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Pecularities of nanoparticle reflection from a barrier

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This work is devoted to molecular dynamics modelling of collision of nanoparticle having a small number of degrees of freedom with a structureless plain. It is established that velocity of nanoparticle after collision can exceed the initial one. The main system parameters, which determine nanoparticle behavior, are established.

Работа посвящена моделированию столкновения с плоскостью наночастицы с небольшим числом внутренних степеней свободы методом молекулярной динамики. Установлено, что при отражении наночастицы от плоскости, её конечная скорость может превышать начальную. Установлено соотношение параметров системы, которое определяет поведение наночастицы.

Особливості відбиття наночастинки від бар'єра. *М.А.Ратнер, А.В.Тур, В.В.Яновський.*
Робота присвячена моделюванню методом молекулярної динаміки зіткнення наночастинки із невеликою кількістю ступенів свободи з площиною. Встановлено, що відбиття від безструктурної площини може призвести до збільшення швидкості наночастинки понад початкову. Встановлено співвідношення параметрів системи, яке визначає таку поведінку наночастинки.

1. Introduction

Interest to the properties of particles with a small number of degrees of freedom has been growing recently due to intensive researches of nanoobjects (see e.g. [1]). It is clear, that, with a diminishing particle size, the number of degrees of freedom decreases. One of the general properties of physical bodies concerns regularities of their collision with a structureless plain or with each other. Thus, it is important to investigate the influence of small number of internal degrees of freedom on the pattern of such collisions. A simple model for the investigation of collision with a plane for a nanoparticle with a small number of degrees of freedom was proposed in the work [2]. Such composite particle consists of a shell with several particles inside it [2]. The shell as well as the internal particles can move along a chosen direction only colliding with each other absolutely elastically. In other words, the internal degrees of freedom interact with each other and with a shell absolutelly elastically and energy dissipation is not taken into account. Despite of the simplicity of proposed model, the obtained results are quite of general character and,

in a certain sence, relate also to a scattering of more complex particles with a small number of degrees of freedom. It is interesting to emphasize, that such composite particles have been realized also experimentally. The example of such structurally composite particles are molecules of rotaxanes [3] and nanotube peapods [4, 5].

For macroscopic bodies with a very large number of internal degrees of freedom, the collision with a structureless plane is described by the relation $\nu_2 = -e\nu_1$. Here ν_1 is particle velocity prior to its collision with a plane, ν_2 is its velocity after the collision, e is the recovery coefficient, that is determined by the properties of particle material and does not depend on the particle velocity. For real macroscopic particles, the relation $0 < e < 1$ is always valid. In other words, particle velocity afer the collision with an immobile plane can only diminish. The existence of another possibility was discovering in the work [2] due to using a simple model. It turned out, that for the collision with a plane of a composite particle with a small number of degrees of freedom, the unusual regimes can be observed.

In the given work, the collision with a plane of more realistic particles with a small number of degrees of freedom is investigated. Using the molecular dynamics method, a particle, consisting from a relatively small number of atoms was modeled. Molecular dynamics methods have now found wide range of applications in physics and chemistry of solid matter [6] and for modeling clusters consisting of several to several thousands atoms (see e.g. [7, 8]). In the given work, atoms, constituing the particle, interact via Lennard-Jones potential. The collision of such particle with a structureless plane was modeled. The collision velocities of nanoparticle are restricted to nondestructing ones. As a result, new regularities of collision of such particles with a plane were established. In particular, the generalized collisional law was obtained, where particle properties are determined by two coefficients, one of which corresponds to recovery coefficient while another can be naturally called transformation coefficient. The revealed regularities predict the existence of anomalous mode of nanoparticle scattering from a massive plane. In this mode, the velocity of a reflected particle exceeds that of an incident one. At the same time, conseration laws are obeyed with a high degree of precision.

2. The purpose of the work and formulation of the problem

In the given work, the main regularities are considered of the collision of structurally complicated nanoparticle with a structureless plane. The collision velocities of nanoparticles are restricted to nondestructing ones. Initially, atoms with the mass $m = 39.9$ a.u. in the nanoparticle formed a cubic lattice with interatomic distance $a = 4.816$ Å. In the model, the number of atoms N was chosen equal to 64 and 512. Atoms were interacting according to Lennard-Jones potential with the following parameters, taken for Argon atoms: $\sigma = 3.405$ Å, $\varepsilon = 0.0104$ eV. On the first stage of the calculations, the system is relaxed to the 2 K temperature during 20 ps. Then, the heating of the system is realized using the following procedure. All atoms of the nanoparticle are given random displacements. Then, system is relaxing again during 20 ps. The displacement range was chosen in such a way that system reached a given temperature ($T = 10$ K or 25 K) after the relaxation. The characteristic collision time between nanoparticle atoms is estimated as $\tau = \sigma(m/\varepsilon)^{1/2} \sim 5.16 \cdot 10^{-14}$ s, so that chosen relaxation time is large enough for the system to reach equilibrium.

Naturally, the initial crystal structure is changing depending on the temperature value. Thus, at lower temperatures ($T = 10$ K) it is preserved, while at higher ones ($T = 25$ K) it becomes hardly noticeable (Fig. 1). The equations of motion are solved numerically via velocity Verlet algorithm [9–11] with a time step $dt = 10^{-6} \div 10^{-5}$ τ. The temperatures, chosen for modeling, are lower than melting temperature of Argon $T = 83.4$ K, which provides for nanoparticle stability (Fig. 1).

For the nanoparticle with a given N, the number Q of random realizations is created with the given temperature T. For the particles, containing $N = 64$ atoms, $Q = 50$, while for those, containing $N = 512$ atoms, $Q = 25$. For each random realization, the collision with a structureless plain is modeled. To impart the directed motion to the particle, all its atoms are given at the same moment of time the addition to the velocity ν_1 in the direction, normal to the plane. (It is checked beforehand, that the initial center of mass velocity vector equals to zero one). After that, the numerical solving of motion equations is conducted by the described above method. As soon as any

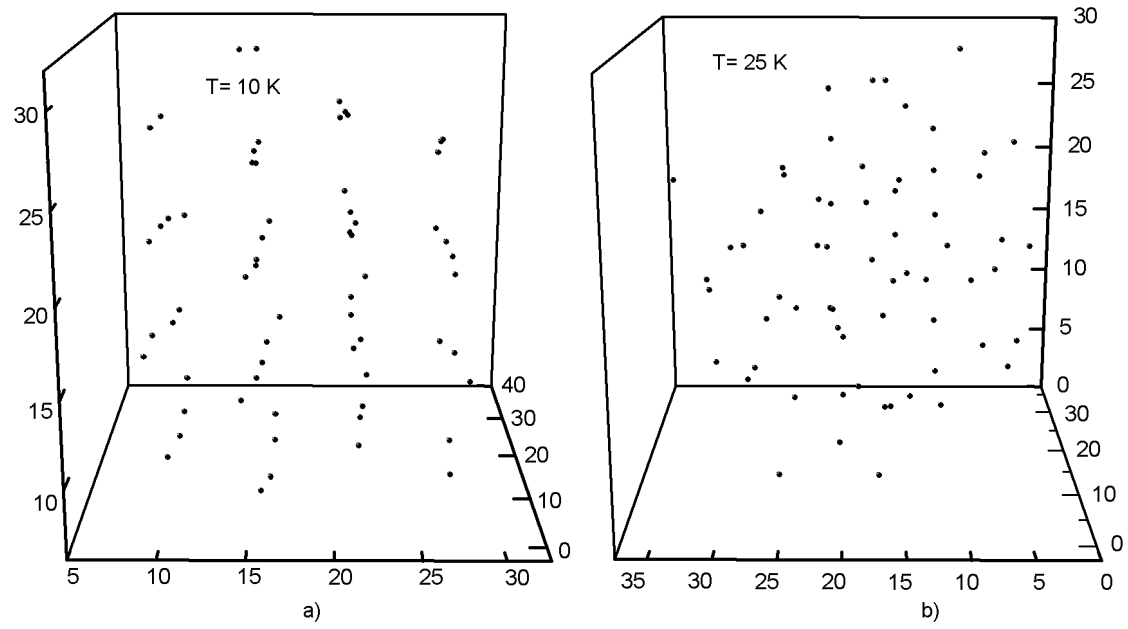

Fig. 1. The positions of nanoparticle atoms in a chosen moment of time are shown, in the left figure (a) temperature is $T = 10$ K, in the right one (b) $T = 25$ K.

nanoparticle atom reaches the plain, its velocity components are instantly changed to their mirror images, then motion equation solving is conducted in the previous mode. The range of nanoparticle initial velocities is changed from 25 to 220 m/s. These velocities do not cause the destruction of nanoparticle.

3. The numerical results

Let us begin with investigating the dependence of the velocity of nanoparticle reflected from the plane on its initial velocity. In the case of macroscopic bodies, such dependence is simple enough: $\nu' = -e\nu$ and is reduced to the linear law. Here e is the recovery coefficient (known as Newton coefficient), that is determined by the material properties and does not depend on the initial velocity of the body, colliding with the plane. Defining the effective recovery coefficient as $e_{ef} = |\nu_2/\nu_1|$, let us consider its dependence on the dimensionless velocity of the direct motion of the nanoparticle in the normal to the plane direction.

$$q = \frac{\nu_1}{\nu_T}. \qquad (1)$$

Here ν_T is the characteristic velocity of the thermal motion of nanoparticle atoms, and is defined as $\nu_T = (2E_{kin}/m)^{1/2}$, where E_{kin} is average kinetic energy of the system, related to one atom. All the dependences, presented below, are averaged over Q random realizations and temperatures $T = 10$ K and 25 K.

The dependence of effective recovery coefficient e_{ef} on $qN^{1/3}$ is presented in Fig. 2. The multiplier $N^{1/3}$ is introduced in order to demonstrate the universal dependence of the effective recovery coefficient on the number of atoms, contained by nanoparticle. First of all, the obtained dependence e_{ef} on $qN^{1/3}$ is close to the inversely proportional one. This implies that introduced in such a way recovery coefficient depends not only on the material properties, but also on the velocity of incident particle. This is a principal difference from the nondependence of e_{ef} on the velocity of an incident structureless macroscopic body. In other words, such coefficient does not fit as a material characteristics that determines the collision law of nanoparticle with a structureless plane. This principally leads to the necessity of introducing another collision law for nanoparticle or particles with a small number of degrees of freedom.

Besides this, the obtained dependence of effective recovery coefficient demonstrates one more unusual property, that can not be realized for macroscopic colliding bodies. Namely, for macroscopic bodies, the reflected velocity can be only less than incident one. For nanoparticles, as it follows from the modeling results, at $qN^{1/3} << 1$, the velocity of a reflected particle is large

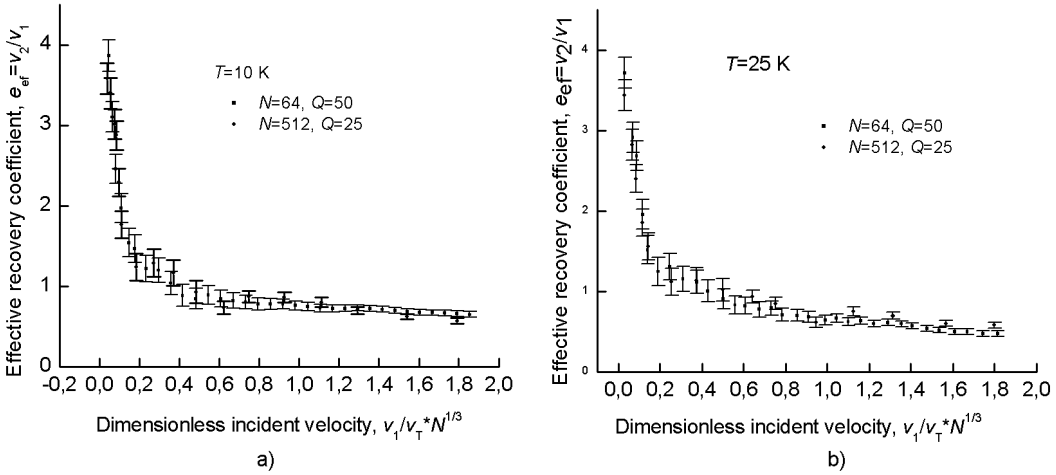

Fig. 2. The effective recovery coefficient $e_{ef} = \nu_2/\nu_1$ as a function of the relation of incident velocity to the thermal one, $q = \nu_1/\nu_T$ and of number of atoms in nanoparticle, N. In the left figure (a), temperature is $T = 10$ K, data, corresponding to nanoparticle, containing $N = 64$ atoms are indicated by squares; data, relating to $N = 512$, are indicated by circles. The vertical segments corresponds to calculating error. In the right figure (b), similar dependences are shown at temperature $T = 25$ K.

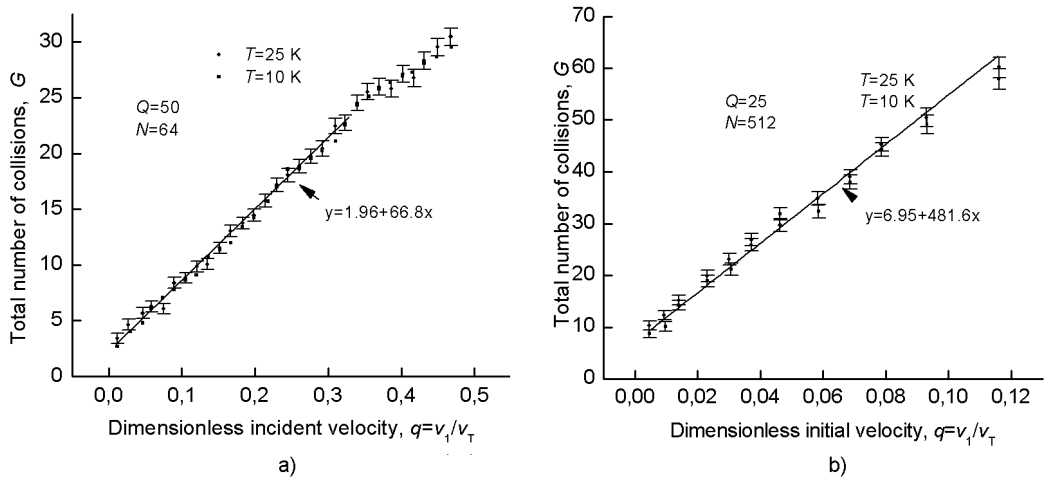

Fig. 3. Number of collisions, G, of nanoparticle atoms with the plain dependent on relation of incident velocity to the thermal one, $q = \nu_1/\nu_T$. Data in the left figure (a) correspond to the nanoparticle, containing $N = 64$ atoms. Data, relating to the temperature $T = 10$ K, are indicated by squares while those relating to $T = 25$ K are indicated by circles. In the right figure (b), similar dependences are shown for $N = 512$. The linear dependence is observed in a wide velocity range $0 < \nu_1 < \nu_T/2$.

by an absolute value than that of the incident one. Of course, conservation laws are not violated in this case. Such reflection regime is accompanied by the cooling of internal degrees of freedom of nanoparticle. With an increase of q, reflected velocity, of course, becomes smaller by an absolute value than initial one and decreases slowly which is accompanied by heating of the nanoparticle (the total energy of the particle is preserved during modeling up to 10^{-6} %). The performed modeling gives the critical value q_{cr}, at which transition occurs from $e_{ef} > 1$ to $e_{ef} < 1$

$$q_{cr} \sim 0.4/N^{1/3}. \quad (2)$$

It is clear, that for macroscopic bodies with a gigantic number of internal degrees of freedom, $N \to \infty$ and $q_{cr} \to 0$, so that it is impossible to observe the described phenomena. It is worth to note, that, as it follows from Fig. 2, the form of dependence e_{ef} on q, including the critical value q_{cr}, is virtually nondependent on size and temperature of nanoparticles.

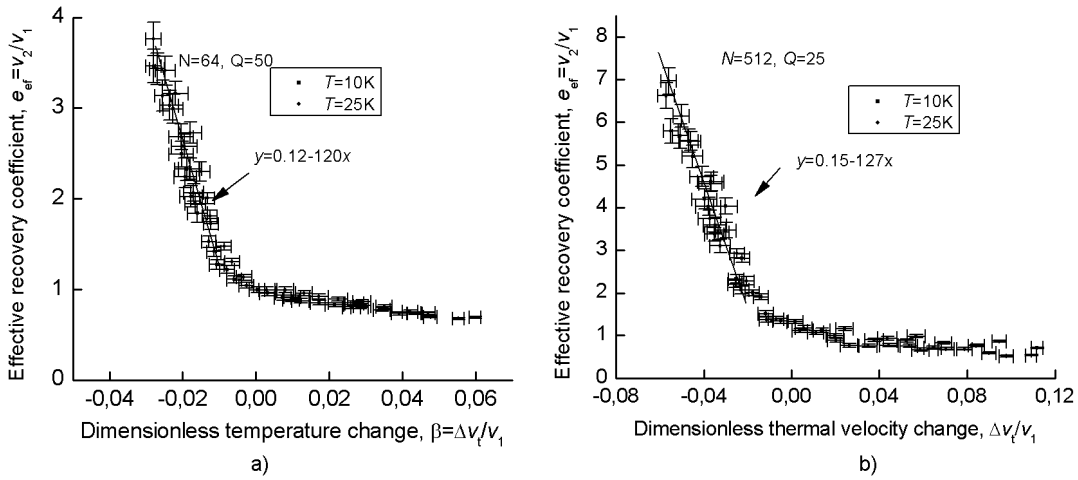

Fig. 4. Dependence of the effective recovery coefficient $e_{ef} = \nu_2/\nu_1$ on the value of $\beta = \Delta\nu_T/\nu_1$. Data in the left figure (a) correspond to the nanoparticle, containing $N = 64$ atoms. Data, relating to the temperature $T = 10$ K are indicated by squares while those relating to $T = 25$ K are indicated by circles. In the right figure (b), similar dependences are shown for $N = 512$.

One more interesting characteristics of the process is G, the full number of collisions of nanoparticle atoms with the plane during their interaction. Numerical data on the dependence of G on q are presented in Fig. 3 for the temperatures 10 K and 25 K. This dependence is linear with proportionality coefficient k close to N. Numerical modeling gives $k = 66.8$ for $N = 64$ and $k = 481.6$ for $N = 512$.

Reverting to establishing the reflection law for the particle with a small number of internal degrees of freedom, let us analyze the dependence of $e_{ef} = \nu_2/\nu_1$ on the relation of the change of mean thermal velocity of nanoparticle atoms to the initial incident velocity ν_1. Let us introduce the notation $\beta = \Delta\nu_T/\nu_1$, where ν_T is thermal velocity change resulting from the collision (with an account of sign). The results of numerical calculations are presented in Fig. 4. It is easy to notice from the figure that, in a wide range of β values, the linear dependence is observed

$$\frac{\nu_2}{\nu_1} = e + k\beta$$

with a proportionality coefficient $k \approx 120$ for $N = 64$ и $k \approx 127$ for $N = 512$. It is interesting to note, that these values are practically nondependent on N. In principle, in the range of $\beta > 0$, the dependence is also close to linear, but with different values of proportionality coefficient. It is important to emphasize that the value of coefficient k does not depend on the particle temperature. Thus, its value is preserved at the temperatures $T = 10$ K and $T = 25$ K within calculating error.

Thus, the generalization of the law of velocity change of the bodies with a small number of degrees of freedom after the collision with a structureless plane takes on a simple form

$$\nu_2 = e\nu_1 + k\Delta\nu_T. \qquad (3)$$

Now, two constants are present in this law, that do not depend on the incident particle velocity, namely e and κ. In a certain sense, these constants depend only on the material properties of the nanoparticle and the wall. It is naturally to preserve the notation of recovery coefficient for e, while β is a new coefficient, that characterizes nanoparticle properties. It is easy to note, that from the law (3) follow the dependences, presented in Fig. 2 as well as the exact reversal proportionality between $e_{ef} = e + k\Delta\nu_T/\nu_1$ and q.

It is worth to note that the value of coefficient k depends on the sign of β. For positive β this coefficient takes on smaller valuer and depends in a differen way on the number of atoms. Preliminary data indicate the inversely proportional dependence on $N^{1/3}$. Thus, value of this coefficient depends on the collisional mode.

4. Conclusions

Let us summarize briefly the results of the modeling. If the particle is reflecting

from a structureless plane, with initial velocity much smaller than velocity of thermal motion of its atoms, the effective recovery coefficient e_{ef} can exceed unity. New collisional law, that determines the velocity of the particle after collision with a wall is established in the present work. The collisional properties of the particles are determined already by two material characteristics, namely by recovery coefficient e, that is always smaller than unity, and by transformation coefficient. With the growth of a number of atoms contained by the nanoparticle, the anomalous mode disappeares. In other words, anomalous collisional properties are inherent to nanoparticles only, whereas for macroscopic bodies such behavior is impossible. The condition of realization $e_{ef} > 1$ is determined by inequality $q_{cr} < 1/(2N^{1/3})$.

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