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# **ARTICLE IN PRESS**

# Small nanoparticles, surface geometry and contact forces

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In this molecular dynamics study, we examine the local surface geometric effects of the normal impact force between two approximately spherical nanoparticles that collide in a vacuum. Three types of surface geometries: (i) crystal facets, (ii) sharp edges and (iii) amorphous surfaces of small nanoparticles with radii R < 10 nm are considered. The impact forces are compared with their macroscopic counterparts described by nonlinear contact forces based on Hertz contact mechanics. In our simulations, edge and amorphous surface contacts with weak surface energy reveal that the average impact forces are in excellent agreement with the Hertz contact force. On the other hand, facet collisions show a linearly increasing force with increasing compression. Our results suggest that the nearly spherical nanoparticles are likely to enable some nonlinear dynamic phenomena, such as breathers and solitary waves observed in granular materials, both originating from the nonlinear contact force.

# 1. Introduction

The discrete nature of nanoscale materials has often revealed surprising phenomena. Nanoscale normal contact force and friction laws depend strongly on the particle contact. A molecular dynamics (MD) study by Luan & Robbins [1] demonstrated that the normal contact force for rough surfaces of solids with amorphous and crystal structures revealed significant departures from the Hertz contact force for quasi-statically contacting elastic, perfect spheres [2]. Atomically rough surfaces on contacting objects influence the contact considerably and local surface geometry in the vicinity of the contact region promotes variations of the contact surface area [1,3].

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Atomic scale surface roughness also dictates impact phenomena in nanoparticles. Gold nanoparticles, for example, can take a near-spherical shape (one of the thermodynamically stable shapes [4]) with the surface of such a nanoparticle comprising crystal steps and terraces, which make them 'rough' and in turn affect the nature of their interactions. The lack of spherical nanoparticle symmetry often leads to more complex dynamics than the Hertz contact theory for perfect spheres. Roll, slide and deflection phenomena of colliding nanoparticles arising from shape asymmetry have been observed elsewhere [5,6].

In dynamics, the coefficient of restitution often suffices to predict the overall behaviour of a dissipative many-body system such as clustering of dissipative particles [7]. Precise measurement of the impact force, however, is critical for certain dynamic systems. A recent MD simulation demonstrated that a one-dimensional chain of nanoscale 'buckyballs' can permit the propagation of a solitary wave [8], which is a non-dispersive propagating wave in a macroscopic granular system discovered by Nesterenko [9]. Realization of the solitary wave at the nanoscale implies that the interaction force between buckyballs is nonlinear. That is, the power of overlap  $\delta$  for the normal contact force  $F_N$  expressed by  $F_N \propto \delta^n$  must satisfy n > 1 so that a spatially localized propagating pulse of energy can be formed [10,11].

Direct observation of the impact force of colliding nanoparticles made by MD simulations has been reported [12–15]. Very large nanoparticles of radius  $R \sim 100$  nm simulated by Tanaka *et al.* [15] show good agreement with the Johnson–Kendall–Roberts (JKR) model, an adhesive contact model based on Hertz contact mechanics, as their shape approaches perfect spheres as the size is increased. However, the nature of impact forces between rough surfaces of colliding *small* nanoparticles is not yet fully understood. Our MD study presents precise details of contact forces for collisions between small nanoparticles having three different contact surface geometries in order to investigate the influence of surface roughness in a systematic fashion. An amorphous nanoparticle as well as nanoparticles with two distinct surface geometries, facets and edges of a face-centred cubic (fcc) crystal, are considered as contact surfaces.

Many MD studies on nanoparticle collisions indicate that nanoparticles are highly elastic if the impact velocity is kept below their material yield point, although a small amount of the initial kinetic energy admittedly dissipates during the impact process [12,16–18]. In addition, the adhesive nanoparticles that collide beyond a critical velocity, determined by the balance between adhesion and elastic energies, actually tend to rebound [6,16,19,20]. Similarly, the repulsive nanoparticles may provide a limiting case for the adhesive nanoparticle with surface energy  $\gamma \rightarrow 0$ . Therefore, we consider both repulsive and adhesive nanoparticles and compare their forces.

Our paper is organized as follows: §2 discusses our nanoparticle models and computational methods. Impact forces for colliding nanoparticles made from amorphous and crystal structures are displayed in §3. The discussion and conclusions are presented in §4. The Hertz contact theory and relevant adhesive contact models are briefly reviewed in appendices C and D.

# 2. Numerical simulations

#### (a) Models

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For an investigation of the dynamic interaction force, nearly spherical nanoparticles  $\xi$  and  $\eta$  of equal radius *R* are prepared. To study the influence of surface roughness, crystal and amorphous structures are employed as base materials for making our nanoparticles. These nanoparticles are modelled by the Lennard–Jones (LJ) potential (see §2b(i)).

101 Crystalline nanoparticles are carved out of an fcc single crystal of solid argon. The resultant 102 nanoparticles have atomic roughness consisting of crystal facets and steps on their exterior 103 surfaces due to their structures (see the nanoparticles in figure 1). We take advantage of the 104 presence of the surface roughness to obtain interaction forces at particular points on the surfaces. 105 The {100} crystal facets are chosen for studying *facet contacts* and some sharp crystal edges are 106 randomly chosen for studying the *edge contact* problem.

107 The amorphous structure is obtained by quenching a molten argon block from temperature T = 70 K to 0.02 K at a rate  $8 \times 10^{10}$  K s<sup>-1</sup> [21,22], followed by equilibrations at  $T_{eq} = 0.02$  K. 108 A nearly spherical nanoparticle is then created by cutting the block in equilibrium (see the insets 109 110 of figure 5). Radial distribution functions computed from our equilibrated nanoparticles confirm the amorphous structure [23]. 111

112 Adhesive and repulsive contacts are achieved by varying the surface energy of nanoparticles, 113 for which modified LJ potentials are used. The variation takes into account reduced interactions 114 through coated or fluid-mediated contact surfaces [24,25]. Nanoparticles with purely repulsive 115 contacts are considered by employing the Weeks-Chandler-Anderson (WCA) potential [26]. We 116 further elaborate on these LJ-based potentials in §2b(ii).

#### (b) Interatomic potentials

120 Our non-equilibrium MD simulations presented here use three interatomic potentials based on 121 the standard 12-6 LJ potential to model adhesive and repulsive nanoparticles. To this end, a 122 modified LJ potential described in equation (2.1) is introduced, which contains a parameter 123  $c_{\alpha\beta}$  in the second term, where  $\alpha, \beta \in \{\xi, \eta\}$ . This parameter allows us to vary the attraction 124 between atoms, as used in [16,19,20,27]. A situation where  $c_{\alpha\beta} = 1$  recovers the standard LJ 125 potential. 126

> $V(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - c_{\alpha\beta} \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] & (r_{ij} < r_{c}), \\ 0 & (r_{ij} \ge r_{c}). \end{cases}$ (2.1)

The  $r_{ij}$  denotes an interatomic distance between *i*th and *j*th atoms,  $\sigma$  is the distance at which the potential is zero, and  $\epsilon$  is the depth of the potential. The potential is truncated and shifted at  $r_{ii} = r_c$  to get rid of a discontinuity that stems from the truncation. The attraction parameter  $c_{\alpha\beta}$ and cut-off  $r_c$  are varied depending on our purposes as described below.

For all potentials considered, the parameters for argon atom  $\sigma = 0.3405$  nm and  $\epsilon = 1.654 \times$  $10^{-21}$  J are used [18].

#### (i) Intrananoparticle potential

We use the standard LJ potential to model the individual nanoparticle, for which  $c_{\xi\xi} = c_{\eta\eta} = 1$  in equation (2.1) ( $\alpha = \beta = \xi$  or  $\eta$ ). The interaction between a pair of atoms *i* and *j* within a nanoparticle (labelled by  $\xi$  or  $\eta$ ) is computed with this standard LJ potential. In other words, the computation is carried out only if  $i, j \in \xi$  or  $i, j \in \eta$ .

#### (ii) Surface interaction

149 We consider three types of surface interactions between two nanoparticles  $\xi$  and  $\eta$ , namely: weak 150 adhesion, strong adhesion and pure repulsion. The parameter sets described below apply only 151 to a pair of atoms i and j that, respectively, belong to colliding nanoparticles  $\xi$  and  $\eta$ , i.e.  $i \in \xi$ 152 and  $i \in \eta$ . 153

For adhesive nanoparticles, the attraction parameter value  $c_{\xi\eta} = 0.2$  or  $c_{\xi\eta} = 1$  is set to achieve weakly or strongly adhesive contacts, respectively. In both cases  $r_c = 2.5\sigma$  is used, as is standard.

155 To attain purely repulsive nanoparticles, the WCA potential is adopted as used in [1,18]. It is a variation of the standard LJ potential with  $c_{\xi\eta} = 1$  and a cut-off  $r_c = 2^{1/6}\sigma$  at which the potential 156 takes its minimum value. Therefore, the tail of the potential is null at  $r_{ij} > r_c$ , which makes the 157 158 potential purely repulsive.

The parameters and cut-offs explained here are summarized in table 1. 159

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**Table 1.** LJ potential parameter sets,  $c_{\alpha\beta}$  ( $\alpha = \xi$  and  $\beta = \eta$ ) and  $r_c$ , for surface interaction between nanoparticles  $\xi$  and  $\eta$  considered in this study.

| surface interaction | $\mathcal{L}_{lphaeta}$ | r <sub>c</sub>     |
|---------------------|-------------------------|--------------------|
| weak adhesion       | 0.2                     | 2.5σ               |
| strong adhesion     | 1                       | 2.5σ               |
| pure repulsion      | 1                       | 2 <sup>1/6</sup> σ |

### (c) Computation

Equations of motion for argon atoms are solved by the velocity Verlet algorithm with integration time step  $\Delta t = 1.08 \times 10^{-14}$  s for crystalline nanoparticles [18]. We confirmed that at shorter time steps the nanoparticles had no substantial differences in collision phenomena [18]. An integration time step  $\Delta t = 4.3 \times 10^{-15}$  s for amorphous nanoparticles is used.

All the nanoparticles prepared are initially relaxed over sufficient time steps in the canonical (constant-temperature) ensemble at temperature  $T_{eq} = 0.02$  K. After the relaxation, the nanoparticles are brought into head-on collision in the *z*-direction at a relative impact velocity  $v_{imp} = |\mathbf{v}_{\xi} - \mathbf{v}_{\eta}|$  in the microcanonical (constant-energy) ensemble. The  $\mathbf{v}_{\xi}$  and  $\mathbf{v}_{\eta}$  denote the centre-of-mass velocities for the nanoparticles  $\xi$  and  $\eta$ , respectively.

Our MD simulations presented hereafter are carried out by LAMMPS [28] with modification to its source code to adopt the modified LJ potential equation (2.1) for adhesive nanoparticles.

# 3. Simulation results

We present our simulation results in this section for impact phenomena found in our adhesive and repulsive nanoparticles. Impacts on crystal edges, crystal facets and amorphous surfaces are, respectively, discussed in §§3a–c. For visualization of nanoparticles VMD [29] is used unless otherwise stated.

# (a) Impact on crystal edges

We consider cases where two fcc crystalline nanoparticles collide such that they first come into contact on at least one crystal edge on either of the nanoparticles.

#### (i) Force between nanoparticles

The nanoparticles dealt with herein possess a weak surface force resulting from a low attraction  $c_{\xi_n} = 0.2$  set in equation (2.1). We use a dimensionless impact force defined as an ensemble averaged normal force as described in appendix A, unless otherwise noted. Impact forces of adhesive nanoparticles colliding at an impact velocity  $v_{imp}$  are displayed in figure 1a for small radius R = 2.7 nm (number of simulations K = 1000) and (b) for large radius R = 7.4 nm (number of simulations K = 100). The solid and dashed lines, respectively, represent average forces in the loading and unloading stages. The impact velocity of the nanoparticles is varied from 20 to  $52 \text{ m s}^{-1}$ , which is in the elastic collision regime. The overlap  $\delta$ , defined in appendix B, is hereafter non-dimensionalized by *R*, denoted by  $\delta := \delta/R$ .

205 Owing to the relatively long-range surface interaction, the approaching nanoparticles undergo 206 a net attractive force prior to the beginning of contact at  $\tilde{\delta} = 0$ . This causes acceleration of the 207 nanoparticles, and hence the incoming velocity becomes higher in the negative force region [30]. 208 In the weakly adhesive contacts, however, the increase in the impact velocity is negligible due to 209 the low surface energy associated with  $c_{\xi\eta} = 0.2$ .

210 Beyond the overlap, where the surface attractive and compressional elastic forces balance out, 211 the impact force continues to increase as the nanoparticles deform further. The force-overlap 212 plots in the compressional region for both sizes show the nonlinear response to the impact loads.



**Figure 1.** Average impact forces for weakly adhesive edge contacts. Solid and dashed lines represent loading and unloading forces, respectively. The insets in (*a*) and (*b*) show the force-overlap curves for purely repulsive edge contacts. (*a*) Adhesive nanoparticles of R = 2.7 nm, (*b*) adhesive nanoparticles of R = 7.4 nm. (Online version in colour.)

Although the attractive force exists, the compressional force is much higher and predominant in the impact velocity range considered. If the impact velocity is set low enough, the attractive force would no longer be negligible as the compressional elastic force decreases. At a velocity below a threshold, determined by the Weber number, nanoparticles actually stick together [6,16,20,27]. In the velocity range and the weak adhesion considered, nanoparticles do not adhere together.

The unloading force for the departing nanoparticles at a given impact velocity is lower than the loading force in most of the overlap range shown. This hysteresis observed in the force-overlap curves, which is also typical in colliding viscoelastic bodies, indicates the loss of translational kinetic energy of the nanoparticles during collision. The existence of energy dissipation corroborates earlier findings: the coefficient of restitution of colliding nanoparticles is less than one if the impact velocity is sufficiently high [12,16–18,20,27]. At an impact velocity as low as the thermal velocity, the coefficient of restitution may exceed one [12,16,17,31,32]. Vibrations [33] and crystal structure changes [31] caused by collision may account for the microscopic energy dissipation.

Despite the impact velocity variations considered, all the loading forces agree well up to their maximum forces displayed here, and hence a dynamic effect on the force associated with strain rate is not appreciable. On the other hand, the unloading force gets smaller as the impact velocity is increased, indicating that the energy dissipates more at a higher impact velocity. This velocity dependence is a reasonable result as energy dissipation of colliding viscoelastic spheres [34,35] and nanoparticles [16,36] gradually increases with increasing impact velocity.

In addition, in order to examine the role of the surface force, purely repulsive contacts, modelled by the WCA potential, are also simulated. The impact forces averaged over 100 simulations for the repulsive nanoparticles with edge contact are shown in the insets of figure 1*a*,*b*. The forces are now purely compressional loads due to the absence of surface forces, but they are nearly indistinguishable from those for the weakly adhesive nanoparticles in the same figures. If we take a closer look at the magnitudes of both forces of the small nanoparticles in (a), the difference is found to be 20% or less. This quantitative difference may stem from the subtlety in identifying when the contact begins at the nanoscale [37,38], as described in appendix B. On the other hand, the large nanoparticles in (b) show good agreement as their large radius tends to diminish the effect of points of contact. 

#### (ii) Contact model for weakly adhesive nanoparticles

The nonlinear and partly negative impact forces of the weakly adhesive nanoparticles suggest that there may be a contact force model that could be inferred on the basis of continuum contact

266 models. We attempt to determine a suitable continuum contact force for our weakly adhesive267 nanoparticles if it exists.

The JKR model is one of the widely used adhesive contact models, in which surface adhesion 268 269 within the mutual contact surface of two elastic objects is taken into account [39]. This model 270 is valid for large compliant solids that allow a large elastic deformation due to surface force. 271 On the contrary, small stiff solids in contact with each other that experience a small elastic 272 deformation can be modelled by the Derjaguin–Muller–Toporov (DMT) theory, another adhesive 273 continuum contact model that considers surface force outside the contact surface [40]. Both 274 models are grounded in a quasi-static elastic contact, i.e. resulting contact forces have no velocity 275 dependence. In general, the DMT contact model is suited for nanoscale mechanical contact often 276 seen in spherical microscope tip-substrate interactions [41], whereas the JKR contact theory is 277 appropriate for contacting large nanoparticles [15].

A dimensionless quantity called the transition parameter, denoted by  $\lambda$ , helps determine the transition between DMT and JKR contact models for given material properties and the size of elastic spheres in contact through their adhesive surfaces [42,43]. The form of this parameter is given by equation (D1) in appendix D. Typically,  $\lambda < 0.1$  for the DMT limit and  $\lambda > 5$  for the JKR limit. An adhesion map created by Johnson & Greenwood [44] conveniently provides an appropriate contact model for the estimated value of the transition parameter.

According to our calculation (described in appendix D), the weakly adhesive nanoparticle with the coefficient  $c_{\xi\eta} = 0.2$  in the LJ potential, from which the surface energy  $\gamma = 0.0380\epsilon/\sigma^2$  is obtained, has the transition parameter  $\lambda \sim 0.04$ . The value falls in the range of the DMT or Hertz contact models in the adhesion map, depending on the compressive force relative to the surface force. It implies that our weakly attractive nanoparticles are stiff and thus undergo a relatively small elastic deformation induced by the surface force.

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The DMT contact force  $F_{\text{DMT}}$  consists of the Hertz contact force  $F_{\text{H}}$ , described in appendix C, and the constant surface force  $F_{\text{s}} = -4\pi \gamma R^*$ :

$$F_{\rm DMT} = F_{\rm H} + F_{\rm s},\tag{3.1}$$

where  $R^* = R/2$  is the reduced radius of the nanoparticles. To verify the applicability of the DMT or the Hertz contact model, we compute contact forces  $F_{DMT}$  and  $F_{H}$  from equation (3.1) and equation (C1), respectively, and compare them with the impact force of the weakly adhesive nanoparticles from our MD simulations.

In figure 2*a*, loading force data for the weakly adhesive nanoparticles at  $v_{imp} = 52 \text{ m s}^{-1}$  are 301 depicted by dark grey dots. The DMT force  $F_{\text{DMT}}$  and Hertz force  $F_{\text{H}}$  non-dimensionalized by 302 303  $2\pi\gamma R^*$  are shown in the same plot as a dotted line and a dash-dotted line, respectively. For  $F_{\rm H}$ , 304 reduced Young's modulus  $E^*$  (see appendix C for the definition of  $E^*$ ) is set to  $E^* = 50.6\sigma/\epsilon$ 305 determined by fitting to the impact force data. It is difficult to distinguish the DMT and Hertz 306 forces plotted in the figure. The substantially equal forces are obtained as a result of the weak surface force  $F_s$  compared with the compressional force for the impact velocity range considered. 307 308 The dimensionless surface force  $F_{\rm s} := F_{\rm s}/(2\pi\gamma R^*) = -2$ , whereas the impact forces,  $F_{\rm N}$ , at the 309 maximum overlap from the simulations are of the order of  $10^2$ . The gap between the magnitudes 310 of the forces is large enough to neglect the surface adhesive force. Thus, the Hertz contact 311 theory is a legitimate contact model to apply to elastic spheres having such a low-surface 312 energy.

The loading force points for the small nanoparticles in figure 2*a* are scattered widely. The scatter is caused by the surface roughness, that is, large deviations in the points of contact from their mean radius *R*. Aside from the scatter, the impact forces are well described by the Hertz contact force. This feature is also observed for the large nanoparticles in figure 2*b*. Unlike the small nanoparticles, the force data shows the smaller scatter, due to their relatively spherical shape, and the points appear to converge to the Hertz contact force.



**Figure 2.** Impact loads for weakly adhesive small and large crystalline nanoparticles are shown in (*a*) and (*b*), respectively. The impact velocity of the nanoparticles is  $v_{imp} = 52 \text{ m s}^{-1}$ . Only randomly selected data points are shown for visual clarity. Hertz and DMT forces for corresponding elastic spheres of the same radii *R* in quasi-static contact, respectively, computed by equations (C 1) and (3.1) are also plotted. (*a*) Small nanoparticles of R = 2.7 nm, (*b*) large nanoparticles of R = 7.4 nm. (Online version in colour.)

#### (iii) Strongly adhesive nanoparticles

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We consider another limiting case, namely small nanoparticles with strong surface force, and scrutinize the influence of the rugged surfaces of small nanoparticles on the impact force and associated contact model. To this end,  $c_{\xi\eta} = 1$  is set in equation (2.1) for the internanoparticle interaction to increase the surface energy of the nanoparticles. The strong adhesion represents the interaction between bare crystals [24].

This internanoparticle interaction leads to a surface energy of  $\gamma = 1.014\epsilon/\sigma^2$  determined from our separate simulation described in appendix D. In fact, this surface energy is much higher than the surface energy  $\gamma = 0.0380\epsilon/\sigma^2$  for the weak adhesion case ( $c_{\xi\eta} = 0.2$ ). The surface energy for the strongly adhesive nanoparticles yields the transition parameter  $\lambda \sim 0.35$ , and the value is found to be in the zone bounded by DMT and JKR zones. Therefore, we compare the impact forces with the DMT force given by equation (3.1) and the JKR force given by equation (3.2).

$$F_{JKR} = \frac{4E^*a^3}{3R^*} - 2\sqrt{4\pi E^* \gamma a^3} \\ \delta_{JKR} = \frac{a^2}{R^*} - \sqrt{\frac{4\pi a\gamma}{E^*}}.$$
(3.2)

The impact forces for the strongly adhesive nanoparticles at  $v_{imp} = 52 \text{ m s}^{-1}$  in the loading 359 phase are shown as grey dots in figure 3. The Hertz, DMT and JKR forces computed with the 360 361 higher surface energy  $\gamma = 1.014\epsilon/\sigma^2$  and the reduced Young's modulus  $E^* = 50.6\epsilon/\sigma$  determined 362 in the previous section are also drawn in the same plot as dashed-dotted, dotted and dashed lines, 363 respectively. They are offset by  $\delta = 0.043$  towards the positive overlap direction (figure 2). The offset value is the exact distance between the potential minima for  $c_{\xi_n} = 0.2$  and 1 in equation (2.1) 364 365 and is introduced to rectify the points of contact deviated because of the different positions of the 366 minima.

Evidently, the Hertz contact theory is no longer valid in this regime. The impact force points spread out, but their average force displayed by a solid line has attractive force comparable with its maximum force, and thus adhesion cannot be neglected in the colliding nanoparticles. The average impact force is higher than the DMT force, and rather close to the JKR force. The DMT contact model overestimates its surface force  $F_s$  in equation (3.1) and ends up in the contact force



**Figure 3.** Loading forces for strongly adhesive crystalline nanoparticles ( $c_{\xi\eta} = 1$ ) of radii R = 2.7 nm at impact velocity  $v_{imp} = 52 \text{ m s}^{-1}$ . Only randomly selected data points are shown for visual clarity. Hertz, DMT and JKR forces for corresponding elastic spheres of the same radii R in quasi-static contact, respectively, computed by equations (C 1), (3.1) and (3.2) are also plotted. (Online version in colour.)



**Figure 4.** Impact forces for nanoparticles of radius R = 2.7 nm that experience facet contact. (*a*) Weakly adhesive nanoparticles and (*b*) repulsive nanoparticles. In (*a*) dotted straight line illustrate the linearly increasing impact forces. (Online version in colour.)

 $F_{\text{DMT}}$  lower than the average impact force of the strongly adhesive nanoparticles. By contrast, the JKR force successfully predicts the average impact force except for high compression at  $\tilde{\delta} > 0.2$ .

# (b) Impact on facets

The nanoparticles undergoing the crystal facet contact displayed in figure 4 have a large contact
surface area and this contact makes a marked distinction in force from the crystal edge contact.
The impact on the facets completely alter the dynamic response of the colliding nanoparticles.
Consequently, the impact force between the nanoparticles is not expressed by the Hertz contact
force in equation (C 1) as we will see below.

421 The symbols in figure 4*a* present loading and unloading forces for the weakly adhesive facet 422 contact. The attractive forces for the facet contact are stronger than those for the edge contact 423 because of higher work of adhesion arising from the larger interacting surface area. Colliding 424 with the large facets leads to the loading and unloading forces notably higher than those for the



**Figure 5.** Average impact forces for weakly adhesive amorphous nanoparticles of radius *R*. The dashed-dotted lines depicted are the Hertz contact forces with different Young's moduli. (*a*) R = 2.8 nm, (*b*) R = 6.2 nm. (Online version in colour.)

edge contact displayed in figure 1. The facet contacts show linearly increasing forces with respect
to overlap if the nanoparticles are compressed sufficiently. We confirm that the contact surface
areas in the sufficiently compressed region remain unchanged during elastic collision, contrasted
with the evolving contact surface areas that occur in the Hertz and relevant adhesive contact
models. The unchanging contact surface areas result in the linear response.

446 Additionally, simulations for purely repulsive nanoparticles with the facet contact are carried 447 out in order to compare them with the weakly adhesive nanoparticles. The impact forces for the 448 repulsive contact are plotted in figure 4*b*. All the forces exhibit a distinctive behaviour in the 449 loading phase: a spike at  $\delta \sim 0.115$  followed by a slow velocity-dependent increase in the forces. 450 The intricate force profile does not admit a simple expression in terms of overlap unlike the forces 451 in figure 4*a* or the Hertz force.

In the edge contact cases discussed earlier, adhesive and repulsive nanoparticles have a similar dynamic response, and hence we have suggested that the force of the repulsive nanoparticles can be substituted for that of the weakly adhesive nanoparticles without loss of generality of the obtained nonlinearity. However, the exclusion of surface force for the facet contact results in large deviations from the adhesive contact. Thus, dynamical phenomena of the adhesive nanoparticles involving the facet contact cannot be inferred from the repulsive nanoparticles as opposed to the aforementioned edge contacts.

# (c) Impact on amorphous surfaces

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The exteriors of the amorphous nanoparticles in figure 5 look more spherical than those of the crystalline nanoparticles in figure 1. Although the disordered arrangement of the surface atoms cause the small roughness, the arrays of atomic steps and associated sharp edges seen in the crystalline nanoparticles are clearly absent. The facet-free nanoparticle having a weak surface force is, therefore, expected to recover the Hertz or derivatives of the Hertz Laws as we have demonstrated in the edge contacts.

Figure 5a,b, respectively, plot the impact force-overlap curves for small and large nanoparticles 468 469 having amorphous structures with a low-surface force originating from the coefficient  $c_{\xi_n} = 0.2$  set 470 in equation (2.1). The forces were averaged over 100 simulations with different initial conditions. 471 The impact forces of the incoming nanoparticles for the given velocities confirm the validity of 472 the Hertz contact force if the reduced Young's modulus for small and large nanoparticles is set 473 to  $E^* = 37.9$  and  $41.1\epsilon/\sigma$ , respectively. The results here are analogous to the edge contact cases 474 presented earlier. The Hertz contact theory is thus a pertinent theory to nanosale contact problems for the weak surface interaction. 475

For the recoiling nanoparticles, the impact forces show an interesting dissimilarity from those of the edge contact. The unloading forces of the large nanoparticles depicted in figure 5*b* by

(b) flattened surface after collision



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**Figure 6.** (a) Radius change  $\Delta R$  for (1) large crystalline nanoparticles (NPs) with edge contact (R = 7.4 nm), (2) large amorphous nanoparticles (R = 6.2 nm) and (3) small amorphous nanoparticles (R = 2.8 nm) before and after collision. (b) Cross sections of the large amorphous nanoparticles after collision. The nanoparticles collide at impact velocity 25 m s<sup>-1</sup>. The red dashed arcs are displayed for a quide to plastic deformation of the surface of the right nanoparticle. Yielding for the Q4 large NP with the facet contact occurs at impact velocity  $v_{imp} > 52 \text{ m s}^{-1}$  [18]. (Online version in colour.)

499 dashed lines drop back to zero at varying positive overlaps distant from  $\delta = 0$ . This obviously means that the nanoparticles do not recover their undeformed shape prior to the collision, and 500 501 that the impact probably induces plastic deformations.

502 Comparing the radii before and after collision, we quantify the plastic deformations observed. 503 Let *R* be the radius before collision and R' be the radius after collision. We take a normalized 504 difference  $\Delta R := (R - R')/R$  and plot it in figure 6a as a function of the impact velocity. For 505 comparison purposes, radius changes,  $\Delta R$ , for the small amorphous nanoparticles and the 506 crystalline nanoparticles with the edge contact are also displayed in the same figure.

507 The large amorphous nanoparticles show the increasing plastic deformation from 1% to 4% in  $\Delta R$  as the impact velocity is increased up to  $32 \,\mathrm{m \, s^{-1}}$ . On the other hand, the radius change 508 509 of the large crystalline nanoparticles with the edge contact stays around 0.2–0.3% in the velocity range between  $v_{imp} = 20-41 \text{ m s}^{-1}$  where their structural integrity is preserved. The values for the 510 edge contact are only 10% of those of the amorphous nanoparticles. For the small amorphous 511 512 nanoparticles large radius changes  $\Delta R > 1\%$  are also found. The large radius changes observed 513 imply that there are visible plastic deformations. Indeed, the amorphous nanoparticles before and 514 after collision displayed in figure 6b reveal a locally flattened surface on the right nanoparticle, 515 accompanied by the rearrangement of atoms triggered by the impact.

516 This type of plastic deformation is not observed in the crystalline nanoparticles at the same 517 velocity. At the transition between the elastic and plastic deformations, crystalline nanoparticles 518 begin to crack and dislocations generated on the contact area propagate through the nanoparticles 519 [18,27,45,46]. On the other hand, the underlying mechanism of plastic deformation in amorphous 520 solids, such as metallic glasses, is generally shear band formation instead of dislocation. The shear 521 band is a narrow region in which a collective rearrangement of atoms occurs and large shear 522 strains are concentrated. The contribution from the rearrangement in amorphous solids to the local strain can be probed by the nonaffine square displacement  $D^2$  of atoms introduced by Falk 523 524 & Langer [47]. A shear band would be visualized as a thin layer of a region of high nonaffine 525 square displacements if it exists.

526 We show the nonaffine square displacement fields for representative large amorphous 527 nanoparticles before and after collision in figure 7. The displacement fields are computed and 528 visualized by OVITO [48]. It turns out that surface atoms involved in contact have high nonaffine 529 square displacements and the displacements propagate underneath the contact surfaces. The 530 unevenly distributed high displacements in the interiors of the nanoparticles do not show



**Figure 7.** Nonaffine square displacement  $D^2$  of each atom on a cross section of the large amorphous nanoparticles is presented by colour, computed with a cut-off 1.5 $\sigma$  for identifying neighbour atoms. Their impact velocity is  $v_{imp} = 31 \text{ m s}^{-1}$ , which is the highest velocity considered. (Online version in colour.)

evidence of shear bands but might be potential initiation sites of shear bands if the nanoparticles are further compressed [49]. Plastic deformations in the amorphous nanoparticles are relatively localized on and in the vicinity of the contact surfaces while the rest remains intact. Accordingly, the localized plastic deformations and average impact forces having hystereses confirm that even at a low impact velocity the amorphous nanoparticles are effectively elastic but much more dissipative than the corresponding crystalline nanoparticles with the edge contact.

#### (d) Contact surface area

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561 562 The loading forces of the weakly adhesive nanoparticles have successfully been fitted to the Hertz contact force, and therefore, the Hertz contact model is partially corroborated in nanoscale contact dynamics under the conditions we have imposed. The results suggest that other relevant quantities in continuum contact mechanics would also agree with our nanoparticle findings. From the nonlinearity found in the impact forces for edge and amorphous surface contacts, an expanding contact area in response to the impact force is expected to coincide with the Hertz contact area. We, therefore, test the validity of the contact model by comparing the contact radius *a*, which gives contact area  $\pi a^2$ , formed between colliding weakly adhesive nanoparticles and that of the Hertz model described by equation (C 2).

We define contact area A as the product of the number  $N_{\rm a}$  of contacting atoms and the projected 563 area  $A_a$  of an atom suggested by Mo *et al.* [50]. It follows that the contact radius is  $a := \sqrt{N_a A_a / \pi}$ . 564 565 A conventional definition for a contact radius based on the gyration radius [38] has often been used in the literature for contacting nanoparticles. However, as contact radii we computed from 566 the former definition were found to be closer to the contact radius the Hertz contact model 567 568 predicts, contact radii hereafter are computed by the method provided by Mo et al. From our simulations, the projected areas A<sub>a</sub> for crystalline and amorphous nanoparticles are, respectively, 569 determined as  $0.9434\sigma^2$  and  $0.9297\sigma^2$ , computed with a method using the radius distribution 570 function described in [51]. 571

572 Non-dimensionalized contact radii  $\tilde{a} := a/R$  for fcc crystal and amorphous nanoparticles are 573 displayed in figure 8*a*,*b* and *c*,*d*, respectively. Moreover, the dotted lines represent the prediction 574 from the Hertz contact model. Although the contact radii data and the Hertz contact radius in 575 each plot have a strong correlation, Hertz's contact radius underestimates the simulation data. 576 Comparing the simulation and theoretical results, we find that the small nanoparticles in (*a*) and 577 (*c*) have 10–30% disparities, whereas the large nanoparticles in (*b*) and (*c*) have 5% or less.

The departures of the contact radii from the Hertz contact model observed here are inconsistent with the excellent agreement between the impact forces and the Hertz contact model. This discrepancy indicates that the continuum models are not versatile enough to consistently predict every nanoscale mechanical property of such small nanoparticles. Knowing the small but finite deviation of the contact radius for the large nanoparticles, we may be able to apply the continuum mechanics to large nanoparticles.



**Figure 8.** (a-d) Variation of dimensionless contact radius  $\tilde{a}$  with dimensionless loading force  $\tilde{F}_N$  for weakly adhesive crystalline and amorphous nanoparticles at impact velocities  $v_{imp} = 52 \text{ m s}^{-1}$  (red dots) and  $32 \text{ m s}^{-1}$  (blue dots), respectively. Only **Q4** randomly selected points are shown in the plots in order for visual clarity. Contact radius from the Hertz contact theory is plotted by a dotted line in each plot. (Online version in colour.)

# 4. Discussion and conclusion

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We have presented the mechanical interactions and associated deformations of two
 approximately spherical nanoparticles that undergo a head-on collision obtained by means of
 non-equilibrium MD simulation. We have compared our numerical results with repulsive and
 adhesive continuum contact models.

To study the effects of atomic scale surface roughness and structure that are present 613 in nanoparticles, monocrystalline and amorphous nanoparticles were prepared. Crystalline 614 615 nanoparticles possess crystal facets, steps and sharp edges on their surfaces, while amorphous nanoparticles have comparatively smooth surfaces, although some atomic roughness stemming 616 from the disordered structure still remains. We considered three different contact regimes: 617 618 edge, facet and amorphous surface contacts. Furthermore, the surface energy of contacting 619 nanoparticles was varied to investigate what continuum contact models can apply to these 620 nanoparticles.

In our simulation results, the impact force data in the loading phase for the weakly adhesive
 nanoparticles with the edge contact show nonlinear interactions. Furthermore, the forces are
 described by the Hertz contact force in the given velocity range as the surface force is negligibly
 small compared with the compressional force exerted in response to the impact.

We found that there is a transition from the Hertz contact force to the JKR contact force when the surface energy of nanoparticles experiencing the edge contact is increased. The strongly adhesive nanoparticles have impact forces that are in good agreement with the JKR contact force.

The mutual contact surface area for the weakly adhesive edge contacts expands qualitatively in the same manner of the Hertz contact model, which is essential to the nonlinearity in the impact forces mentioned above. However, in the edge contact case, the Hertz contact model underestimates the contact radius data by 5–30%, depending on the sizes of the nanoparticles. The discrepancy between the force and contact radius indicates that the continuum contact theory does not consistently predict the contact force and radius of colliding small nanoparticles at a time.

635 Contrasted with the edge contact, the impact on the facets causes dynamic properties to 636 considerably deviate from predictions of the Hertz contact theory. This facet contact yields a

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Table 2. Contact model for average impact forces obtained for our nanoparticles.

|  | amorphous    | crystalline nanoparticle | crystalline nanoparticle |  |
|--|--------------|--------------------------|--------------------------|--|
|  | nanoparticle | edge contact             | facet contact            |  |
| weak surface energy ( $\epsilon_{\xi\eta}=$ 0.2) | Hertz        | Hertz/DMT                | linear                   |  |
| strong surface energy ( $c_{\xi\eta} = 1$ )      | —            | JKR                      | —                        |  |

linearly increasing force with increasing overlap because the mutual contact surface area for that contact does not expand at all as long as they elastically collide.

For a system in which orientation of the nanoparticles cannot be controlled, the possibility of precise facet contact is not high. Overall collisional behaviour of the nanoparticles is thought to be dominated by edge contact; hence, Hertz contact theory is valid in this regard. However, a crystallographic orientation-controlled system [52–54] may have to consider the non-Hertz interactions we have demonstrated if the nanoparticles are compelled to impact on facets together.

Additionally, collisions of weakly adhesive amorphous nanoparticles, which have a rather
 spherical shape, were simulated to examine the influence of facet-free surface structure. Their
 loading forces are also described by the Hertz contact force. In spite of the fact that the impacts
 induced small permanent deformation on the mutual contact surfaces for the given velocities, the
 contact radius data of the amorphous nanoparticles are closer to the Hertz contact radius than
 the edge contacts.

The nonlinear contact forces shown in our simulations consistent with the Hertz contact model suggest that a one-dimensional chain of nanograins may allow us to observe propagating nondispersive compressional waves, as confirmed in particulate media [10,11]. The nonlinearity found in our nanoparticles would open up possibilities of potential applications at the nanoscale that utilize the wave propagations for impact transmission [55] and impact mitigation [56–58].

The impact forces of purely repulsive nanoparticles achieved by the WCA potential and the weakly adhesive nanoparticles agree only if the edge contact occurs. For the facet contact, the exclusion of the adhesion between nanoparticles dramatically changes the force, and large deviations in forces from the weakly adhesive contacts were found. The use of the repulsive nanoparticles may result in some unrealistic dynamical phenomena caused by the inconsistent force if the facet contact occurs.

Finally, we summarize the contact models in table 2 for our crystalline and amorphous nanoparticles, based on their average impact forces in the loading phase.

672 Data accessibility. This article has no additional data.

Authors' contributions. Y.T. participated in the design of the study, implemented most of simulations, analysed
the simulation data and drafted the manuscript. M.E.B. ran simulations, analysed the simulation data and
corrected the manuscript. S.S. designed the study, carried out the data analysis, helped draft the manuscript
and reviewed the manuscript. All the authors gave their final approval for publication.

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# <sup>681</sup> Appendix A. Calculation of impact force

683 An impact force  $\mathbf{F}_{\xi\eta}$  acting on the mutual contact surfaces formed between two nanoparticles 684  $\xi$  and  $\eta$  in contact is computed by summing the individual interatomic forces  $\mathbf{f}_{ij} = -\nabla V(\mathbf{r}_{ij})$  for 685 a pair of atoms *i* and *j* that are positioned in separate nanoparticles  $\xi$  and  $\eta$ , respectively. The 686 expression for the force  $\mathbf{F}_{\xi\eta}$  is given by 687

$$\mathbf{F}_{\xi\eta} = \sum_{i\in\xi} \sum_{j\in\eta} \mathbf{f}_{ij}.\tag{A1}$$

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690 Depending on a choice from the potentials considered and the separation between the 691 nanoparticles, the force  $f_{ii}$  determined leads to compressive or tensile loads  $F_{\xi\eta}$  that cause 692 deformation of the nanoparticles during a head-on collision.

693 The normal component  $F_N$  of the impact force  $\mathbf{F}_{\xi\eta}$  is obtained in such a way that  $F_N = \mathbf{F}_{\xi\eta}$ . 694  $d_{\xi\eta}/|d_{\xi\eta}|$ , where  $d_{\xi\eta}$  is the instantaneous centre-of-mass distance of the colliding nanoparticles  $\xi$ 695 and  $\eta$  in a direction parallel to a line segment between the centres of the colliding nanoparticles. 696 Although the direction of  $\mathbf{d}_{\xi\eta}$  is initially aligned with the *z*-axis, thermal vibrations, slip and 697 rotation that break the reflectional symmetry of the system frequently result in a small deflection 698 of the contacting nanoparticles. The direction of  $\mathbf{d}_{\xi\eta}$  during and after the collision does not 699 necessarily match the *z*-axis, accordingly.

Ensemble averaged normal force  $(F_N(\delta))$  at an overlap  $\delta$  is computed from a set of normal forces  $\{F_N^k\}$  in an interval  $[\delta, \delta + \Delta \delta)$  by

$$\langle F_{\rm N} \rangle = \frac{1}{K} \sum_{k=1}^{K} F_{\rm N}^k. \tag{A 2}$$

The *k* and *K* denote the *k*th initial condition and the number of simulations carried out for a given impact velocity, respectively. We introduce a dimensionless force  $\langle F_N \rangle := \langle F_N \rangle / 2\pi \gamma R^*$ , and it is used to show the nanoparticle impact force. The quantities  $R^*$  and  $\gamma$ , respectively, stand for reduced radius and surface energy of nanoparticles, whose definitions are given in appendices C and D.

# Appendix B. Point of contact

Owing to the surface roughness of the nanoparticles considered, they are far from perfect spheres whose geometries are characterized only by their radius. To compare with continuum contact models for contacting elastic spheres, the radii of the nanoparticles must be obtained. We provide a method to compute the radius R of a nanoparticle averaged over N simulation runs as follows.

When two identical adhesive nanoparticles approach one another, atoms on their surfaces initially feel attractive forces. Further approach switches the forces from attraction to repulsion. We define the switching point as the onset of *contact* of individual atoms. Upon the very first contact at time  $t_0$ , the radius  $R_k$  for a particular simulation k is defined by  $R_k := |r_k^{cm}(t_0) - r_k^{cm}(t_0)|$  $r_{\eta}^{\rm cm}(t_0)|/2$ , where  $r_{\xi,\eta}^{\rm cm}$  represent the centres of the nanoparticles  $\xi$  and  $\eta$ . It follows that the average radius is described by  $R = (1/K) \sum_{k=1}^{K} R_k$  for K simulations performed with different initial conditions.

With the average radius, an instantaneous overlap at time t is now defined by  $\delta(t) := 2R - 2R$  $|r_{\xi}^{\rm cm}(t) - r_n^{\rm cm}(t)|$ . Note that this definition could result in negative overlap values if atomic ridges formed on the surfaces come into contact.

# Appendix C. Hertz Law

Hertz derived a normal compressive force  $F_{\rm H}$  between two quasi-statically contacting elastic spheres that have smooth surfaces [2,59]. The force is expressed in terms of overlap  $\delta_{\rm H} = (2R - d)$ for two identical spheres of diameter 2R and centre-to-centre intersphere distance d under compression,

$$F_{\rm H} = \kappa_{\rm H} \delta^n_{\rm H'} \tag{C1}$$

where n = 3/2 and  $\kappa_{\rm H} = (4/3)E^*R^{*1/2}$ . The reduced Young's modulus is  $E^* = E/[2(1 - \nu^2)]$  with 736 Young's modulus *E* and Poisson ratio  $\nu$ . The reduced radius is  $R^* = R/2$  for identical spheres 737 738 of radius R. The contact force grows nonlinearly with increasing overlap. The underlying mechanism that yields the nonlinearity is the varying mutual contact surface area between the 739 spheres as a function of compression. The shape of the contact surface in the theory is assumed 740 to be a circle with radius  $a_{\rm H}$ , from which its area is  $\pi a_{\rm H}^2$ . General contact surface shapes and 741 their resultant contact forces including Hertz force are discussed in [60]. The geometrical relation 742

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Figure 9. A simulation model of contacting blocks used to estimate the (100) surface energy  $\gamma$ .

between the displacement and the contact area under compression gives  $a_{\rm H} = \sqrt{R^* \delta_{\rm H}}$ . Hence, the contact area expands in proportion to the square root of the overlap  $\sqrt{\delta_{\rm H}}$ . The relation between the contact radius and force is described by

$$a_{\rm H}^3 = \frac{3R^*}{4E^*}F_{\rm H}.$$
 (C2)

# Appendix D. Surface energy and adhesive contact models

There are a number of adhesive contact models based on the elasticity theory, for example, JKR [39], Maugis-Dugdale [43], DMT [40] and Bradley models [61]. These models may suitably be chosen for specific materials by means of a dimensionless transition parameter  $\lambda$ , introduced by Maugis [43] by modifying the Tabor parameter [42].

$$\lambda = 1.16 \left( \frac{R^* \Delta \gamma}{E^{*2} z_0^3} \right). \tag{D1}$$

In this equation, work of adhesion  $\Delta \gamma = 2\gamma$  is needed to create a new surface, surface force range  $z_0$ ,  $E^*$  reduced Young's modulus, and  $R^*$  reduced radius are used. We compute the transition parameter to identify a suitable adhesive contact model for our weakly and strongly adhesive nanoparticles. To this end, we need the surface energy  $\gamma$  for both nanoparticles.

The surface energy for our nanoparticle is estimated by additional MD simulations for the (100) surface of an fcc crystal. The energies of two identical blocks  $U_1$  and  $U_2$  are independently determined by performing energy minimization. Now, the two blocks are placed such that their (100) surfaces are in the equilibrium position, and this allows them to interact each other via a given potential. The energy of these blocks  $U_{12}$  is now lower due to the presence of the attraction through the (100) surfaces. The energy difference per unit area gives the surface energy  $\gamma$  of the (100) surface of area *A* from the following equation (figure 9).

$$\gamma = \frac{U_1 + U_2 - U_{12}}{(2A)}.$$
 (D2)

The surface energy  $\gamma = 0.038\epsilon/\sigma^2$  in the weak attraction case,  $c_{12} = 0.2$ , is obtained from our simulations. The transition parameter computed by equation (D 1) is  $\lambda = 0.04$  with  $z_0 = 1.468\sigma$ , which is the equilibrium position for the LJ potential in equation (2.1). According to the adhesion map [44], this parameter value suggests that the DMT model or the Hertz model may be a suitable model for the contacting nanoparticles with the low-surface energy (table 3).

Likewise, the transition parameter for the strongly adhesive nanoparticles is computed. The surface interaction between the nanoparticles is governed by the standard LJ potential

Q2

Q3

#### Table 3. Transition parameter.

| attraction strength<br><sub>C12</sub> | surface energy $\gamma~(\epsilon/\sigma^2)$ | transition parameter $\lambda$ |
|---------------------------------------|---|--------------------------------|
| 0.2                                   | 0.038                                       | 0.04                           |
| 1.0                                   | 1.014                                       | 0.35                           |

equation (2.1). The surface energy  $\gamma = 1.014\epsilon/\sigma^2$  obtained by the simulation method stated above yields the transition parameter  $\lambda = 0.35$ , assuming  $z_0 = 1.12\sigma$ . In the adhesion map, this value lies in the intermediate zone between JKR and DMT models [44].

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