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Molecular Dynamics of Surface-Moving Thermally Driven Nanocars

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Abstract: We developed molecular models describing the thermally initiated motion of nanocars, nanosized vehicles composed of two to four spherical fullerene wheels chemically coupled to a planar chassis, on a metal surface. The simulations were aimed at reproducing qualitative features of the experimentally observed migration of nanocars over gold crystals as determined by scanning tunneling microscopy. Coarse-grained-type molecular dynamics simulations were carried out for the species "Trimer" and "Nanotruck", the simplified versions of the experimentally studied nanomachines. Toward this goal, we developed a version of the rigid body molecular dynamics based on the symplectic quaternion scheme in conjunction with the Nose−Poincare thermostat approach. Interactions between rigid fragments were described by using the corrected CHARMM force field parameters, while several empirical models were introduced for interactions of nanocars with gold crystals. With the single adjusted potential parameter, the computed trajectories are consistent with the qualitative features of the thermally activated migration of the nanocars: the primary pivoting motion of Trimer and the two-dimensional combination of translations and pivoting of Nanotruck. This work presents a first attempt at a theoretical analysis of nanocars' dynamics on a surface by providing a computationally minimalist approach.

Introduction

Fullerene-based nanometer-sized molecular structures, called nanocars, which have demonstrated a wheel-like rolling motion along metal surfaces,[1–3] are among the artificial molecular systems that mimic some of the properties of biological molecular motors. The latter include active enzyme molecules that move progressively along such tracks as protein filaments or nucleic acids by transforming chemical energy into mechanical work.[4] Nanocars are single-molecule vehicles composed of two to four spherical fullerene wheels that are chemically coupled to a planar chassis and sometimes bearing a loading bay. Their thermally initiated migration on the surface of gold crystals was determined by scanning tunneling microscopy techniques.[3]

To support the eventual goals of these studies, specifically the understanding and control of surface transport by such entities, it is important to develop theoretical models of nanocars and explore modern computational approaches for detailed analyses of their motion. Molecular dynamics (MD) simulations provide a convenient tool for the investigation of such complex dynamic systems. Theoretical computations are supposed to reproduce the observed features of the thermally activating surface movements of nanocars.[2,3] According to these experimental findings, a four-wheeled nanocar remained stationary on the gold surface up to 170 °C, and as the temperature increased to 200–225 °C, the molecule began to move in two dimensions (2D) through a combination of both translation and pivoting. When a three-wheeled nanocar was heated to 225 °C, only occasional

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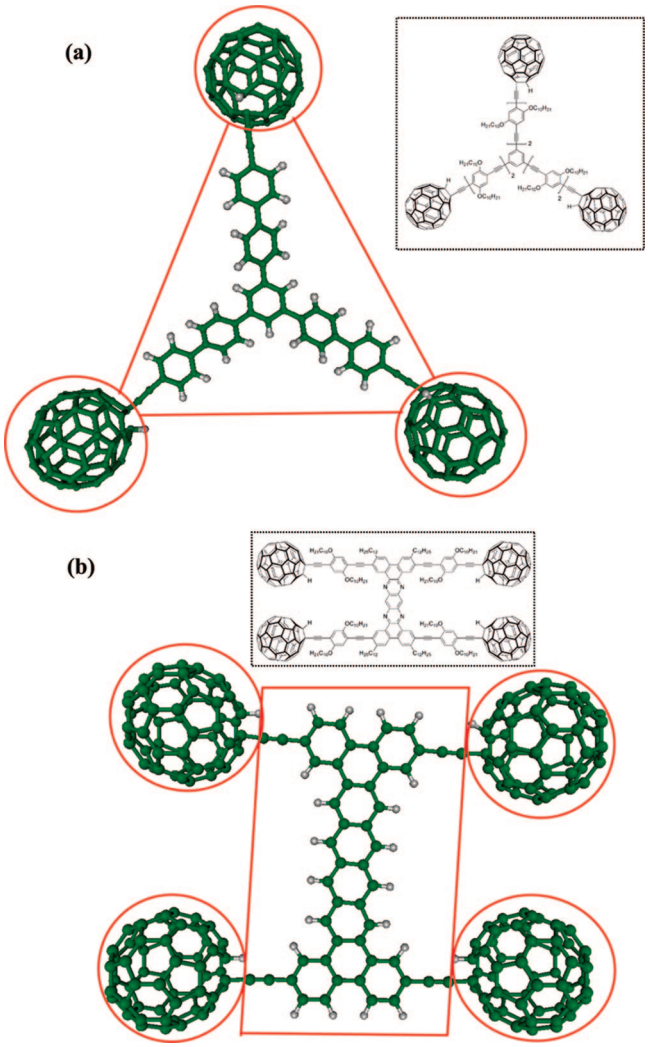

Figure 1. Molecular models of nanocars used in molecular dynamics simulations: (a) Trimer and (b) Nanotruck. The insets show chemical structures of the parent nanocars.[3] Partitioning the molecules into rigid fragments (four for Trimer and five for Nanotruck) is clarified by the red lines.

surface diffusion was observed, and the majority of motion was pivoting in space around a central pivot point. The MD models that are capable of replicating these physical movements may be used in the future to understand and optimize the fabrication of the next generation of nanocars.

In this work, we consider two hydrocarbon analogs of fullerene-based nanocars originally designated[3] as "Trimer" (a three-wheeled vehicle) and "Nanotruck" (a four-wheeled vehicle). The panels of Figure 1 illustrate the models, showing chemical structures of the parent nanocars in the insets and the corresponding analogs considered here and shown in ball-and-stick representations. Starting with the structures of the experimentally studied species[3] (insets in Figure 1), we introduced simplifying modifications to the molecular structure in order to reduce computational expenses in this first attempt to model nanocar dynamics. Specifically, we kept the alkynyl connectors (−C≡C−) to the fullerene wheels, but we replaced the other alkynyl moieties with direct aryl−aryl linkages. As discussed below, we maintained the rigidity of the parent chassis (insets in Figure 1) by using the rigid body MD simulations. The most significant features of the parent nanocars, the rolling motion of the wheels, should be the same in our model vehicles.

For simulations of the thermally activated surface transport of the nanocar models, we applied an original version of the rigid-body molecular dynamics, an extension of the previous approach.[5] This method allowed us to concentrate on the most essential dynamical features of nanovehicles on the surface: the wheels were allowed to rotate, but the wheels and chassis were represented by rigid fragments. As shown in Figure 1, four rigid fragments (three wheels and a chassis) were assumed for Trimer, and five rigid fragments (four wheels and a chassis) were considered for Nanotruck. Application of rigid-body MD helped us to drastically reduce an array of internal coordinates, to simplify forms of interaction potentials, to decrease the amount of potential parameters, and to afford fairly long MD trajectories.

In preliminary steps, we implemented and tested several algorithms of rigid-body MD in the canonical ensemble (NVT) and found that the symplectic quaternion scheme described, in particular, by Miller et al.,[6] in conjunction with the Nose−Poincare thermostat approach,[7] was an optimal choice for constant temperature molecular dynamics calculations of nanocars. It should be noted that, in this work, similarly to other molecular dynamics investigations, we did not study how the presence of a thermostat influences the dynamics of nanocars.

All MD runs were performed for an integration time step of 1 fs. The trajectories were typically about 5 ns lengths. Interactions between rigid fragments were modeled by the site–site potential composed of the Lennard-Jones and Coulomb functions in eq 1.

$$E_{\alpha\beta} = \sum_{i\in\alpha}\sum_{j\in\beta}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}}\right\} \qquad (1)$$

Here, i and j are the indices of atoms belonging to fragments α and β, respectively, r_{ij} is the distance between atoms i and j, and q_i and q_j are partial charges on the respective atoms. Potential parametrization was basically consistent with the CHARMM27 force field[8,9] but corrected in this work as explained below. The hydrogen atoms were assigned to type HA(1) with the parameters $\epsilon = 0.022$ kcal/mol and $\sigma = 1.32$ Å; the carbon atoms were assigned to type CA(11), except those connecting fullerene wheels with the chassis (see Figure 2). For the latter, type CC(12) was assumed. The Lennard-Jones parameters of all carbon atoms were taken as $\epsilon = 0.070$ kcal/mol and $\sigma = 1.9924$ Å. The partial charges on atoms were determined in *ab initio* quantum chemical calculations in the RHF/6-31G** approximation by using the PC GAMESS program[10] as the Mulliken charges for the compounds benzene, biphenyl, biphenylacetylene, and phenylfullerenylacetylene, occurring as fragments of model nanovehicles (Figure 1). The atom types and computed partial charges are shown in Figure 2. The remaining fullerene carbon atoms were assumed to be CA(11)-type atoms with zero partial charge.

The parameters required for the bonded interactions when using the CHARMM force fields were selected as follows. For the CA(11)−CC(12) stretching term: $k_b = 320.0$ kcal/mol and $r_0 = 1.400$ Å. For the CA(11)−CC(12)−CA(11)

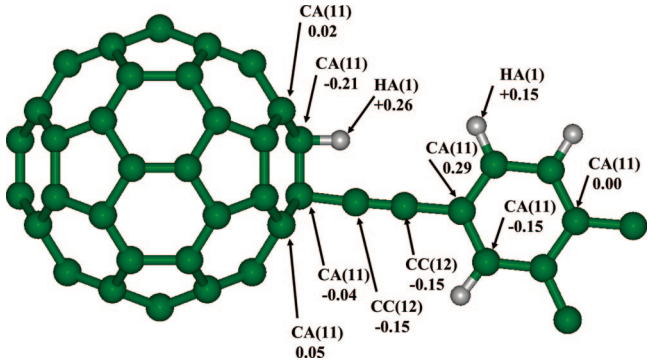

Figure 2. An assignment of the atoms in the model nanocars (Figure 1) to the CHARMM force field types and their partial charges as computed by *ab initio* calculations in this work.

bending term: $k_a = 40.0$ kcal/mol and $\theta_0 = 170.0°$. For the CA(11)−CC(12)−CC(12) bending term: $k_a = 40.0$ kcal/mol and $\theta_0 = 120.0°$. The torsional terms were excluded because of their negligible contribution to the total energy. Some precautions were introduced to the computer code for the bending potential in order to exclude singularities of the potential when the CA(11)−CC(12)−CC(12) angle approached 180°. We verified that such a constructed total interaction potential was consistent with the small rotational barrier (1.0 kcal/mol) of the fullerene-wheel structures without a surface, as estimated in ref 3.

Several models have been considered for the nanocar−surface interaction potentials assuming that each atom of a nanocar experiences an external force from the resting metal. All models are based on the pairwise 12–6 Lennard-Jones potential function in eq 2:

$$E_W = 4\epsilon\left[\left(\frac{\rho}{d}\right)^{12} - \left(\frac{\rho}{d}\right)^{6}\right] \tag{2}$$

where d is the distance from a particular atom of a nanocar to a specific point in the metal. We considered parameters of these interaction potentials close to the values reasonable for a description of the gold crystals. In particular, the lattice parameter $a = 4.07$ Å was taken from the *fcc* gold lattice.[11] We found in preliminary calculations that the geometry parameter ρ in eq 2 did not strongly affect the essential features of nanocar dynamics. Therefore, we selected the value corresponding to the gold van der Waals atomic radius 1.66 Å.[11]

The most uncertain parameter in eq 2 is the potential well depth ϵ. An initial selection was the value 0.47 kcal/mol corresponding to the molecular mechanical parameters of metals (Ca^{2+}, Ba^{2+}) from the AMBER force field set;[12] however, we allowed its large variations within 2 orders of magnitude, from 4.7 to 0.094 kcal/mol. In recent MD simulations of gold nanoparticles inside carbon nanotubes, Schoen et al. used the 12–6 Lennard-Jones potential function with parameters $\epsilon = 0.3$ kcal/mol and $\rho = 3$ Å for interactions between gold and carbon atoms, conditions reasonably consistent with our choice. Narrowing the range of the suitable values of ϵ and better theoretical justification of ϵ are subjects of our current work.

Within the simplest *Model-W*, each atom of a nanocar interacts with a structureless metal surface (or with a rigid *wall*) calculated by the potential (eq 2), where d is the distance from an atom to the surface plane. Correspondingly, the only nonzero components of forces acting on the machine's atoms are directed along the normal to the surface. Summation over all atoms of a vehicle defines a total interaction potential E_W. As discussed below, this model is capable of explaining the thermal activation of Trimer's pivoting but fails to describe translations of Nanotruck.

The more advanced *Model-L* assumes certain features of a *lattice* atomic structure of metals. When this model is applied, the current coordinates of a nanocar's atom are projected on the surface plane, and the nearest to this point from the surface atom of the *fcc* lattice serves as a reference node to construct the interacting shell. To this end, several (9 or 25) nearest lattice points from the surface layer and from the one underneath the surface contribute to the interaction potential calculated as a sum of the terms defined by eq 2. The procedure is repeated for all atoms of a nanocar. This is the most computationally expensive approach for molecular dynamics calculations.

Model-P takes into account the 2D *periodicity* of the surface potential. The corresponding total potential E_P acting on a nanocar is related to the wall-like potential E_W by eq 3:

$$\begin{aligned} &E_P(x, y, z) = f(x, y)\, E_W(z) \\ &f(x, y) = f(x + na, y + ma) \\ &f(x, y) = 1 + \frac{\left[\sin^2\left(\frac{\pi x}{a}\right) + \sin^2\left(\frac{\pi y}{a}\right)\right]}{2} \end{aligned} \tag{3}$$

where coordinates z are counted along the normal to the metal surface, coordinates x and y are in the surface plane, n and m are integers, and a is the lattice parameter. Application of this model allows us to qualitatively describe the translational motion of nanocars.

We also considered a model accounting for charge polarization of the metal. In this approach, we introduced, for each atom with a nonzero partial charge in the nanocar's structure, its image inside the metal with a charge of the opposite sign. Then, the Coulombic contributions from the nanocar−metal interactions were added to the total interaction potential E_W. Since no noticeable improvements over other models were found, we do not further discuss the results of this approximation.

The most essential results of MD simulations are as follows. In complete accord with experimental observations,[2,3] pivoting around the central point was the primary movement for Trimer. With *Model-L*, surface rotations mixed with weak displacements of Trimer were observed. At temperatures lower than 300 K (27 °C), the nanocar remained stationary; at $T = 400$ K (127 °C), the mobility was initiated, and at $T = 500$ K (227 °C), we could observe an apparent rotational rolling motion. The sensitivity of the results to the parameter ϵ of eq 2 is demonstrated in Table 1. These data show that surface dynamics of model nanocars depend on the parameters of this simple potential (eq 2) in a complicated fashion; we do not observe monotonous behavior of the computed trajectories by varying ϵ.

We illustrate the pivoting motion of Trimer on the gold surface in Figure 3 as well as in the animated movies

Table 1. Dependence of the Mode of Surface Movement of Trimer (Figure1a) on the Parameter ϵ of Potential eq 2[a]

temperature, K	ϵ = 4.7 kcal/mol	ϵ = 0.47 kcal/mol	ϵ = 0.094 kcal/mol
300	weak rotation, no displacement	no rotation, no displacement	weak rotation, weak displacement
500	rotation, no displacement	weak rotation, weak displacement	rotation, displacement
600	rotation, no displacement		

[a] Other parameters of potential eq 2 are as follows: ρ = 1.66 Å and a = 4.07 Å.

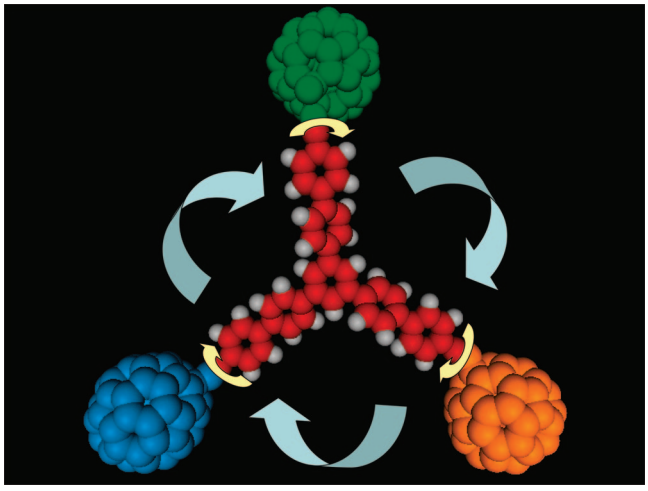

Figure 3. The pivoting mode of surface movement of Trimer. The animated movies are presented in the Supporting Information (trimer_300K.avi and trimer_500K.avi).

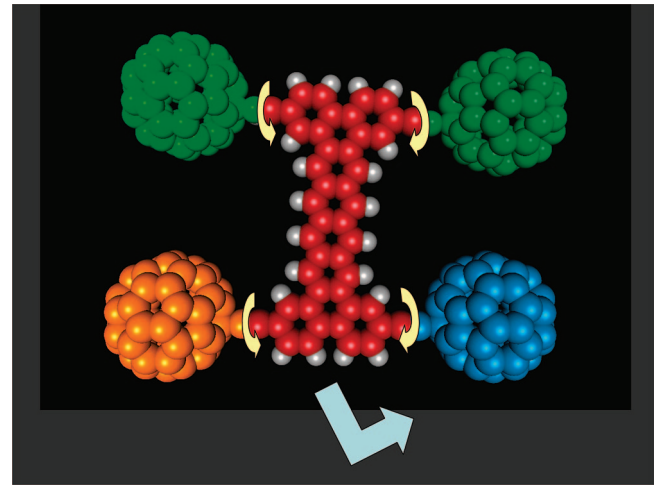

Figure 4. The mode of surface movement of Nanotruck. The animated movies are in the Supporting Information (ntruck_300K.avi and ntruck_500K.avi).

presented as Supporting Information: trimer_300K.avi (T = 300 K) and trimer_500K.avi (T = 500 K). These data refer to simulations with *Model-L* with the potential parameters ρ = 1.66 Å, a = 4.07 Å, and ϵ = 4.7 kcal/mol. Application of *Model-P* permits the observation of a combination of strong rotations and non-unidirectional displacements of Trimer along the surface.

If we define the rotational velocity, k_{rot}, of Trimer as the ratio of the (noninteger) number of rotation circles (for example, 5.5 at T = 600 K) to the trajectory length (5 ns) and assume the temperature dependence of the rotational velocity in the Arrhenius form (eq 4):

$$k_{rot} = A\, e^{-\frac{E_a}{RT}} \qquad (4)$$

then plotting the values k_{rot} versus T^{-1} (300 K $\leq T \leq$ 800 K) allows us to estimate the slope of the graph and, therefore, an activation energy barrier E_a for thermally driven Trimer rotation. With the trajectories of *Model-W,* such an estimate results in E_a values between 3 and 4 kcal/mol.

For the four-wheeled Nanotruck, an application of *Model-W* was an unsuccessful attempt to detect the 2D movement of the vehicle. However, applications of *Model-P* or the more expensive *Model-L* allowed us to observe a combination of both translation and pivoting. Within the latter models, the use of potential parameter ϵ = 4.7 kcal/mol in eq 2, corresponding to the strongest interaction of Nanotruck with the metal surface, precluded migration of the nanovehicle even at higher temperatures (400 and 500 K). For the smaller values of ϵ, a desired type of motion (two-dimensional combination of both translation and pivoting) could be observed. We illustrate the movement of Nanotruck on the gold surface in Figure 4 as well as in the animated movies

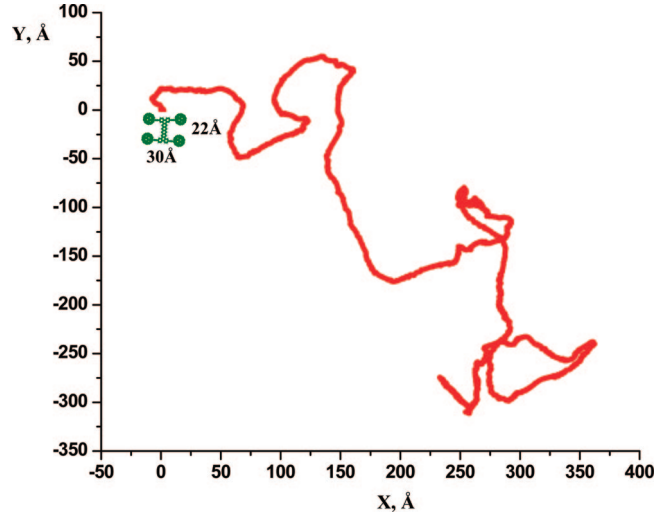

Figure 5. Two-dimensional trajectory of Nanotruck in the surface plane (X,Y) as computed with *Model-L* at T = 500 K. The shape of the moving molecule is shown for comparison in green.

in the Supporting Information: ntruck_300K.avi (T = 300 K) and ntruck_500K.avi (T = 500 K). These data refer to simulations with *Model-L* with the potential parameters ρ = 1.66 Å, a = 4.07 Å, and ϵ = 0.47 kcal/mol.

In Figure 5, we show a typical 2D trajectory of Nanotruck at T = 500 K as computed with *Model-L* with the potential parameter ϵ = 0.47 kcal/mol. According to these MD simulations, the nanovehicle can experience large-scale migrations, especially compared to its size, shown in green in Figure 5.

Our results indicate that lattice structure and periodicity of the surface play a critical role in the dynamics of thermally

driven nanocars. This suggests the following mechanism of transport: nanocars are bound to the surface by strong bonds (covalent or electrostatic), and they move along the surface by overcoming the barriers with the help of thermal fluctuations; that is, the dynamics of nanocars are an activated process. The experimentally determined existence of a temperature threshold below which no motion is observed, and the strong temperature dependence of the dynamics, supports the computational findings here.

To summarize the results of this work, we emphasize that molecular models have been developed for surface-moving analogs of fullerene-based nanocars, which successfully reproduce experimentally observed[2,3] thermal activation and dynamical features of the nanovehicles. This paper presents a first attempt in the theoretical analysis of these complex systems by providing a computationally minimalist approach that allows one to understand the essential features of nanocar dynamics upon a surface. Our theoretical analysis suggests that the dynamics of nanocars is an activated process that strongly depends on the structure and periodic properties of the surface. In addition, we provide an estimate for the activation energy of thermally driven rotation of Trimer (3–4 kcal/mol) that can be measured in experiments to test the validity of our approach.

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Supporting Information Available: Animated movies of typical trajectories of Trimer and Nanotruck. This material is available free of charge via the Internet at http://pubs.acs.org.

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