table A1: vdW-DF-cx results for primitive-cell lattice structures when permitting unconstrained unit-cell relaxations. They are all slightly distorted fcc as reflected in the lattice constants \((a, b, c)\) and unit-cell solid angles \((\alpha, \beta, \gamma)\).

| Molecule  | Lattice system | \(a/b/c\) (Å) | \(\alpha/\beta/\gamma\) (°) | \(V\) (Å³) |
|-----------|----------------|----------------|---------------------------|-----------|
| C60-Ih    | Triclinic      | 13.92/14.15/14.14 | 91.2/90.8/90.9           | 696       |
| C70-D5h   | Orthorhombic   | 16.26/13.94/14.33 | 90.0/90.0/90.0           | 812       |
| C76-D2    | Orthorhombic   | 16.95/13.66/13.91 | 90.0/90.0/90.0           | 905       |
| C84-D2    | Triclinic      | 16.09/15.76/15.34 | 90.3/88.4/90.0           | 972       |

Panel (a) of Fig. A2 shows the primitive (one molecule) and super-cell (four molecules) geometries that we have used to model the fullerene crystals, as illustrated with C\(_{60}\). We assume that fullerenes are in crystal structures that are variations of fcc. Cohesive energies are extracted for (super-cell) geometries that have been fully relaxed with the consistent-exchange vdW-DF-cx version, using the BFGS quasi-newton algorithm as available in variable-cell calculations (‘vc-relax’) with the QUANTUM ESPRESSO package. We find no observable deformation of the individual fullerenes in any of the approximate-ground-state crystals structures that we have studied.

Table A1 reports the details of fully unrestrained vdW-DF-cx characterization of the optimal structure of fullerenes, when forced into a primitive cell (panel (a) of Fig. A2). Unconstrained relaxation was chosen, because we do not, except for the C\(_{60}\) crystal, have access to experimental information about alignment of fullerene symmetry axis and of the fullerene crystal. This vdW-DF-cx characterization yielded the following identification of the nature of optimal structures: triclinic (rhombohedral) crystal symmetry for C\(_{60}\) and C\(_{84}\) (for C\(_{70}\) and C\(_{76}\)). From these structures, we extracted the vdW-DF-cx results for the sublimation energies \(E_s\) and for the wall-to-wall separations \(d_{ww}\) (estimated as the distance to the nearest vertex or bond or facet on one molecule to the corresponding motif on the neighboring molecules). These results have been reported in the main text.

The C\(_{60}\) crystal motivates further theoretical characterizations because there is experimental data on structure \[65\]. We note that while our unconstrained relaxation (modeling a primitive cell) predicts a triclinic structure, the actual structure deviation is small (see Table A1). This difference is, in fact, expected. The ground state should have two different alignments of the symmetry axis relative to the crystal directions \[65\]. In choosing a primitive modeling, we are, on principle grounds, prevented from fully representing the actual C\(_{60}\) crystal ground state.

For a deeper discussion, we consider the role of the molecular orientation in the C\(_{60}\) crystal both in a primitive cell containing one molecule and in an improved modeling relying on 4 molecules per unit cell; the second modeling approach is illustrated in panel (b) of Fig. A2. The C\(_{60}\) crystal undergoes a phase transition at 260K. Above that temperature, all molecules can be considered equivalent, having free rotations, in a fcc primitive cell with one C\(_{60}\) molecule. Below this temperature, however, the C\(_{60}\) crystal is still fcc, but then in a super-cell configuration of unknown size. There is no free rotation but a forced alignment of the major symmetry axis with the [111] direction of the fcc crystal cell. One can experimentally assign a rotational-angle value, \(\phi\), for molecules in the low-temperature systems \[65\]. However, the alignment must vary over the fcc-type super cell (of unknown size) which has a mixture of alignments: 15 % molecules in a rotational configuration R\(_{98}\) and about 85 % in R\(_{98}\).

Figure A3 summarizes the additional structure exploration that we have done to test the ability of vdW-DF-cx to characterize the structural motifs of the C\(_{60}\) ground state. The figure shows the sublimation-energy variation that results in a single-molecule unit-cell modeling as we vary the alignment of the major symmetry axis with the [111] crystal axis, all in an fcc structure; since the major axis has a three-fold symmetry, it is only necessary to explore constrained relaxations in the range \(0 < \phi < 120\). Tracking the relaxations in vdW-DF-cx, we thus identify a set of meta-stable configurations, red dots, with specific rotations but with a range of structural symmetries, as further described in Table A2. This class of metastable fcc structures differs qualitatively from the...
The structure identified as ‘Fm ¯3 mix’ is an example of individual molecules to relax to different orientation values. Alignment. In a super cell, however, we can allow individual ground state. If we furthermore take the dashed line as an approximation for how such additional local minima would be distributed in energies, then we can expect optimal rotational values at around $\phi \approx 40^\circ$ and $\phi \approx 100^\circ$. It is heartening that these angles coincide with those that emerge as most prevalent in the mixture description obtained in the experimental characterization of C$_{60}$, evident as vertical blue lines in Fig. A3.

Table A2 also reveals that structural optimization in the super cell indicates a very small preference for mixing different molecular rotations. Here again the relaxation is constrained to the experimentally observed major-axis alignment. In a super cell, however, we can allow individual molecules to relax to different orientation values. The structure identified as ‘Fm3 mix’ is an example of an energetically favorable such meta-stable configuration. Like the actual but unknown ground-state super cell, this structure is characterized by having a mixture of molecular rotations.

Finally, Table A3 lists the sublimation energies that arises when the [111] crystal axis (red line) is assumed to align with either the major or the secondary symmetry axis for the C$_{60}$ crystal. For a single-molecule modeling, and among the cases with major-axis alignment, we find a best case, Fm3 R111°, with a sublimation energy that lies with 0.1 meV/atom of that of the triclinic structure with the secondary-axis alignment. Also, although the energy differences are still very small, the $E_b$ ordering is reversed when instead we consider the best four-molecule super cell case (with correct alignment), denoted ‘Fm3 mix’.

Overall, we find that the vdW-DF-cx is able to reflect the known structural motifs of the C$_{60}$ crystal (although the C$−60$ ground state is not fully known): (a) preference for a fcc-type super-cell configuration with a mixture of rotational angles, (b) a preference for having predominantly a $\phi = 100^\circ$ rotational state, and (c) a per-molecule volume value, which for the most-favurable super-cell representation, lies within 2 percent of the experimentally observed value, 692 Å$^3$. We take this vdW-DF-cx progress as an indication that it can be used to predict the binding structures of the set of investigated nano-structured materials and that it is a good starting point for exploring energy scaling laws.

### Appendix B: Asymptotic binding in vdW-DF-cx

Here we will show that vdW-DF-cx predicts equilibrium binding energies of fullerene solids in agreement with experiment, even though, as anticipated in Ref. 20, it is not accurate for the asymptotic interaction of a fullerene pair.

We have extracted the C$_b$ values that correspond to an asymptotic vdW-DF-cx description, following prior discussions of the nature of the vdW-DF binding 12 64. For the finite fullerene structures, this leads to a determination of the C$_b$ coefficients using Eq. (5)-(7) of Ref. 53. The following information is presented to permit a discussion of differences in the asymptotic description from the hollow-shell model 53.
TABLE A3: Comparison of geometries and binding energies of C\textsubscript{60} crystals in metastable cubic/rhombohedral structures (in which the [111] crystal axis is kept aligned with major symmetry axis) and in alternative triclinic structures (in which [111] is found to be aligned with the secondary C\textsubscript{60} symmetry axis). The former is a characteristics of the experimentally observed ground state, while the latter is what emerges in unconstrained relaxations in the one-molecule primitive cell.

| Symmetry                        | Lattice system | a/b/c (Å) | α/β/γ (°) | V (Å\textsuperscript{3}) | d\textsubscript{ww} (Å) | E\textsubscript{b} (meV/atom) |
|---------------------------------|----------------|-----------|------------|--------------------------|---------------------|-------------------------------|
| 0.835 Fm\textsubscript{3} R98°  | Cubic          | 14.04     | 692        |                          |                     |                               |
| +0.165 Fm\textsubscript{3} R38°|                 |           |            |                          |                     |                               |
| Experiment [63]                 |                |           |            |                          |                     |                               |
| -                               | Triclinic      | 13.92/14.15/14.14 91.2/90.8/90.9 | 969 | 3.05 | 34.8 |
| Fm\textsubscript{3} R0°         | Cubic          | 14.10/14.10/90.0/90.0/90.0 | 701 | 3.06 | 34.0 |
| Fm\textsubscript{3} R111°       | Rhombohedral   | 14.07/14.07/14.07 90.4/90.4/90.4 | 697 | 3.11 | 34.7 |
| vdW-DF-cx; primitive cell       |                |           |            |                          |                     |                               |
| -                               | Triclinic      | 13.90/14.08/14.04 91.2/91.0/90.8 | 687 | 2.93 | 36.1 |
| Fm\textsubscript{3} mix         | Rhombohedral   | 13.96/13.96/13.96 90.7/90.7/90.7 | 679 | 2.96 | 36.8 |
| vdW-DF-cx; 4 molecules/unit cell|                |           |            |                          |                     |                               |

In the vdW-DF method, we work with a local-field susceptibility \( \alpha \) and corresponding external-field susceptibility \( \alpha_{\text{ext}} = \alpha/(1 + 4\pi\alpha) \). This susceptibility (or plasmon propagator) depends on two spatial coordinates but can be represented in a gradient expansion. When investigating the asymptotic interactions, the relevant limit is \([12, 64]\):

\[
\alpha_{\text{ext, asym}}^{\text{vdW-DF}}(iu, r) \to \frac{n(r)}{u^2 + [9g_0(r)^2/(8\pi)]^2}.
\]  (B1)

This susceptibility limit is directly set by the inverse length scale \( g_0 \) that enters in the specification of the local plasmon dispersion \([12, 14, 64]\). We compute this susceptibility limit from the electron-density variation \( n(r) \) that we have established in the underlying (full) vdW-DF-cx calculations.

From the approximation Eq. \([B1]\) we determine, in turn, the asymptotic vdW-DF-cx description of nanostructure interaction from a Casimir-Polder expression of the molecular C\textsubscript{6} coefficients, using a numerical imaginary-frequency integration. The result is a description similar to Eq. \((17)\) of Ref. \([12]\). We note that this C\textsubscript{6} limit is not an exhaustive representation of the full, regular vdW-DF-cx calculations, for reasons explained in Refs. \([12, 14, 83, 64]\).

Table \([B1]\) reports our numerical extraction of such vdW-DF-cx based C\textsubscript{6} coefficients for fullerenes with various number of carbon atoms \( N \), here contrasted with TDHF-based values cited in Table 3 of the main text. In general, the nonlocal-correlation part of vdW-DF \([12]\) (same as in vdW-DF-cx) leads to good C\textsubscript{6} values for small-to-medium sized molecules \([65]\). However, for the hollow fullerenes, the vdW-DF-cx values are about half the size of the results of the shell-model analysis based on TDHF calculations \([53]\). Also, the vdW-DF-cx results for C\textsubscript{6}/\( N^2 \) is nearly independent of \( N \). Thus the vdW-DF-cx descriptions do not reflect the C\textsubscript{6} nonadditivity that is expressed in the TDHF-based C\textsubscript{6} description \([54]\) and hollow-sphere model.

The vdW-DF-cx functional slightly overestimates the nanostructure binding energies \( E_b \), but it is still useful for mapping the energy scaling as it is accurate on structure characterizations (Appendix A and Refs. \([5, 59, 70, 66]\), as well as for nanostructure energy differences \([51, 22, 67, 59]\). Table B1 also reports a comparison of the vdW-DF-cx results for fullerene sublimation energies \( E_b \) and raw experimental observations (no thermal correction); Table \([B1]\) reports the comparison when the finite-temperature effect is removed from the experimental values.

For the C-PAH dimers in the sandwich or AA configuration, CCSD(T)-based best estimates of the binding energy per atom for benzene, naphthalene, and anthracene \([66]\) are 13.2, 17.8, and 21.1 meV per carbon atom, versus the vdW-DF-cx values of 17.4, 22.4, and 25.0 meV per carbon atom, respectively. For the corresponding benzene, naphthalene, and anthracene molecu-
lar crystals, the measured suplimation energies are 22, 41, and 40 meV per carbon atom, versus the vdW-DF-cx values of 25, 46, and 44 meV per carbon atom [22]. Thus vdW-DF-cx captures the right trends with increasing particle size (being in these cases about 4 meV per carbon atom higher than the best available estimates).

Moreover, vdW-DF-cx is accurate in first-principle characterizations of nanostructure-energy differences. It has proven useful for the description of both elastic deformations energies [8, 53, 58, 60] and lattice vibrations [57, 60]. For example, it can accurately reproduce the measurement of all all libration modes in the naphthalene molecular crystal, characterizing the phonon dispersion to within 1 meV (without any experimental input on the molecular-crystal structure) [60].

Some of us have previously (independently) discussed that it is possible for a density functional to fail in the asymptotic description but still be accurate at binding separations [14, 21]. The vdW-DF-cx description of the fullerene crystals gives in example: Appendix A shows that vdW-DF-cx does give an accurate description of structural motifs in fullerene crystals at binding separation even if vdW-DF-cx is not accurate for (and does not give nonadditive) C₆ coefficients, Table [51]. We also note that the vdW-DF-cx is nonadditive in a different sense, namely in its description of the nonlocal correlation interaction at binding separations [67].

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