Origin of the size-dependence of the equilibrium van der Waals binding between nanostructures

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Nanostructures can be bound together at equilibrium by the van der Waals (vdW) effect, a small but ubiquitous many-body attraction that presents challenges to density functional theory. How does the binding energy depend upon the size or number of atoms in one of a pair of identical nanostructures? To answer this question, we treat each nanostructure properly as a whole object, not as a collection of atoms. Our calculations start from an accurate static dipole polarizability for each considered nanostructure, and an accurate equilibrium center-to-center distance for the pair (the latter from experiment, or from the vdW-DF-cx functional). We consider the competition in each term \(-C_{2k}/d^{2k}\) (\(k = 3, 4, 5\)) of the long-range vdW series for the interaction energy, between the size dependence of the vdW coefficient \(C_{2k}\) and that of the \(2k\)-th power of the center-to-center distance \(d\). The damping of these vdW terms can be negligible, but in any case it does not affect the size dependence for a given term in the absence of non-vdW binding. To our surprise, the vdW energy can be size-independent for quasi-spherical nanoclusters bound to one another by vdW interaction, even with strong nonadditivity of the vdW coefficient, as demonstrated for fullerenes. We also show that, for low-dimensional systems, the vdW interaction yields the strongest size-dependence, in stark contrast to that of fullerenes. We illustrate this with parallel planar polycyclic aromatic hydrocarbons. Other cases are between, as shown by sodium clusters.

I. INTRODUCTION

Conventional Kohn-Sham density functional theory (DFT) has reached a high level of sophistication and achieved practical success, due to the good balance between efficiency and achievable accuracy. In recent years, many reliable semilocal density functionals have been proposed [1–9] and some of them have been widely used in electronic structure calculations. However, these conventionally constructed DFT methods often produce large errors for molecular complexes and solids [10, 11], interface problems [11], and ionic solids [12]. A fundamental reason is that, while conventional DFT methods can give an accurate description of the short-range part, the long-range vdW interaction is missing in these methods.

The long-range vdW interaction is an important nonlocal correlation due to instantaneous electric charge fluctuations. It affects many properties of molecular complexes and solids [13–21], layered materials [10, 22–23], and ionic solids [12, 24]. It has been shown that performances of conventional DFT methods can be substantially improved with a vdW correction. A number of accurate vdW corrections have been developed. Most of them are based on atom pairwise effective models [25–29], while a few of them [26, 30–33] go beyond atom pairwise models. These models are very accurate for small or medium-size intermolecular interaction and have been widely used in electronic structure calculations, but errors may grow with system size or number of atoms in a system and can seriously affect the performances of vdW-corrected methods, as system size approaches the nanoscale. For example, it has been shown that, while the dispersion-corrected atom pairwise model PBE+D2 is accurate for the binding of a pair of small molecules, the errors become large for fullerenes [21, 36]. It is known that an important source of errors is the nonadditivity of the vdW coefficients [37], due to electron delocalization and many-body (e.g., three-body) interactions [38, 39].

Additivity means that the multipole polarizability of a nanostructure scales linearly with \(N\), the number of atoms in it, and that each vdW coefficient \(C_{2k}\) between identical nanostructures scales as \(N^2\), the behavior predicted by atom pairwise interactions. As we will see, this expectation is rarely exact even for the dipole polarizability and for \(C_6\), and never for higher-order contributions. A proper treatment of non-additivity requires treating each nanostructure as a whole object, and not as a collection of atoms.

In solids, a particle at \(I\) not only interacts with another particle at \(J\), but also with pairs \(JK\) of other particles, etc. The energy of vdW interaction of a particle at \(I\) with all others can be written as a many-body expansion [39–42]

\[
E_{\text{vdW}}(I) = \sum_J E_{\text{vdW}}^{(2)}(IJ) + \sum_{JK} E_{\text{vdW}}^{(3)}(IJK) + \cdots
\]

where \(E_{\text{vdW}}^{(2)}\) is the two-body contribution, while \(E_{\text{vdW}}^{(3)}\) accounts for the three-body contribution.

II. TWO-BODY VDW INTERACTION ENERGY

A model for the two-body vdW interaction energy is usually developed from the asymptotic expansion of the
vdW interaction at large separation, which can be written as
\[
E_{\text{vdW}}^{(2)} = -(C_6/d^6)f_{d,6}(d/d_{\text{vdW}}) - (C_8/d^8)f_{d,8}(d/d_{\text{vdW}}) - (C_{10}/d^{10})f_{d,10}(d/d_{\text{vdW}}),
\]
where \(d\) is the distance between the centers of two interacting density fragments and \(f_{d,k}\) is the damping function \([44, 48]\), with \(d_{\text{vdW}}\) being the sum of vdW radii.

In the development of vdW corrections, there are two important tasks. One is the calculation of vdW coefficients, and the other is the design of a proper damping function, according to the short-range interaction from a semilocal DFT. The former involves important many-body effects and has received most attention. It was shown \([21]\) that in nanostructured materials such as fullerenes, \(f_{d,2k}(d/d_{\text{vdW}} \sim 1) \approx 1\). The sum of vdW radii can define the minimum separation between the centers of density fragments for nanostructured materials without formation of a covalent bond. The center-to-center distance can be written as \(d = d_{\text{vdW}} + \Delta\), with \(\Delta\) being determined by the nature of the interaction. It can be positive, zero (i.e., direct contact), or negative. For nanostructures bound at equilibrium by only the vdW interaction, \(d/d_{\text{vdW}}\) is of order unity, and nearly independent of system size (as we will show), so even when damping is important for the interaction energy it is not important for the size-dependence of each term in Eq. (2).

The two-body vdW coefficients can be calculated from the dynamic multipole polarizability via the Casimir-Polder formula \([40]\),
\[
C_{2k}^{AB} = \frac{(2k - 2)!/(2\pi)^{k-2}}{(2l_1!)(2l_2)!} \int_0^\infty d\omega \alpha_{l_1}(i\omega)\alpha_{l_2}(i\omega) \alpha_{l_1}^{(0)}(i\omega)\alpha_{l_2}^{(0)}(i\omega)\left(\omega^2_1 + \omega^2_2\right),
\]
where \(l_2 = k - l_1 - 1\). The required dynamic multipole polarizability can be modelled with the spherical-shell model. Since the electron density in nanostructures is nearly independent of system size or number of atoms in a system, we may simplify the spherical-shell model with the single-frequency approximation (SFA) \([52, 51]\), in which we assume that (i) only valence electrons in the outermost subshell of an atom in a molecule are polarizable, and (ii) the density is uniform inside the effective or vdW radius \(R_i\) and zero otherwise. This model is particularly useful for nanostructures or larger systems, in which the electron density is slowly-varying \([52, 54]\).

The only required input is the static polarizability which can be obtained from accurate \(ab\) initio methods.

Within the SFA, the model dynamic multipole polarizability takes the simple expression
\[
\alpha_{l}^{\text{SFA}}(i\omega) = R_i^{2l+1} \frac{\omega^2_1 + \omega^2_2}{\omega^2_1 + \omega^2_2 + u^2} \frac{1 - \rho_l}{1 - \beta_l\rho_l},
\]
where \(R_i\) is the effective outer radius of the shell defined below [Eq. 4], \(\beta_l = \omega^2/\omega^2 + u^2(\omega^2 + u^2)\) describes the coupling of the sphere and cavity plasmon oscillations, and \(\rho_l = (1 - t_l/R_i)^{2l+1}\) describes the shape of the shell, with \(t_l\) being the shell thickness \([52, 53]\). In the static limit, the model dynamic multipole polarizability reduces to the true static polarizability, i.e., \(\alpha_{l}^{\text{SFA}}(0) = \alpha_{l}^{(0)}\) for fullerenes, we set \(t_l = 3.4\) bohr.

\(\omega_l = \omega_p\sqrt{(2l + 1)/(2l + 2)}\) is the average sphere plasmon frequency, \(\omega_1 = \omega_p\sqrt{(l + 1)/(2l + 1)}\) is the cavity plasmon frequency, and \(\omega_p = \sqrt{4\pi\rho}\) is the average plasmon frequency of the extended electron gas, with \(\rho = \bar{N}/V_i\) and \(V_i\) being the effective vdW volume and \(\bar{N}\) the total number of valence electrons in the outermost subshell \((\bar{N} = 2\) for carbon atom, while for B and N atoms, \(\bar{N} = 1, 3\)).

For a classical conducting shell of uniform density, the static dipole polarizability is related to the static dipole polarizability by \(\alpha_l^{(0)} = [\alpha_l^{(0)}]^{(2l+1)/3}\). The vdW radius is defined by
\[
R_i = [\alpha_l^{(0)}]^{1/(2l+1)},
\]
with \(R_1 = R_2 = R_3 = [\alpha_l^{(0)}]^{1/3}\). The preceding formula, which predicts the static higher-order polarizabilities from the static dipole polarizability, is valid for slowly-varying densities, but only approximately true for strongly inhomogeneous densities such as atoms and ions \([12]\). It can be shown that the average electron density \(\bar{n}\) within the shell is nearly a constant for nanostructures such as fullerenes. Therefore, we can write
\[
E_{\text{vdW}}^{(2)} = -\frac{\alpha_{l_1}^{(0)}(\omega_1)\alpha_{l_2}^{(0)}(\omega_2)f_{11}(\bar{n}_A, \bar{n}_B)}{\left(\alpha_{l_1}^{(0)}(\omega_1)^{1/3} + \alpha_{l_2}^{(0)}(\omega_2)^{1/3} + \Delta\right)^6} - \frac{\alpha_{l_1}^{(0)}(\omega_1)\alpha_{l_2}^{(0)}(\omega_2)f_{12}(\bar{n}_A, \bar{n}_B) + P_{21}}{\left(\alpha_{l_1}^{(0)}(\omega_1)^{1/3} + \alpha_{l_2}^{(0)}(\omega_2)^{1/3} + \Delta\right)^8} - \frac{\alpha_{l_1}^{(0)}(\omega_1)\alpha_{l_2}^{(0)}(\omega_2)f_{13}(\bar{n}_A, \bar{n}_B) + P_{22} + P_{31}}{\left(\alpha_{l_1}^{(0)}(\omega_1)^{1/3} + \alpha_{l_2}^{(0)}(\omega_2)^{1/3} + \Delta\right)^{10}},
\]
where \(f_{12}, f_{13}(\bar{n}_A, \bar{n}_B)\) represents the integral over the imaginary frequency \(i\omega\), whose explicit expression can be extracted from Ref. \(56\). \(P_{21}, P_{22}\) and \(P_{31}\) represent the terms containing \(\alpha_{l_1}^{(0)}(\omega_1)\alpha_{l_2}^{(0)}(\omega_2)\), \(\alpha_{l_1}^{(0)}(\omega_1)\alpha_{l_2}^{(0)}(\omega_2)\), and \(\alpha_{l_1}^{(0)}(\omega_1)\alpha_{l_2}^{(0)}(\omega_2)\), respectively. Note that Eq. (5) is valid for any two nanostructures, no matter whether they are identical or not. Consider a sequence of systems in which system size or number of atoms in a system increases from the initial \((i)\) to final \((f)\) size. The static multipole polarizability also changes from \(\alpha_{l_1}^{(0)}(\omega_1)\) to \(\alpha_{l_1}^{(f)}(\omega_1)\). Here \(\delta_l\) is the nonadditivity of the static multipole polarizability measuring the deviation of the conventional value \(\alpha_{l_1}^{\text{conv}, f}(\omega_1)\) of the true value \(\alpha_{l_1}^{(f)}(\omega_1)\). For example, \(\delta_{1} = 0.2\) for the dipole polarizability of fullerenes \([54, 52]\), and \(-0.084\) for sodium clusters evaluated from the dipole polarizability of Ref. \(54\). As seen below, even when \(\delta_1 = 0, \delta_l > 0\) for \(l \geq 2\).

In the preceding paragraph, \(\delta_l\) is a measure of nonadditivity of the static multipole polarizability, as explained above. It is given by \([54, 55] \delta_{l_1} = \left[(2l + 1)(1 + \delta_{l_1}) - 3\right]/(3 - (1/3)(2l + 1) - \delta_{l_1}(\ln N_{f_1}/\ln N_{f_2})\right), where the second term is a correction to the first term. For \(N_{f_1} = 1\) or \(N_{f_1} \ll N_{f_2}\), the second term vanishes. Then, we obtain \(\delta_2 = (2 + 6\delta_{l_1})/3\) and \(\delta_3 = (4 + 7\delta_{l_1})/3\). Substituting the expression for the nonadditivity of the static multipole polarizability into
TABLE I: Terms of the van der Waals interaction energy for a pair of identical fullerenes in a fullerene solid [21] with the nearest neighbor center-to-center separation $d_{cc}$ obtained from fcc experimental lattice constants [60, 61], and for a pair of identical sodium clusters. The dipole polarizabilities of Na$_4$ and Na$_8$ are from Ref. [54], while that of Na$_{19}$ is obtained as $\alpha_1(0) = (R + \delta)^3$, with $R = N^{1/3}r_s$ and $\delta = 1.5$ bohr [52]. $d_{cc}$ is calculated as the distance between the centers of mass of two sodium clusters by putting them side by side [53] (AA stacking for (Na$_{19}$)$_2$) with Quantum ESPRESSO [54] using the vdW-DF-cx functional [51]. All quantities are in atomic units. The reference values for $C_6$ are from Ref. [53] for fullerenes and Ref. [56] for sodium clusters, except for Na$_{19}$, which is taken as an average of Na$_{12}$ and Na$_{20}$. The calculated vdW coefficients [51, 52] are obtained from the hollow-sphere model within SFA of Eq. (9). A minus sign “−” in front of all the vdW interactions has been suppressed.

| $d_{cc}$ (Å) | $\alpha_1$ | $C_6/v^{10}$ | $C_{10}/v^{14}$ | $C_{14}/v^{18}$ | $C_{18}/v^{22}$ | $C_{20}/v^{26}$ | $C_{24}/v^{30}$ | $\Delta(t)$ | $C_{6}/C_{10}/C_{14}/C_{18}/C_{20}/C_{24}$
|------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|------------|----------------------------------|
| C$_{60}$-C$_{60}$ | 536.6 | 100.1 | 98.91 | 356.9 | 105.9 | 396.0 | 18.9 | 16.3 | 1.16 | 2.6 | 2.2 | 2.4 | 2.0 | 0.13 |
| C$_{70}$-C$_{70}$ | 659.1 | 141.6 | 144.7 | 601.8 | 205.7 | 711.1 | 20.1 | 17.4 | 1.16 | 2.7 | 2.2 | 2.5 | 2.2 | 0.13 |
| C$_{78}$-C$_{78}$ | 748.3 | 178.2 | 184.2 | 836.1 | 311.9 | 1027 | 20.8 | 18.2 | 1.14 | 2.6 | 2.2 | 2.5 | 2.2 | 0.14 |
| C$_{84}$-C$_{84}$ | 860.4 | 207.7 | 213.3 | 1019 | 400.2 | 1281 | 21.5 | 18.6 | 1.16 | 2.9 | 2.2 | 2.5 | 2.2 | 0.13 |
| Na$_{19}$-Na$_4$ | 511.6 | 16.80 | 17.28 | 51.40 | 13.75 | 57.89 | 13.9 | 16.9 | 0.81 | -2.7 | 3.6 | 6.3 | 10 | 0.55 |
| Na$_{18}$-Na$_8$ | 883.9 | 52.48 | 55.68 | 251.3 | 98.47 | 342.5 | 15.7 | 19.2 | 0.82 | -3.3 | 3.7 | 6.8 | 11 | 0.59 |
| Na$_{19}$-Na$_{19}$ | 1804 | 241.9 | 250.5 | 1941 | 1249 | 3389 | 16.5 | 24.3 | 0.68 | -7.8 | 12.4 | 35.3 | 84 | 3.74 |

Eq. (4) and considering $A = B$ leads to a dramatically simplified size-dependence of the vdW interaction energy between nanostructures,

$$E_{vdW}^{(2)} = \frac{-[\alpha_1(0)]^2 f_1(\tilde{n})}{(2[\alpha_1(0)]^{1/3} + \Delta R)^6} + \frac{\alpha_1(0)[\alpha_2(0)]^2 f_2(\tilde{n})}{(2[\alpha_1(0)]^{1/3} + \Delta R)^8},$$

where $R = (N_1^{1/3} + \delta)/N_1^{1/3}$. This is the main result for the two-body vdW interaction. We can see from Eq. (6) that the size-dependence of the two-body vdW interaction depends upon the difference $\Delta$ between the true center-to-center distance and the sum of the vdW radii. When $\Delta$ is close to 0, the vdW attraction reduces to the value it takes initially for $\Delta = 2[\alpha_1(0)]^{1/3}$ and we are almost unable to observe the size dependence of the vdW interaction. When $\Delta$ is large and positive, the vdW attraction is rather weak. When $\Delta$ is negative, a stronger (e.g., covalent) bond may form between nanostructures. But in both cases, the size-dependence of the vdW interaction should be observed. We will demonstrate these observations with fullerenes, sodium clusters, and polycyclic aromatic hydrocarbons as follows.

### III. THREE-BODY VDW INTERACTION ENERGY

In solids, a molecule or ion core not only interacts with another molecule or ion core, but also simultaneously interacts with other two or more species. Three-body vdW interaction is much weaker [12, 38, 50, 42] than two-body vdW interaction. Here we only consider the most important lowest-order dipole-dipole-dipole interaction. The asymptotic form of the three-body interaction energy is given by $E_{vdW}^{(3)}(IJK) = C_9[3\cos(\theta_I)\cos(\theta_J)\cos(\theta_K) + 1]/(d_{IJ}d_{IK}d_{JK})^3$, where $d_{IJ} = |I - J|$ are the sides of a triangle, and $\theta_I, \theta_J, \theta_K$ are the internal angles of the triangle formed by $d_{IJ}d_{IK}d_{JK}$. $C_9$ is the three-body vdW coefficient, which can be calculated with the dipole polarizability from

$$C_9 = \frac{3}{\pi} \int_{0}^{\infty} du \alpha_1(iu)\alpha_1(iu)\alpha_1(iu).$$

Substituting the dipole polarizability of Eq. (8) into the expression for the three-body vdW coefficient [Eq. (9)] and performing the integration over the imaginary frequency, we can obtain an expression for the three-body coefficient. Next we consider identical nanostructures. Making use of an analysis similar to that for the two-body interaction, we can easily obtain the final expression for the size dependence of three-body vdW interaction energy

$$E_{vdW}^{(3)} = \left[\alpha_1(0)^3 f(\tilde{n}, \theta_I, \theta_J, \theta_K)\{(2[\alpha_1(0)]^{1/3} + \Delta_{IJ}/R)\right.$$  

$$\left.\times (2[\alpha_1(0)]^{1/3} + \Delta_{JK}/R)(2[\alpha_1(0)]^{1/3} + \Delta_{IK}/R)\right]^{-3},$$

which is similar to the two-body vdW interaction, with $R$ being defined below Eq. (4). If the $\Delta_{IJ}, \Delta_{IK},$ and $\Delta_{JK}$ are all small, the three-body interaction is also size independent. Otherwise, it is size-dependent. This is very similar to the two-body interaction, but its effect on the total vdW interaction is small.

Summarizing, our size-dependence of the vdW interaction energy for identical nanostructures is formulated in terms of the hollow-sphere model within the SFA of Eq. (9). This model is valid for both spherical and non-spherical nanostructures of slowly-varying densities, because non-sphericity [51, 54] can enter the model via the input static polarizability $\alpha(0) = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ obtained from accurate ab initio calculations. But Eq. (9) is only instructive for quasi-spherical nanostructures at equilibrium center-to-center distance between them. It is least instructive for finite low-dimensional parallel nanostructures, for which the center-to-center distance at equilibrium is nearly independent of system size. In this
case, the size-dependence of the vdW interaction energy mainly arises from the size dependence of vdW coefficients. As such, we can employ the asymptotic formula of Eq. (2) directly to study its size dependence, as exemplified here with polycyclic aromatic hydrocarbons. For nanostructures of infinite length such as nanotubes, the situation is more complicated and will not be discussed.

Finally, it is worth pointing out that the vdW interaction energy can also display a size-dependence in the case of nonzero $\Delta$, even when the vdW coefficients are additive. This suggests that this phenomenon can be also described with an atom pairwise model \cite{20, 22, 26}.

**IV. SIZE-DEPENDENCE STUDY OF NANOSTRUCTURES**

**A. Fullerenes**

Fullerene is an important material with many remarkable properties such as great chemical stability and high sublimation or cohesive energy, leading to a variety of applications \cite{54, 55}. Its properties resemble those of graphene in the large-size limit, such as zero-energy gap and binding energy \cite{54}. In fullerene solids, the vdW interaction is dominantly important, while covalent interaction between fullerene molecules is negligibly small \cite{21}. The shape of fullerenes is quasispherical and the electron density on the surface of fullerenes is nearly uniform. Therefore, they are ideal model systems for the study of the vdW interaction energy.

Table II for fullerene solids shows that both the leading-order and higher-order vdW interactions, $-C_{2k}/d^{2k}$, are nearly size independent. This is because $\Delta$ values are all small, compared to the sum of vdW radii $d_{vdW} = 2a_1(0)^{1/3}$. Table II also shows the comparison of expensive TDHF calculations and model polarizability-based calculations for $C_6$. From Table II we can see the good agreement of our model $C_6$ with TDHF values. The size independence of fullerene pair interactions may not be valid for other near neighbor (NN) pair interactions, because for other NN pair interactions, $\Delta$ increases, while $d_{vdW}$ is a constant. But the influence of other NN pair interactions is small, leading to the near size-independence of fullerene pair interaction. Table II also shows the very slow convergence of the vdW series for the interaction energy between two fullerenes at equilibrium, as anticipated by Refs. \cite{21, 55}.

The same analysis will also apply to the three-body vdW interaction energy. To demonstrate the size independence of the three-body interaction energy, we first evaluate the three-body vdW coefficient in each fullerene solid with Eq. (4). Then we evaluate the three-body vdW interaction. The results are also displayed in Table II. From Table II we can observe that, similar to the two-body vdW interaction, the three-body interaction is also size-independent, confirming our prediction.

**B. Sodium clusters**

Sodium cluster is a simple-metal cluster. It was shown that a sodium cluster can form a giant atom \cite{65, 66}. Therefore, the pair interaction between sodium clusters can form a covalent bond. This leads to an intermolecular distance between centers of two sodium clusters significantly shorter than the sum of the vdW radii of sodium clusters, $d_{vdW}$. To confirm this, we have calculated the distance between the centers of mass of two identical sodium clusters $\langle N_{A_2} \rangle$ ($D_{2h}$), $\langle N_{A_3} \rangle$ ($T_d$), and $\langle N_{A_{10}} \rangle$ ($D_{2h}$) by putting them side by side, with Quantum ESPRESSO using the vdW-DF-cx functional \cite{31}, which has proven accurate in nanostructures \cite{54}. In this calculation, the energy cutoff is 30 hartree and only $\Gamma$ points are included in the k-mesh. The results are displayed in Table II. From Table II we can see that cancellation of the size dependence between vdW coefficients and the vdW radii is incomplete. We have also repeated the calculation of the distance between the centers of mass of sodium cluster pair $\langle N_{A_2} \rangle$ by putting them head to head and head to tail (see Supplemental Material). The results are shorter, compared to that for side to side, suggesting that the cancellation of the size dependence between vdW coefficients and the vdW radii in incomplete in all the cases. In other words, the vdW interaction between sodium clusters is indeed size dependent. Table II also shows the comparison of the vdW coefficients obtained from the ab initio method and the hollow-sphere model within the SFA. From Table II we see that the model calculation is in good agreement with more expensive ab initio values.
TABLE II: Terms of the van der Waals interaction energy between two identical polycyclic aromatic hydrocarbons (PAHs) of AA stacking with the nearest neighbor center-to-center separation $d = d_{cc}$ obtained from the vdW-corrected vdW-DF-cx nonlocal functional \[31\]. All quantities are in atomic units (hartrees for energy, bohrs for distance). The vdW coefficients are evaluated from the hollow-sphere model within the SFA of Eq. \[3\] with $t_{l} = R_{l}$, where the average valence electron density $\bar{n} = N/v$ \[51\]. The reference values of $C_{l}$ are from TDQDFT (time-dependent DFT) calculations \[67, 68\]. The input static dipole polarizabilities are taken from TDHF calculations \[68\]. The higher-order multipole polarizabilities are estimated from the conventional formula of Eq. \[3\]. We have used a density $\bar{n} = 0.0468$. A minus sign “−” in front of all the vdW interactions has been suppressed.

|       | $\alpha$ | $C_{6}/10^{10}$ | $C_{8}/10^{10}$ | $C_{10}/10^{10}$ | $d_{cc}$, \(\text{nm}\) | $d_{vdW}$, \(\text{nm}\) | $(C_{6}/d_{cc})10^{10}$ | $(C_{8}/d_{cc})10^{10}$ | $(C_{10}/d_{cc})10^{10}$ |
|-------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\text{C}_{6}\text{H}_{6}-\text{C}_{6}\text{H}_{6}$ | 68.23 | 17.73 | 17.93 | 15.65 | 11.35 | 7.69 | 1.00 | 0.87 | 1.28 | 1.57 |
| $\text{C}_{10}\text{H}_{12}-\text{C}_{10}\text{H}_{12}$ | 176.6 | 100.3 | 108.5 | 178.5 | 244.0 | 7.37 | 0.97 | 6.77 | 20.5 | 51.6 |
| $\text{C}_{18}\text{H}_{12}-\text{C}_{18}\text{H}_{12}$ | 244.8 | 175.1 | 199.0 | 407.1 | 691.8 | 7.30 | 0.96 | 13.1 | 50.5 | 161.0 |

C. Polycyclic aromatic hydrocarbons (PAHs)

Finally, we have studied the size dependence of the vdW interaction energy between two identical PAHs with AA stacking. For such a geometry, a recent calculation with the vdW-DF-cx has shown \[51\] that the plane-to-plane distance is only shrinking a little with system size, due to the fact that the vdW force also increases with system size, but the vdW coefficients per carbon atom increase rapidly with system size as we go from $\text{C}_{6}\text{H}_{6}$, $\text{C}_{10}\text{H}_{12}$, $\text{C}_{14}\text{H}_{10}$, to $\text{C}_{18}\text{H}_{12}$, owing to the nonadditivity. This leads to a rapid increase of the vdW interaction with system size. From Table III we can observe that, even when the molecules are highly non-spherical, the model vdW coefficients (Eq. \[3\] with $t_{l} = R_{l}$) are still accurate, compared to the more expensive time-dependent DFT-B3LYP calculations, suggesting the reliability of our results. In our calculations, the plane-to-plane distance of 2,3-Benzanthracene \[51\] was used for $\text{C}_{18}\text{H}_{12}-\text{C}_{18}\text{H}_{12}$.

To see the damping effect on the vdW interaction energy, we calculate the ratio of the center-to-center distance over the sum of the vdW radii $d_{cc}/d_{vdW}$ and the center-to-center distance of PAHs over the benzene-to-benzene distance $d_{cc}(\text{C}_{6}\text{H}_{6}, \text{C}_{6}\text{H}_{6})/d_{cc}(\text{C}_{6}\text{H}_{6}, \text{C}_{6}\text{H}_{6})$. The former are all displayed in Table III while the latter are displayed in Table III. From Table II, we see that all the ratios are nearly independent of system size, except for $\text{Na}_{19}\text{Na}_{19}$. This means that the damping function should not change the size-dependence of the vdW interaction energy. The reason for this is the cancellation of the size-dependences of the equilibrium center-to-center distance and vdW radii. From Table III we can also see that the ratios are nearly the same for PAHs, because the plane-to-plane distance of PAHs should not be size-dependent.

Figure III shows the comparison of the dipole-dipole interaction energy term $-C_{6}/d_{cc}$ for identical fullerene pairs, sodium cluster pairs, and PAH pairs. From Fig. III we observe that the size dependence of fullerene pairs is nearly a constant, while that of PAH pairs yields the strongest size dependence. The size-dependence of the vdW interaction between sodium clusters is between these two extreme cases. From Tables II and III we also see similar size dependences for higher-order interactions.

V. CONCLUSION

In conclusion, we employ the model polarizability and the experimental center-to-center distance (for fullerenes) or the distance from the vdW-DF-cx functional (for sodium clusters and PAHs) to study the size dependence of the vdW energy at the equilibrium distance. The former offers a good description of vdW coefficients via the Casimir-Polder formula, while the latter is accurate in the prediction of the center-to-center equilibrium distance, but inaccurate in the vdW coefficients for some nanostructures such as fullerene \[3\] and \[51\]. The dependence of the vdW interaction energy on system size or number of atoms is a common feature for nanostructures. It arises from the competition between the size-dependences of the vdW coefficients and the center-to-center distance. In this work, starting from the asymptotic long-range vdW interaction, we have derived an expression for the size-dependence of the vdW interaction, which is valid for identical nanostructures. We have studied the size-dependence of the vdW interaction for fullerenes, sodium clusters, and PAHs. Our calculations show that, for two identical nearest neighbor fullerenes in a fullerene solid, the vdW interaction is size-independent. This is unexpected, given that the vdW coefficients of fullerenes have very strong nonadditivity \[51\] or non-linear effects, due to the electron delocalization. However, for low-dimensional nanostructures, the vdW interaction shows the strongest size-dependence. We illustrate this with planar PAHs. For sodium clusters, the size-dependence of the vdW interaction is between those of fullerenes and PAHs.

VI. SUPPLEMENTARY MATERIAL

This material provides the details of different molecular geometries of sodium cluster.
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