Negative Normal Restitution Coefficient Found in Simulation of Nanocluster Collisions

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The oblique impacts of nanoclusters are studied theoretically and by means of molecular dynamics. In simulations we explore two models—Lennard-Jones clusters and particles with covalently bonded atoms. In contrast with 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 a 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 hundred atoms.

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Introduction.—Inelastic collisions, where part of the 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, $\mathbf{g}'$ (prime states for the postcollision value), and the impact speed, $\mathbf{g}$

$$e = -\frac{\mathbf{g}' \cdot \mathbf{n}}{\mathbf{g} \cdot \mathbf{n}}. \tag{1}$$

The unit intercenter vector $\mathbf{n} = \mathbf{r}_{12}/|\mathbf{r}_{12}|$ at the collision instant ($\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$) 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 1, that is, $0 \leq e \leq 1$. This is a common statement in the majority of mechanical textbooks, 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 [3–5] and second, it can exceed unity for a special case of oblique collisions with an elastoplastic plate [6], 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 have been studied in detail numerically [7–10]. It was observed that the surface effects, due to the direct intercluster 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 [7]; 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 atoms of a different sort, such as for H-passivated Si nanospheres [8]. These particles can rebound from a substrate, keeping their form unaltered after an impact [8]. The bouncing nanoclusters demonstrate a surprising effect—the normal restitution coefficient can exceed unity even for strictly head-on collisions [9].

In this Letter we investigate the oblique impact of nanoclusters with the reduced adhesion by means of molecular 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 always yields 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 $\phi(r) = 4\epsilon[(\sigma_{\mathrm{LJ}}/r)^{12} - (\sigma_{\mathrm{LJ}}/r)^{6}]$ for

the interaction between two atoms in the same cluster and the modified LJ potential $\phi_{\rm int}(r) = 4\epsilon[(\sigma_{\rm LJ}/r)^{12} - c(\sigma_{\rm LJ}/r)^6]$ for the interaction between atoms in two different clusters. Here the cohesive parameter $c = 0.2$ controls the adhesive force [9,10] between clusters, while ϵ, $\sigma_{\rm LJ}$, and r are, respectively, the depth of the potential well, the diameter of the repulsive core, and the distance between two atoms. The nanoclusters of $N = 500$ atoms were prepared by the two-step temperature quench to obtain a rigid amorphous particle [11]. The radius of nanocluster $d/2$ was defined as the maximum distance between the center of mass of the nanocluster and the atom on the surface, so we find $d = 10.46\sigma_{\rm LJ}$. For the model B we adopt the Tersoff potential [12] for the covalent Si-Si, Si-H, and H-H bondings. 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 2.4 nm.

We fix the modulus of the relative intercluster velocity $\mathbf{v}_1(0) - \mathbf{v}_2(0) = \mathbf{v}_{12}(0) = \mathbf{V}$ and set it to $V = 1.0\sqrt{\epsilon/m}$ and 1850 m/s for the model A and B, respectively. We vary the incident angle γ 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. Because of rough atomic surfaces of the clusters, this results in varying contact configurations at each impact. Hence, for every incident angle γ 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, $\xi_n(t) = d - |\mathbf{r}_{12}(t)| = d - r_{12}(t)$. 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

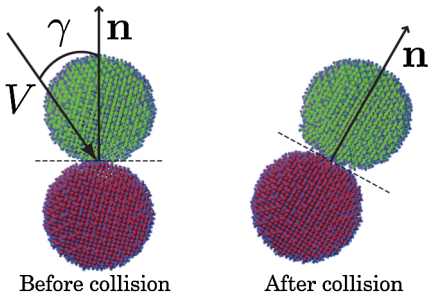

FIG. 1 (color online). Initial (left) and final stage (right) of the nanocluster collision. The initial relative velocity is $\mathbf{v}_{12}(0) = \mathbf{V}$ and the incident angle is γ. The unit normal $\mathbf{n}$ specifies the orientation of the contact plane. For large γ a noticeable reorientation of this plane is observed. Here the collision of H-passivated Si nanospheres (model B) is shown.

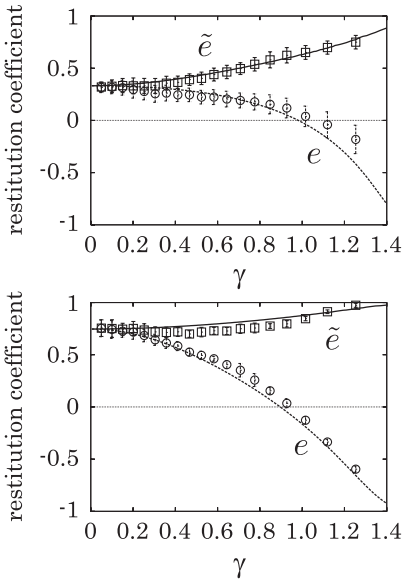

FIG. 2. Dependence on the incident angle γ of the normal restitution coefficients e, and $\tilde{e}$ according to the standard definitions (4) and modified definition (5). Open circles and squares are, respectively, the MD results for e and $\tilde{e}$, while dashed and solid lines correspond to theoretical predictions. The upper panel refers to model A and the lower panel to model B. Note that the coefficient e is always positive.

negative for large incident angles γ. 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 $\mathbf{n}(t) = \mathbf{r}_{12}(t)/r_{12}(t)$, significantly alters during the collision [Fig. 1]. This is quantified by the angle α between the initial and final orientations of $\mathbf{n}(t)$,

$$\cos\alpha = \mathbf{n}(0)\cdot\mathbf{n}(t_c). \tag{2}$$

The dependence of α on the incident angle γ is shown in Fig. 3. If α is large, the normal restitution coefficients becomes negative [Fig. 2].

Modified definition of e.—To analyze this effect, consider the relative velocity of particles at their contact,

$$\mathbf{g} = \mathbf{v}_{12} + \frac{d}{2}[\mathbf{n}\times\omega_{12}] = -\dot{\xi}_n\mathbf{n} + r_{12}\dot{\mathbf{n}} + \frac{d}{2}[\mathbf{n}\times\omega_{12}], \tag{3}$$

where $\omega_{12} \equiv \omega_1 + \omega_2$ and we use $\mathbf{v}_{12} = \dot{\mathbf{r}}_{12}$ 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 [14], $\mathbf{n} = \mathbf{n}(0)$. Neglecting angular velocities [note that $\omega_{1/2}(0) = 0$] we find for the restitution coefficient

$$e = -\frac{\mathbf{g}(t_c)\cdot\mathbf{n}(0)}{\mathbf{g}(0)\cdot\mathbf{n}(0)} = \left|\frac{\dot{\xi}_n(t_c)}{\dot{\xi}_n(0)}\right|\cos\alpha - \frac{d\sin\alpha\dot{\alpha}}{V\cos\gamma}, \tag{4}$$

where we take into account that $\mathbf{g}(0)\cdot\mathbf{n}(0) = -\dot{\xi}_n(0) = -V\cos\gamma < 0$, $r_{12}(t_c) = d$, and $\dot{\xi}_n(t_c) < 0$. For head-on collisions, when $\gamma \to 0$ and $\alpha \to 0$ [see Fig. 3] the second term in the right-hand side (r.h.s.) of Eq. (4) is negligible and e is positive. For oblique impacts, γ and α are large and the second term prevails, yielding a negative e.

Hence, the negative restitution coefficient is a consequence of a significant reorientation of a contact plane during a collision. For hard particles with a small collision duration the reorientation of $\mathbf{n}$ is small and may be neglected [13]; this usually holds true for macroscopic bodies. Nanoclusters, however, are very soft particles with small Young's modulus [15]. The duration of their impact t_c is relatively large and the reorientation of the contact plane is significant.

As it follows from the Eq. (4), the standard definition of e characterizes not only the normal motion along $\mathbf{n}(t)$ [the first term on the r.h.s. of Eq. (4)], but also the change of the normal $\mathbf{n}(t)$ [the second term on the r.h.s. of Eq. (4)]. Therefore, it is worth defining the restitution coefficient, which describes pure normal motion. The respective modification of the standard definition reads

$$\tilde{e} = -\frac{\mathbf{g}(t_c)\cdot\mathbf{n}(t_c)}{\mathbf{g}(0)\cdot\mathbf{n}(0)} = \left|\frac{\dot{\xi}_n(t_c)}{\dot{\xi}_n(0)}\right|. \tag{5}$$

Here we use Eq. (3) for $t = t_c$ and take into account that $\dot{\mathbf{n}}\cdot\mathbf{n} = 0$ for a unit vector $\mathbf{n}$. Note, that the modified restitution coefficient $\tilde{e}$ 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 γ) 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 noninertial frame, rotating with the angular velocity $\mathbf{\Omega}$, perpendicular $\mathbf{n}$, so that $\dot{\mathbf{n}} = \mathbf{\Omega}\times\mathbf{n}$. To compute the normal force acting between two nanoclusters we apply the impact theory for

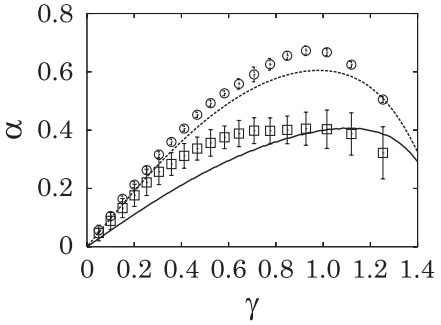

FIG. 3. Dependence of the angular displacement $\alpha = \arccos[\mathbf{n}(0)\cdot\mathbf{n}(t_c)]$ of the unit normal $\mathbf{n}$, Eq. (2), on the incident angle γ. Open squares and circles are the MD results for the model A and B, respectively. Solid and broken lines are the corresponding theoretical predictions, $\alpha = \int_0^{t_c}\Omega(t)dt$ (see text for detail).

macroscopic viscoelastic adhesive spheres [4,5]. It contains the JKR force [16], which accounts for elastic interactions via the Herzian force F_H and for adhesive interactions via the Boussinesq force F_B,

$$F_H - F_B = \frac{4a^3}{Dd} - \sqrt{\frac{6\pi\sigma}{D}}a^{3/2}. \tag{6}$$

It also contains the dissipative force [5],

$$F_D = \dot{a}\eta\left(\frac{12a^2}{Dd} - \frac{3}{2}\sqrt{\frac{6\pi\sigma}{D}}a^{1/2}\right). \tag{7}$$

Here, a is the contact radius of the colliding nanoclusters, related to the normal displacement ξ_n as

$$\xi_n = \frac{4a^2}{d} - \sqrt{\frac{8\pi\sigma Da}{3}}, \tag{8}$$

and $D = (3/2)(1-\nu^2)/Y$ is the elastic constant with the Young modulus Y and the Poisson ratio ν. From the independent numerical simulations we estimate $Y = 88.3\epsilon/\sigma_{\mathrm{LJ}}^3$ and $\nu = 0.396$ for model A and $Y = 283$ GPa and $\nu = 0.166$ for model B [15]. The surface tension σ may be expressed via Hamaker constant A_H and the equilibrium distance between atoms at the interface z_0 as $\sigma \simeq A_H/24\pi z_0^2$. We obtain $\sigma = 0.0246\epsilon/\sigma_{\mathrm{LJ}}^2$ and 0.002 89 N/m for the models A and B, respectively. The dissipative constant η, which accounts for the viscoelasticity of the particles' material [4] is used here as a fitting parameter. In the present simulations a good agreement is obtained by choosing $\eta = 0.65\sigma_{\mathrm{LJ}}\sqrt{m/\epsilon}$ and 1.62 fs for models A and B, respectively.

In the noninertial frame, the inertial force must also be taken into account. Its normal component reads [17]

$$F_I = 2\mu\mathbf{v}_{12}\cdot\dot{\mathbf{n}}(t) - \mu x_{12}|\dot{\mathbf{n}}(t)|^2, \tag{9}$$

where $\mu = Nm/2$ is the reduced mass of the nanoclusters. If we assume that the two clusters at a contact move together, we can exploit the conservation of the angular momentum in the form

$$\mu r_{12}^2\Omega = \mu V\sin\gamma d, \tag{10}$$

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

$$F_I = \frac{\mu V^2 d^2}{r_{12}^3}\sin^2\gamma. \tag{11}$$

Combining Eqs. (6)–(11) we obtain the equation of motion for ξ_n,

$$\mu\frac{d'^2}{dt^2}\xi_n + F_H - F_B + F_D + \frac{\mu V^2 d^2}{(d-\xi_n)^3}\sin^2\gamma = 0, \tag{12}$$

where d'/dt denotes the time derivative in the noninertial frame. Solving Eq. (12) for $\xi_n(t)$, we obtain $\tilde{e}$ as it follows from Eq. (5). Taking into account that $\dot{\alpha} = \Omega(t_c)$ we obtain

from Eq. (4) the relation between the standard and modified restitution coefficients,

$$e = \tilde{e}\cos\alpha - \tan\gamma\sin\alpha. \quad (13)$$

The last equation together with the relation $\alpha = \int_0^{t_c} \Omega(t)dt$ may be used to compute the standard coefficient e. The theoretical predictions for the coefficients e and $\tilde{e}$ 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 reorientation 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 [18]. Relevance of the theory for collisions in wet granular systems is also expected [19].

Conclusion.—We perform a detailed study of the oblique impact of nanoclusters theoretically and by means of molecular dynamics. In simulations we use two models: a simplified one based on the LJ 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, $\tilde{e}$, which is always positive and describes only the normal motion of particles independently of their relative reorientation. A simple relation between e and $\tilde{e}$ 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 hundred atoms.

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