Negative normal restitution coefficient for nanocluster collisions

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The oblique impacts of nanoclusters is studied by means of Molecular Dynamics and theoretically. In simulations we explore two models – Lennard-Jones clusters and particles with covalently bonded atoms. In contrast to the case of macroscopic bodies, the standard definition of the normal restitution coefficient yields for this coefficient negative values for oblique collisions of nanoclusters. We explain this effect and propose a proper definition of the restitution coefficient which is always positive. We develop a theory of an oblique impact based on continuum model of particles. A surprisingly good agreement between the macroscopic theory and simulations leads to the conclusion, that macroscopic concepts of elasticity, bulk viscosity and surface tension remain valid for nanoparticles of a few hundreds atoms.

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Introduction. Inelastic collisions, where a part of mechanical energy of colliding bodies transforms into heat, are common in nature and industry. Avalanches, rapid granular flows of sand, powders or cereals may be mentioned as pertinent examples [1, 2]. Moreover, inelastic collisions define basic properties of astrophysical objects, like planetary rings, dust clouds, etc. An important characteristic of such collisions is the so-called normal restitution coefficient $e$. According to a standard definition, it is equal to the ratio of the normal component of the rebound speed, $g'$ (prime states for the post-collision value), and the impact speed, $g$

$$e = \frac{-g' \cdot n}{g \cdot n}. \quad (1)$$

The unit inter-center vector $n = r_{12}/|r_{12}|$ at the collision instant $(r_{12} = r_1 - r_2)$ specifies the impact geometry. Since particles bounce in the direction, opposite to that of the impact, $e$ is positive, $e > 0$, and since the energy is lost in collisions, $e$ is smaller than one, that is, $0 \leq e \leq 1$. This is a common statement in the majority of mechanical textbook, where it is also claimed that $e$ is a material constant. Recent experimental and theoretical studies show, however, that the concept of a restitution coefficient is more complicated: First, it depends on an impact speed [3, 4]; second, it can exceed unity for a special case of oblique collisions with elastoplastic plate [5], where the energy of normal motion can increase at the expense of the energy of tangential motion [6]. Still, it is believed that $e \leq 1$ for a true head-on collision. The concept of a restitution coefficient, as a basic one of the classical mechanics, has been introduced long ago by Newton; it addresses an impact of macroscopic bodies. The increasing interest to nanoparticles, inspired by its industrial significance, raises an important question, to what extent the macroscopic concepts are applicable and whether they acquire new features at a nanoscale.

The collisions of nanoclusters has been studied in detail numerically [7, 10]. It was observed that the surface effects, due to the direct inter-cluster van der Waals interactions, play a crucial role: The majority of collisions of homogeneous clusters, built of the same atoms, lead to a fusion of particles [6]; they do not fuse for high impact speeds, but disintegrate into pieces [7]. This complicates the analysis of restitutive collisions, which may be more easily performed for particles with a reduced adhesion. Among possible examples of such particles are clusters of covalently bonded atoms, especially when their surface is coated by atom of different sort, as for H-passivated Si nanospheres [5]. These particles can rebound from a substrate, keeping their form after an impact unaltered [5]. The bouncing nanoclusters demonstrate a surprising effect – the normal restitution coefficient can exceed unity even for strictly head-on collisions [6].

In this Letter we investigate the oblique impact of nanoclusters with the reduces adhesion by means of Molecul-
ilar Dynamics (MD) and theoretically, using concepts of continuum mechanics. Unexpectedly, we have found that the normal restitution coefficient, as defined by Eq. 1, acquires for large incident angles negative values, \( e < 0 \). We explain this effect by the reorientation of the contact plane during an impact and quantify it. Moreover, we propose a modified definition of \( e \), which preserves its initial physical meaning and yields always positive values. To describe the collision of nanoclusters we develop a continuum theory. Surprisingly, the macroscopic approach quantitatively agrees with MD even at nanoscale.

**MD simulations.** We study two models - a simplified model (A), which mimics interactions of nanoclusters with the reduced adhesion and realistic model (B) for interaction of nanoclusters with covalently bonded atoms - H-passivated Si nanospheres. For the model A, which is less computationally expensive, we adopt the Lennard-Jones (LJ) potential for the covalent Si-Si, Si-H, and H-H bonds. The Si nanospheres, containing 2905 Si atoms arranged in a diamond structure, are fully coated by 852 H atoms. The radius of Si nanosphere is about \( d = 2.4 \text{ nm} \).

We fix the modulus of the relative inter-cluster velocity \( \mathbf{v}_1(0) - \mathbf{v}_2(0) = \mathbf{v}_{12}(0) = \mathbf{V} \) and set it to \( V = 1.0 \sqrt{e/m} \) and \( 1850 \text{ m/s} \) for the model A and B, respectively. We vary the incident angle \( \gamma \) between \( \mathbf{n} \) and \( \mathbf{V} \) (see Fig. 1), so that the normal impact velocity, \( V_n = V \cos \gamma \) is changed. The nanoclusters do not rotate before an impact and have zero angular velocities, \( \omega_1(0) = \omega_2(0) = 0 \). To make an ensemble average, we randomly turn one of the clusters around the axis, passing through its center and perpendicular to the contact plane. Due to rough atomic surfaces of the clusters, this results in varying contact configurations at each impact. Hence, for every incident angle \( \gamma \) we perform averaging over 100 collisions with different contact conditions for model A and over 10 collisions for model B. The clusters’ deformation during an impact is quantified by the normal displacement, \( \xi_n(t) = d - |r_{12}(t)| = d - r_{12}(t) \). We define the beginning of a collision at \( t = 0 \) and the end at \( t = t_c \) through the conditions, \( \xi_n(0) = \xi_n(t_c) = 0 \).

Simulation results for the normal restitution coefficient for the models A and B are shown in Fig. 2 (upper and lower panel respectively). As it is seen from the figure, the restitution coefficient \( e \), defined by Eq. 1, becomes negative for large incident angles \( \gamma \). Such unusual behavior of \( e \) at nanoscales may be understood if we notice that the orientation of the contact plane, characterized by the unit vector \( \mathbf{n}(t) = r_{12}(t)/r_{12}(t) \), significantly alters during the collision, Fig. 1. This is quantified by the angle \( \alpha \) between the initial and final orientations of \( \mathbf{n}(t) \),

\[
\cos \alpha = \mathbf{n}(0) \cdot \mathbf{n}(t_c).
\]

The dependence of \( \alpha \) on the incident angle \( \gamma \) is shown in Fig. 3. If \( \alpha \) is large, the normal restitution coefficient becomes negative, Fig. 2.

**Modified definition of \( e \):** To analyze this effect, consider the relative velocity of particles at their contact,

\[
\mathbf{g} = \mathbf{v}_{12} + \frac{d}{2} [\mathbf{n} \times \omega_{12}] = -\xi_n \mathbf{n} + r_{12} \mathbf{n} + \frac{d}{2} [\mathbf{n} \times \omega_{12}],
\]

where \( \omega_{12} \equiv \omega_1 + \omega_2 \) and we use \( \mathbf{v}_{12} = \mathbf{r}_{12} \) with \( \mathbf{r}_{12} = \mathbf{n}(d - \xi_n) \). In the standard definition of \( e \) and theoretical studies of an oblique impact [13], \( \mathbf{n} \) is taken at the collision instant, that is, its reorientation during the impact is ignored. In experiments, the normal \( \mathbf{n} \) is also determined only once, at the beginning of an impact.
restitution coefficient \( \tilde{e} \cdot n \) can be also seen from Fig. 2 that the magnitude of \( \tilde{e} \) is always positive, Fig. 2. It can be also seen from Fig. 2 that the magnitude of \( \tilde{e} \) for an oblique impact (for large \( \gamma \)) is significantly larger than that for a head-on collision. In what follows we explain the observed behaviors of \( e \) and \( \tilde{e} \) using a simple theoretical model, based on continuum mechanics approach.

Theory of an oblique impact. Consider a non-inertial frame, rotating with the angular velocity \( \Omega \), perpendicular to \( n \), so that \( n = \Omega \times \mathbf{n} \). To compute the normal force acting between two nanoclusters we apply the impact theory for macroscopic viscoelastic adhesive spheres \[\mathbb{1}, \mathbb{3}\]. It contains the JKR force \[\mathbb{16}\], which accounts for elastic interactions via the Herzenman force \( F_B \) and for adhesive interactions via the Boussinesq force \( F_B \),

\[
F_B = \frac{4a^3}{D} - \frac{6\pi \sigma}{D} a^{3/2}.
\]

It also contains the dissipative force \[\mathbb{9}\],

\[
F_D = 4\pi \frac{\alpha^2}{D} \left( \frac{3}{2} \frac{6\pi \sigma}{D} a^{1/2} \right).
\]

Here, \( a \) is the contact radius of the colliding nanoclusters, related to the normal displacement \( \xi_n \) as

\[
\xi_n = \frac{4a^2}{d} - \frac{8\pi \sigma Da}{3},
\]

and \( D = (3/2)(1 - \nu^2)/Y \) is the elastic constant with the Young modulus \( Y \) and the Poisson ratio \( \nu \). From the independent numerical simulations we estimate \( Y = 88.3 \epsilon/\sigma_{LJ}^3 \) and \( \nu = 0.396 \) for model A, and \( Y = 283 \text{ GPa} \) and \( \nu = 0.166 \) for model B \[\mathbb{17}\]. The surface tension \( \sigma \) may be expressed via Hamaker constant \( A_H \) and the equilibrium distance between atoms at the interface \( z_0 \) as \( \sigma \approx A_H/24\pi z_0^2 \). We obtain \( \sigma = 0.0246 \epsilon/\sigma_{LJ}^3 \) and 0.00289 N/m for the models A and B, respectively. The dissipative constant \( \eta \), which accounts for the viscoelasticity of the particles’ material \[\mathbb{3}\] is used here as a fitting parameter. In the present simulations a good agreement is obtained by choosing \( \eta = 0.95 \epsilon/\sigma_{LJ} \sqrt{m/\epsilon} \) and 1.62 fs for models A and B, respectively.

In the non-inertial frame, the inertial force must be also taken into account. Its normal component reads \[\mathbb{18}\],

\[
F_I = 2\mu v_{12} \cdot n(t) - \mu v_{12} |\mathbf{n}(t)|^2,
\]

where \( \mu = N m/2 \) is the reduced mass of the nanoclusters. If we again neglect the angular velocities of particles in the collision (since \( \omega_{1/2}(0) = 0 \), that is, if we assume that the two clusters at a contact move together as a solid dumbbell, we can exploit the conservation of the angular momentum in the form,

\[
\mu v_{12} \Omega = \mu V \sin \gamma d,
\]

where we take into account that \( n \cdot \Omega = 0 \). This yields \( \Omega(t) = V \sin \gamma d/r_{12}^2(t) \) and the inertial force,

\[
F_I = \frac{\mu V^2 d^2}{r_{12}^4} \sin^2 \gamma.
\]
Combining Eqs. (10) – (11) we obtain the equation of motion for $\xi_n$:

$$\mu \left(\frac{d^2}{dt^2} \xi_n + F_H - F_B + F_D + \frac{\mu V^2 d^2}{(d - \xi_n)^3} \sin^2 \gamma \right) = 0,$$

(12)

where $d'/dt$ denotes the time derivative in the non-inertial frame. Solving Eq. (12) for $\xi_n(t)$, we obtain $\delta$ as it follows from Eq. (3). Taking into account that $\dot{\alpha} = \Omega(t_c)$ we obtain from Eq. (4) the relation between the standard and modified restitution coefficients,

$$e = \delta \cos \alpha - \tan \gamma \sin \alpha .$$

(13)

The last equation together with the relation $\alpha = \int_0^t \Omega(t) dt$ may be used to compute the standard coefficient $e$. The theoretical predictions for the coefficients $e$ and $\delta$ are shown on the upper and lower panels of Fig. 2 respectively. The agreement between our theory, which has only one fitting parameter, and MD simulations is rather good. We find that the restitution coefficient of H-passivated Si nanospheres is well reproduced by our macroscopic theory for the incident speed between 20 m/s and 2405 m/s. If, however, the speed exceeds 2500 m/s, the nanospheres melt and fuse upon collisions and the theory fails to describe the impact.

We wish to stress that our theoretical model, developed for nanoclusters, may be relevant for oblique collisions of macroscopic bodies, provided the re-orientation of the contact plane during the impact is not negligible. This may happen for soft cohesive particles with a low Young modulus and large collision time. Relevance of the theory for collisions in wet granular systems is also expected [19].

In conclusion, we perform a detailed study of the oblique impact of nanoclusters by means of Molecular Dynamics and theoretically. In simulations we use two models, a simplified one, based on the Lennard-Jones potential with a cohesive parameter and a realistic model for nanoclusters with covalently bonded atoms. We detect unexpected behavior of the normal restitution coefficient $e$, which becomes negative for large incident angles and explain this effect by the reorientation of the contact plane in the course of collision. We propose a modified definition of the restitution coefficient, $\hat{e}$, which describes only the normal motion of particles, independently of their relative reorientation, and is always positive. A simple relation between $e$ and $\hat{e}$, that may be helpful for experiments is reported. We develop a theoretical model for an oblique impact, based on the continuum mechanics description of colliding particles, and demonstrate that theoretical predictions agree well with simulation results. Hence, we conclude that the macroscopic concepts of elasticity, surface tension and bulk viscosity are well applicable for nano-objects of a few hundreds atoms.

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