Supplementary information

Interaction forces between spherical nanoparticle and flat surface

*Weifu Sun**

School of Materials Science and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

1. Interaction forces between silicon and diamond dissimilar nanospheres

The snapshots of a typical simulation process are shown in Figure S-1.

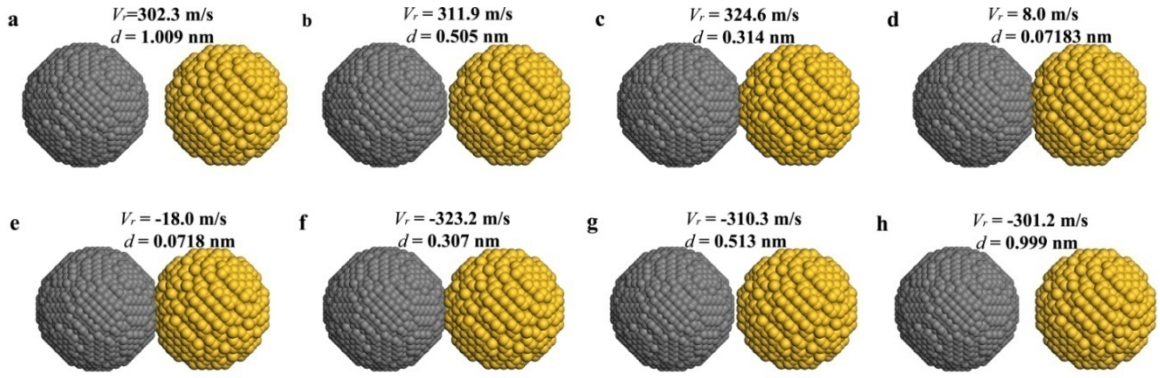

Figure S-1 Snapshots of simulation of a typical head-on collision between neutral diamond nanosphere and silicon nanosphere obtained at (a): 30.65, (b) 32.3, (c): 32.9, (d): 34.0, (e): 34.05, (f): 35.10, (g): 35.75 and (h): 37.35 ps. The initial shortest surface-to-surface separation between two equally-sized silicon nanospheres of about 2.0 nm in radius is 10.0 nm and the initial relative velocity is 300 m/s. V_r>0 denotes they approach towards each other and V_r<0 represents they depart from each other. The d denotes the corresponding shortest surface-to-surface separation, d= r-2R where r is the centre-to-centre separation, R is nanoparticle radius.

The interparticle potentials between diamond and silicon dissimilar nanospheres and the corresponding ratios are displayed in Figures S-2 and S-3, respectively. The same trends as silica nanospheres can be observed from Figures S-2 and S-3. Figure S-2 shows that the same as silica nanospheres,[1] for a given particle size, the magnitudes of both the vdW

attraction and Born repulsion potentials increase with decrease in surface separation; for a given separation, both the magnitudes of vdW attraction and Born repulsion potentials increase with increase in particle size. With decrease in surface separation, the totals of the attraction and repulsion potentials, i.e., the LJ potential, decrease sharply to a minimum, followed by increasing drastically.

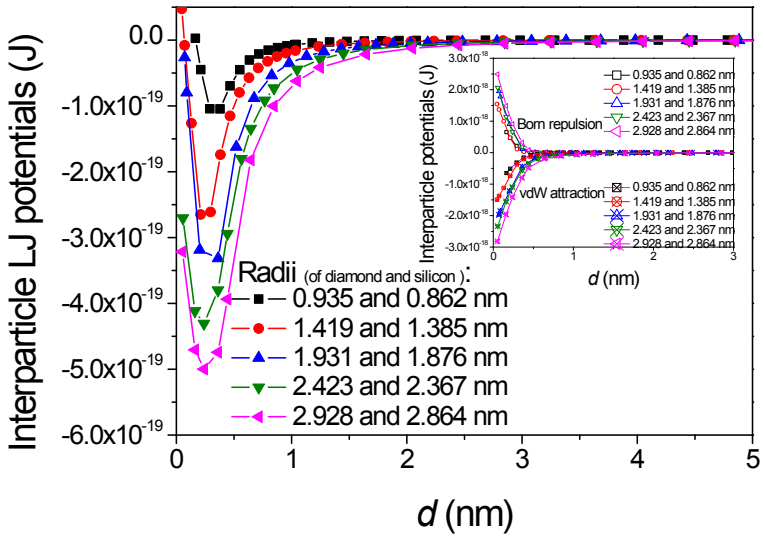

Figure S-2 Interparticle potentials as a function of the surface separation d between two similarly sized silicon and diamond nanospheres.

As observed from Figure S-3, the ratios of interparticle forces obtained from the MD simulation to those predicted by Hamaker approach are also as a function of particle size R and surface separation distance d. With increase in surface separation, the ratios of both vdW attraction and Born repulsion forces first increase sharply from almost zero to a peak around 0.4 nm, then decrease drastically and finally become constant asymptotically. In particular, in most cases, the vdW attraction and Born repulsion forces from the MD simulations are much larger than those from the Hamaker approach. The asymptotically constant ratios of vdW attraction and Born repulsion forces are denoted by k_{vdW} and k_{Born}, respectively. And k_{vdW} and k_{Born} are correlated with particle radius by Eqs. (S-3) and (S-4), respectively. It can be expected that if R becomes large enough, both constant ratios will become equal to unity, implying that the proposed equations of Eqs. (S-1) and (S-2) will produce the same results as those predicted by Hamaker approach using Eqs. (5) and (6).

Therefore following the same approach as silica nanospheres,[1] the interparticle vdW attraction and Born repulsion force can be represented by Eqs. (S-1) and (S-2), respectively. The calculated results from Eqs. (S-1) and (S-2) are in reasonable agreement with the MD simulated results as shown in Figure S-4.

$$F_{\mathrm{MD}}^{\mathrm{vdW}} = \begin{cases} \left(1+373.8e^{-6.5d^{0.3}}\right)F_{\mathrm{Hamaker}}^{\mathrm{vdW}}, & d \geq 0.4\,nm \\ e^{2.50(0.4-d)^{0.62}}F_{\mathrm{Modified},\,d=0.4\ \mathrm{nm}}^{\mathrm{vdW}}, & 0.15 < d < 0.4\ nm \\ \left[1+0.08\left(1-d/0.15\right)^{0.6}\right]F_{\mathrm{Modified},\,d=0.15\ \mathrm{nm}}^{\mathrm{vdW}}, & d < 0.15\,\mathrm{nm} \end{cases} \quad \text{(S-1)}$$

$$F_{\mathrm{MD}}^{\mathrm{Born}} = \begin{cases} \left(1+74.3e^{-5d^{0.8}}\right)k_{\mathrm{Born}}F_{\mathrm{Hamaker}}^{\mathrm{Born}}, & d \geq 0.4\,nm \\ e^{4.34(0.4-d)^{0.5}}F_{\mathrm{Modified},\,d=0.4\ \mathrm{nm}}^{\mathrm{Born}}, & 0.15 < d < 0.4\ nm \\ \left[1+0.295\left(1-d/0.15\right)^{0.8}\right]F_{\mathrm{Modified},\,d=0.15\ \mathrm{nm}}^{\mathrm{Born}}, & d < 0.15\,\mathrm{nm} \end{cases} \quad \text{(S-2)}$$

where k_{vdW} and k_{Born} are determined by Eqs. (S-3) and (S-4), and rms is the calculated average surface roughness of 0.0514 nm.

$$\ln k_{\mathrm{vdW}} = 4.85(\mathrm{rms}/R)^{0.24} \quad \text{(S-3)}$$

$$\ln k_{\mathrm{Born}} = 7.49(\mathrm{rms}/R)^{0.30} \quad \text{(S-4)}$$

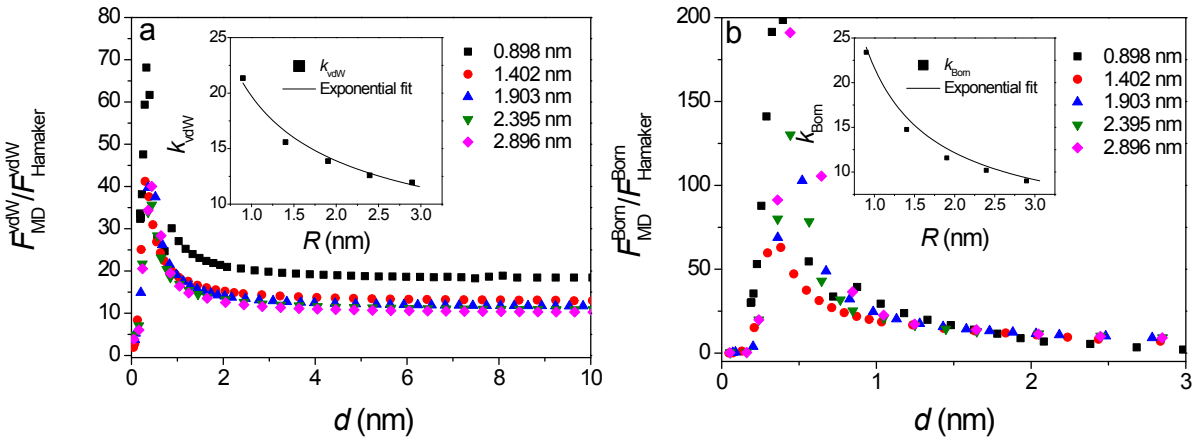

Figure S-3 The ratios of interparticle forces between silicon and diamond dissimilar nanospheres obtained from MD simulations to those from the Hamaker approach: the vdW attraction (a) and the Born repulsion force (b).

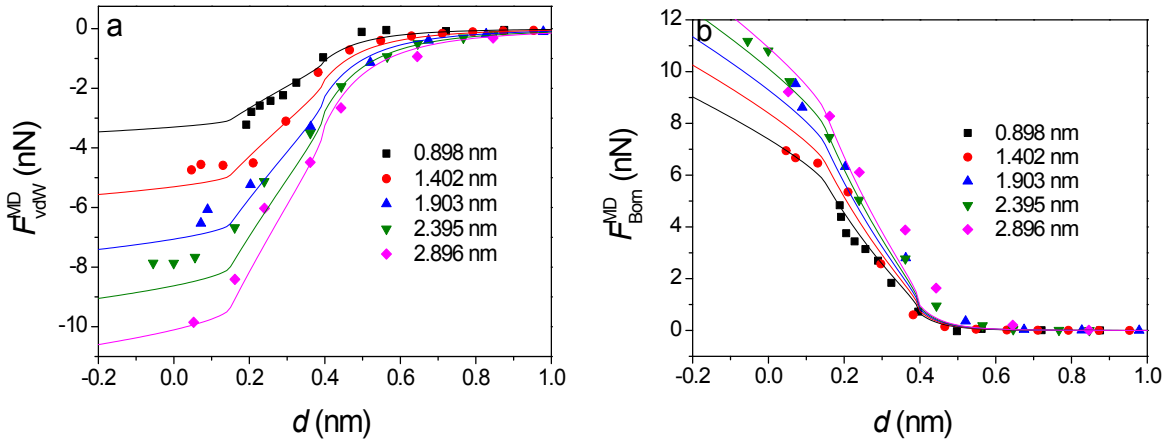

Figure S-4 Interparticle vdW attraction and Born repulsion forces between silicon and diamond dissimilar nanospheres.

2. Interplay between LJ force and mechanical contact force

Figure S-5 demonstrates the interparticle LJ potential E_{LJ}, LJ force F_{LJ}, the contact force F_c as a function of surface separation distance d. It is clear that the LJ potential first decreases to a minimum at d≈0.16 nm, and then increases sharply by decreasing surface separation. By differentiating interparticle LJ potential with respect to surface separation, the as-obtained LJ force also first decreases to a minimum, followed by increasing sharply. The minimum point of LJ potential corresponds to the zero point of LJ force at d≈0.16 nm where the occurrence of mechanical contact force initiates, confirming that due to the intermolecular repulsive forces, the mechanical contact force arises when two surfaces are less than equilibrium separation distance apart.

As observed from Figure S-5b, the pull-off force of 4.0 nm-radius silicon interacting diamond substrate. i.e., the minimum point, is about -4.0 nN. In view of the fact that Hamaker constants of silica[1] (A_{Silica}=6.5×10^{-20} J) and $A_{Si\text{-}C}$=8.3×10^{-20} J are similar, the pull-off force between two 40 nm-radius silica is about -13.2±2.6 nN.[2] But considering the size difference of 4.0 nm and 40 nm, the magnitude of pull-off force obtained in this work is reasonable.

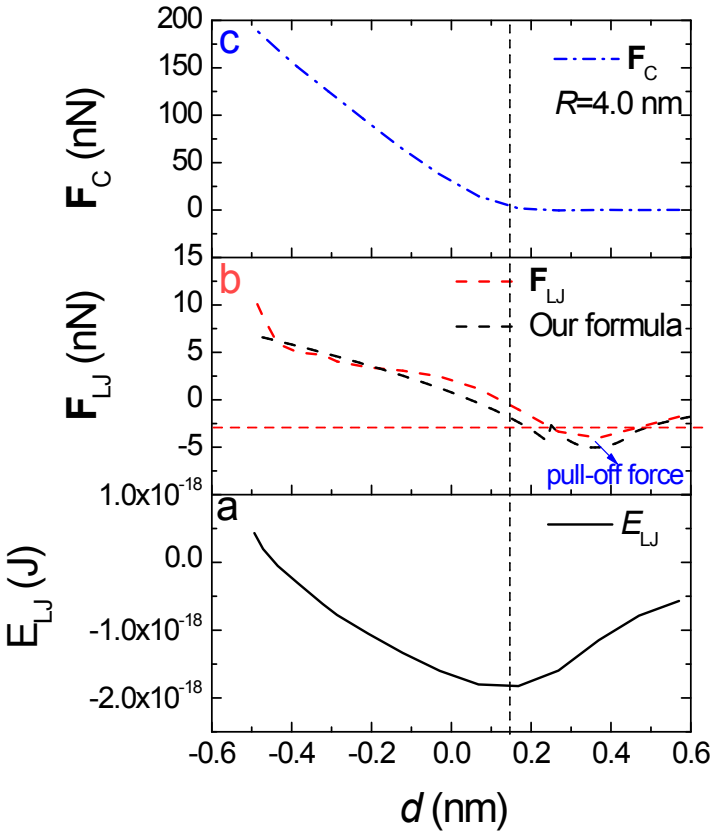

Figure S-5 The interplay between interparticle LJ potentials E_{LJ} (a), LJ forces F_{LJ} (b) and mechanical contact forces F_c (c) between crystalline silicon nanospheres of 4.0 nm in radius and diamond substrate as a function of surface separation. (b): the red dashed line represents MD simulated results while the black dashed line denotes the results calculated from our formula.

3. Measurement of Young's modulus of silicon bulk

The Young's modulus of silicon bulk was separately measured by MD simulations. MD simulations were performed on a simulation cell of $L \times M \times M$ nm^3 (L=8.0, M=6.0), which was filled with silicon molecules as bulk (Figure S-6a). After geometry optimization, MD simulation was first conducted using a NVT ensemble (i.e., constant number of atoms, constant volume and constant temperature) at 300 K running for at least 50.0 ps after equilibration. The equilibrated structure in the final frame was exported and then MD simulations were carried out using NPT ensemble (i.e., constant number of atoms, constant pressure and constant temperature) at 300 K for at least 50.0 ps along the (100) direction,

following geometry optimization. A series of external pressures were applied along the (100) direction, in order to obtain compressive stress-strain curve (Figure S-6b).

Young's modulus is derived from the initial linear part of the typical stress-strain curve (Figure S-6b) of silicon bulk. With increase in stress, the corresponding strain first increases linearly and then increases sharply. The slope of initial linear part (satisfying Hooke's law) was used to derive elastic modulus of ca. 125.5 GPa along the (100) direction of crystalline silicon bulk, which is 3.5% lower than experimental result of 130 GPa,[3] indicating an excellent agreement with each other.

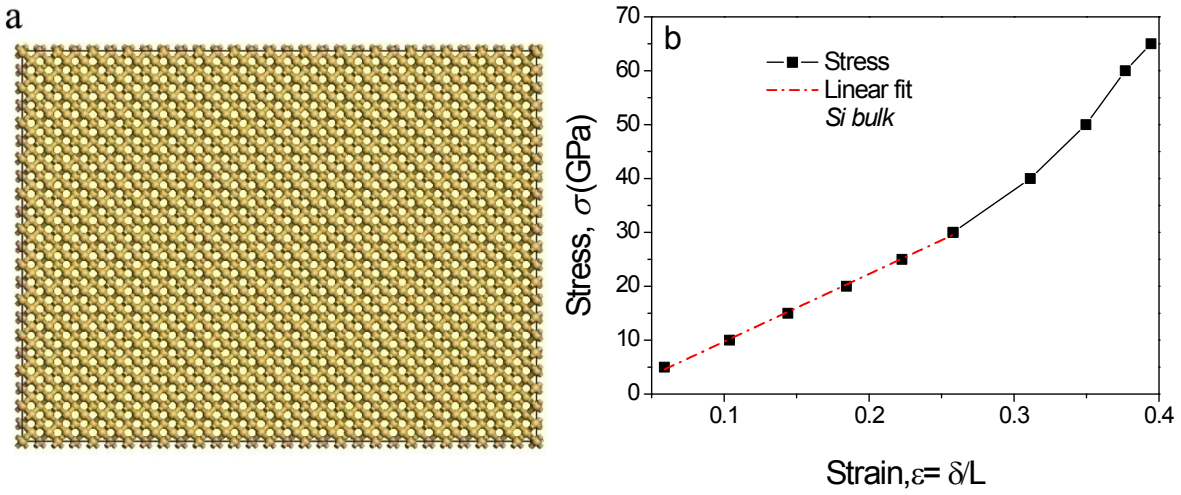

Figure S-6. (a): Simulation model used to measure Young's modulus of silicon counterpart bulk along the (100) direction; (b): Compressive stress-strain curve of silicon bulk.

4. Supplementary nomenclature

Table S-1 Nomenclature for symbols used in this work

Symbol	
A	Hamaker constant
C	the vdW attraction interaction parameter
ε	the potential well depth or strain
σ	the collision diameter of atom
E_{LJ}	interparticle Lennard-Jones potential

E	Young's modulus
E^*	the reduced Young's modulus
R_0	the cut-off radius
R	the defined particle radius $R = \overline{R}$
$\overline{R}$	the averaged radial distance of surface atoms from particle's centre
R^{core}	the radius of particle's core
δ	effective surface thickness
δ_{Max}	the maximum surface thickness
δ_{n}	normal displacement
d	the shortest surface separation along the line of two particles' centres
d_{min}	The minimum surface separation
v	velocity or volume of atom
λ	the ratio of the particle radii of two particles
$\mathbf{F}_{\text{n}}$	total normal force
$\mathbf{F}_{\text{vdW}}$	van der Waals attraction force
$\mathbf{F}_{\text{Born}}$	the short range Born repulsion force
$\mathbf{F}_{\text{c}}$	mechanical contact force

References

1 W. F. Sun, Q. H. Zeng and A. B. Yu, *Langmuir*, 2013, **29**, 2175-2184.

2 L. F. Hakim, J. H. Blackson and A. W. Weimer, *Chem. Eng. Sci.*, 2007, **62**, 6199-6211.

3 M. A. Hopcroft, W. D. Nix and T. W. Kenny, *J. Microelectromech. Syst.*, 2010, **19**, 229-238.