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Physics Procedia 40 (2013) 93 – 99

Physics Procedia

2nd European Conference on Nano Films: ECNF-2012

Molecular dynamics simulations of bio-nano systems with MBN Explorer

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Abstract

We present results of molecular dynamics simulations performed using a multi-purpose computer code *MBN Explorer*.In particular we consider the process of laser induced acoustic desorption of lysine amino acids from the surface of a nickel foil. We analyze the rate of lysine desorption from the nickel foil at different foil accelerations and suggest a simple theoretical model to describe the observed results. We note that despite the universality, the computational efficiency of *MBN Explorer* is comparable (and in some cases even higher) than the computational efficiency of other software packages, making *MBN Explorer* a possible alternative to the available codes.

Keywords: nanostructures simulation, biomolecular simulation, molecular dynamics, multi scale approach

1. Introduction

In recent years, numerous nanosystems possessing unique structural, optical, electric and magnetic properties have been[1]discovered[2–5] The aggregation of atoms and small molecules into clusters, nanoparticles, micro-droplets is a process in which a wide range of complex bio-, nano- and mesoscopic objects can be created. Often, such systems are seen as building blocks for new nanostructured materials with specific tailored properties. Many of these systems have become a subject of intensive investigations because of the variety of potentially important applications[5,7–15].

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doi:10.1016/j.phpro.2012.12.013

In this paper we present results of molecular dynamics simulations obtained using a multi-purpose computer package, MesoBioNano Explorer (*MBN Explorer*), which can be used for advanced theoretical characterization and analysis of a variety of bio- nano systems[1]. The binary files of *MBN Explorer*, the user's guide and a number of representative examples are available upon registration online at http://www.mbnexplorer.com/. The ultimate goal of *MBN Explorer* is to expand the understanding of mechanisms of stability, self-organization and growth, as well as the ways of manipulation and control of bio-nano systems with potential applications in nanotechnology, microelectronics and medicine.

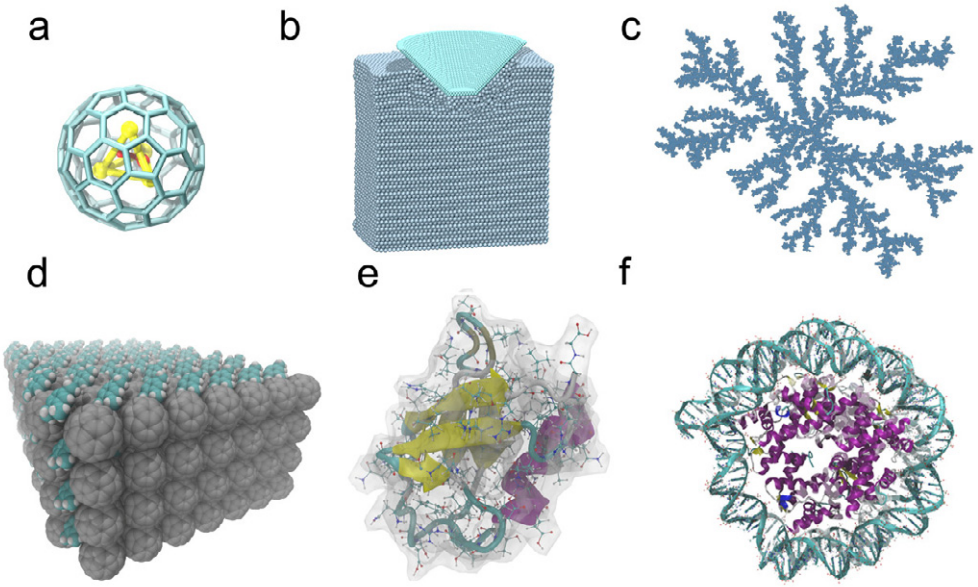

Fig. 1 Variety of molecular systems which can be simulated using *MBN Explorer*: (a) encapsulated clusters, (b) nanoindentation of titanium crystal, (c) nanofractals, (e) proteins, (f) biomolecules, e.g., DNA on the histone. Structure and properties of any of these objects or any of their combinations can be studied using *MBN Explorer*.

Figure 1 illustrates a variety of molecular systems, which can be simulated using *MBN Explorer*. In particular, *MBN Explorer* is suited to compute the system's energy, to optimize molecular structures, as well as to explore the molecular and random walk dynamics. *MBN Explorer* allows to use a broad variety of interatomic potentials, to model different molecular systems, such as atomic clusters[16–18], fullerenes, nanotubes[19], polypeptides, proteins[15-16], composite systems[22–25], nanofractals[26–28], etc.

Many features of *MBN Explorer* are not unique and are implemented in other computer programs developed throughout the last decades. However, a distinct feature of *MBN Explorer*, which makes it different from the already existing codes, is its universality and applicability to a broad range of problems involving different molecular systems of biological and/or non-biological origin. Most of the existing codes are applicable to a particular class of molecular systems, and have thus certain limitations, while*MBN Explorer* goes beyond these drawbacks.

In this paper briefly overview the key functionality of the *MBN Explorer*by illustrating its application on the example of a particular problem: the process of laser induced acoustic desorption of biomolecules from metallic foil.

2. Laser induced acoustic desorption

In this section we describe the molecular dynamics simulations of lysine (Lys) polypeptides desorption from oscillating metallic foil. This process occurs in the course of lifting of biomolecules into the gas phase by means of laser induced acoustic desorption (LIAD) procedure. In LIAD experiments the biomolecules are deposited on a surface of a relatively thin (10 μm) metallic foil[29,30]. The back surface of the foil is irradiated by a laser pulse of nanosecond duration, having the power density of 10 GW/cm^2. The energy of the laser is adsorbed by the material of the foil, which consequently causes the propagation of an acoustic and thermal waves. The propagating waves induce vibration of the foil material which stimulates the desorption of biomolecules from the foil surface to the gas phase.

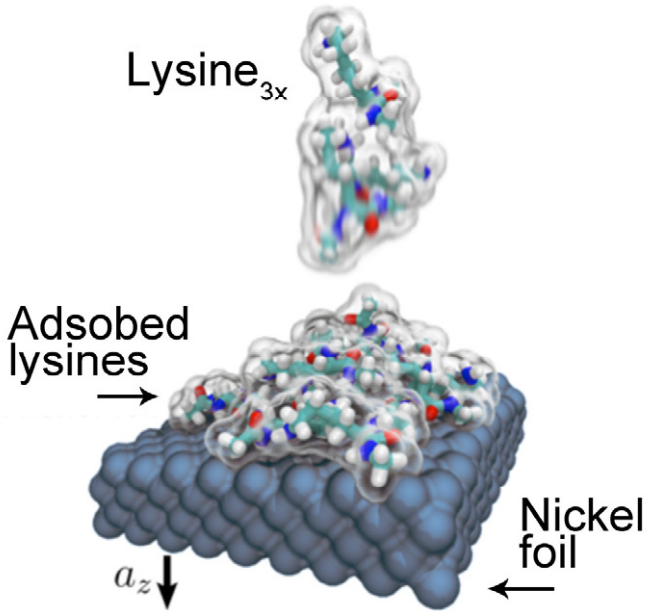

Fig. 2 Desorption of several lysine residues from the surface of a nickel foil. The desorption is caused by acceleration of the foil.

In the considered example we assume that the amplitude of the foil vibration is proportional to the intensity of the laser pulse, and investigate the dependence of the number of desorbed molecules on the laser intensity. Consider the process of longitudinal acoustic wave propagation through the foil in the direction perpendicular to the foil surface, see Fig. 2. The 1D-displacement of the foil surface can be described as:

$$z(t) = A\cos(\omega t + \varphi_0), \tag{1}$$

where z is the coordinate of the foil, t is the time instance, A is the wave amplitude, ω is the foil vibration frequency, and φ_0 is the initial phase. From Eq. (1) follows that acceleration of the foil surface can be written as:

$$a_z(t) = \ddot{z}(t) = -A\omega^2\cos(\omega t + \varphi) \tag{2}$$

Thus, the maximal acceleration of the foil surface, a_{max}, is equal to $A\omega^2$. Let us assume that most of the molecules deposited on the foil surface desorb if $a \approx a_{max}$. We use *MBN Explorer* to investigate the number of desorbed molecules at various maximal accelerations of the substrate.

To illustrate the LIAD procedure we have considered thirteen lysine amino acid deposited on a (111)-nickel surface consisting of four monolayers. The size of the nickel surface in x and y directions was taken equal to 3 nm. The interactions between amino acids were described through the CHARMM22 force field[31] and the interactions between nickel atoms were modeled using the many-body Sutton-Chen potential[32]. Interaction between the atoms of nickel and atoms of lysines were described through the van der Waals potential with ε_{Ni}=0.082394eV and R_{min}=0.63Å, combined with the van der Waals parameters defined in the CHARMM22 force field for lysine atoms. The parameters for the lysine-nickel interaction were chosen in order to match the quantum mechanical calculations of the adsorption of benzene on the nickel surface[33]. The 13×Lys@Ni system was equilibrated for 4 ns at 350 K using Langevin thermostat with a damping time τ=100fs. Reflective boundary conditions were implied along the x,$y$and z directions in order to spatially constrain the system. Thus, the size of the simulation box was chosen as 32, 32, 108Åalong the x, $y$and $z$directions, correspondingly. The cut-off distance for the van der Waals interactions was taken equal to 8Å, while the Coulomb interactions were treated with the cutoff of 12Å. The lower layer of the nickel foil was treated as a "rigid layer" in order to maintain the crystalline-like structure of the substrate, see Fig 2. The integration timestep in the molecular dynamics simulation was set equal to 1 fs.

After equilibration of the system a constant force was applied to the atoms of the lower layer of the foil, see Fig. 2. The foil was accelerated in direction outwards the deposited amino acids. This procedure was performed with the use of the auxiliary system manipulation. We have performed several simulations which correspond to the acceleration of the substrate equal to 2, 3, 4, 4.5 and 5 Å/ps^2, thus the substrate acceleration of 5 Å/ps^2 induces force of 122 pN acting on a lysine amino acid. For each acceleration three independent 0.5 ns long simulations were performed. The initial temperature of the system before acceleration was set equal to 350 K.

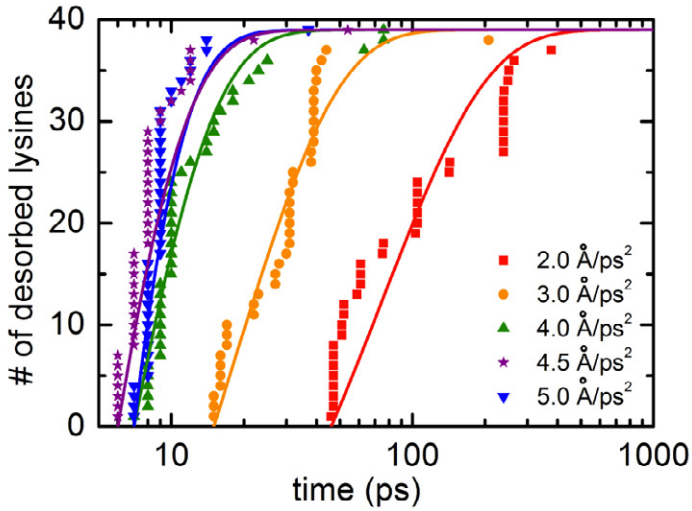

Fig. 3 The number of desorbed lysine residues as a function of time after the start ofnickel-foil acceleration. Symbols show the results of molecular dynamics simulations corresponding to different values of foil acceleration (measured inÅ/ps^2). Solid lines show the theoretical curves obtained by fit of Eq. (5) to the results of molecular dynamics simulations. The figure legend indicates the values of acceleration used in molecular dynamicssimulation.

Due to the acceleration of the foil the loosely bound amino acids are desorbed from the foil surface in the course of the simulation. Figure 2 shows a snapshot of the simulation, which features desorption of a cluster consisting of 3 lysine amino acids. We have defined an amino acid as desorbed if it was separated from the foil surface on more than 50Å. Figure 2 shows the dependence of the number of desorbed amino acids as a function of simulation time for different values of foil acceleration. The desorption rate of an amino acid, λ, depends on the acceleration of the foil. Assuming that each amino acid desorbs independently, it is possible to define the probability for an amino acid to stay on the foil surface as:

$$p(t) = \lim_{\Delta t \to 0}(1 - \lambda t)^{t/\Delta t} = \exp(-\lambda t), \quad (3)$$

where$t$ is time from the beginning of the foil acceleration and Δt is an infinitely small time interval. Thus, the number of desorbed amino acids at any time instance can be calculated as:

$$N(t) = N_0\big(1 - p(t)\big), \quad (4)$$

whereN_0 is the initial total number of amino acids on the foil surface. In the current example N_0 = 39, because we have performed three independent simulations for all acceleration values with 13 amino acids in each simulation.

Inertial forces that are applied to amino acids in the course of foil acceleration lead to rearrangement of contacts between amino acids prior their desorption. In order to account for this effect, we count time in Eq. (4) from the moment of desorption of the first amino acid. Thus, Eq. (4) should be modified as:

$$N(t) = N_0[1 - \exp(-\lambda(t - t_0)], \quad (5)$$

where$t_0$is the time of the first amino acid desorption. We have fitted the results of molecular dynamics simulation with the function defined in Eq. (5) by varying λ. The results of the fit for each acceleration value are shown in Fig. 3 by solid lines. The values of the obtained fit parameter λand the corresponding $t_0$values are summarized in Tab. 1.

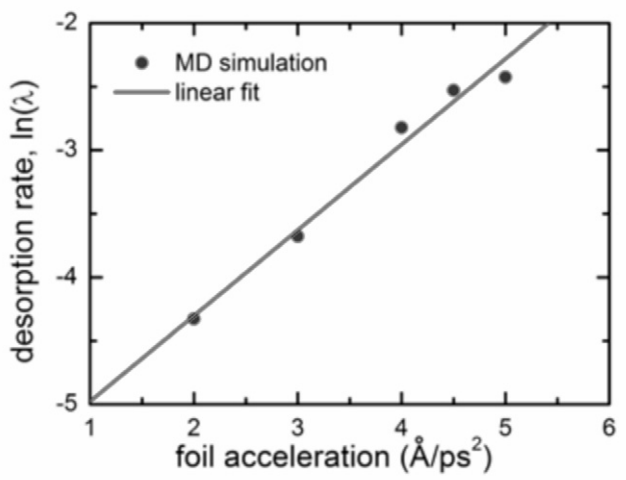

Fig. 4. The dependence of the desorption rate, λ, on the acceleration of the nickel foil.Dots show the results of molecular dynamics simulations. Solid line shows the linear fit ofmolecular dynamics results.

From Figure 3 it is seen that results of molecular dynamics simulations are reasonably fitted by the theoretical model defined in Eq. (5). Figure 4 shows the dependence of the desorption rate λ on the acceleration of the substrate. It is also seen that the logarithm of λ is proportional to the acceleration of the substrate, i.e., λ has an exponential dependence on the acceleration of the foil. This result is consistent with experimental observations[30], where it has been suggested that the LIAD phenomenon cannot be described in terms of simple mechanical shake-off or direct laser desorption.

Table 1. Parameters λ and $t_0$used for the fit of molecular dynamics simulation data shown in Fig. 3.

Acceleration (Å/ps^2)	Ln λ	t_0(ps)
2.0	-4.32	46
3.0	-3.67	15
4.0	-2.82	7
4.5	-2.52	7
5.0	-2.42	6

3. Conclusions

MBN Explorer is a program with several important features, which make it potentially interesting to diverse communities including physicists, chemists, biologists and material scientists. *MBN Explorer* permits energy calculation, structure optimization, molecular and random walk dynamics simulations. The development of a new program for studying molecular structures and dynamics is motivated by the need of a universal extendable code, which would permit investigation of molecular processes on the nano- and meso-scales. Through the combination of advanced MD techniques and simplified coarse-grained models, *MBN Explorer* is suitable for the description of molecular systems on the basis of a multiscale approach, which is not provided by the most of existing standard molecular dynamics codes: the standard codes would require additional input, involving either plugin or module development, to permit the multiscale calculations, while *MBN Explorer* supports it intrinsically.

As an example of *MBN Explorer* extended functionality, the program allows for straightforward simulations using Monte-Carlo-based dynamics, classical molecular dynamics involving a large number of rigid molecules of arbitrary shapes, molecular dynamics simulations of bio-nano systems modeled through a combination of pairwise and many-body potentials (e.g., a gold nanoparticle marker linked to a DNA molecule). In the paper we have considered only one illustrative example, which outline the key features of *MBN Explorer*, but, of course, do not describe all of them, since *MBN Explorer* allows to combine most of its features in a user-friendly manner, permitting simulations of various molecular assemblies in special environments. It is worth noting that although most of the computational features of *MBN Explorer* can be found in other computer packages, *MBN Explorer* is unique because it combines a vast majority of these features into one computationally efficient code. The current version of *MBN Explorer* supports calculations on the multiple CPU cores with sheared memory by means of OpenMP parallelization technique.

MBN Explorer is made compatible with the popular molecular dynamics programs NAMD[34], CHARMM[31] and visualization program VMD[35]. This permits to easily swap files between the programs and prepare molecular systems for simulations in a straightforward way. The visualization support through the VMD program is necessary for analysis of *MBN Explorer*output and the build-in

Tclscripting language in VMD allows to develop specialized plugins to perform the extended analysis of the calculations results.

4. Acknowledgements

We acknowledge the Frankfurt Center for Scientific Computing for providing computer resources that have contributed to the research results reported within this paper. I.S. acknowledges support as a Beckman Fellow. A.Y. thanks the StiftungPolytechnischeGesellschaft Frankfurt am Main for financial support.

References

[1] I. A. Solov'yov, A. V. Yakubovich, P. V. Nikolaev, I. Volkovets, and A. V. Solov'yov, Accepted to J. Comp. Chem. 1–85 (2012).
[2] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109–162 (2009).
[3] S. Ohkoshi, K. Imoto, Y. Tsunobuchi, S. Takano, and H. Tokoro, Nat. Chem. doi:10.1038/nchem.1067 (2011).
[4] L. Adler-Abramovich, D. Aronov, P. Beker, M. Yevnin, S. Stempler, L. Buzhansky, G. Rosenman, and E. Gazit, Nat. Nanotech. **4**, 849–854 (2009).
[5] S. Mann, Nat. Mat. **8**, 781–792 (2009).
[6] N. Withers, Nat. Chem. **doi:10.103**, (2009).
[7] M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko, Nat. Mat. **9**, 101–113 (2010).
[8] G.Ciofani, Expert Opinion on Drug Delivery **7**, 889–893 (2010).
[9] P.D.Yang, R.X.Yan, and M.Fardy, Nano Lett. **10**, 1529–1536 (2010).
[10] G. F. Schneider, S. W. Kowalczyk, V. E. Calado, G. Pandraud, H. W. Zandbergen, L. M. K. Vandersypen, and C. Dekker, Nano Lett. **10**, 3163–3167 (2010).
[11] S. Garaj, W. Hubbard, A. Reina, J. Kong, D. Branton, and J. A. Golovchenko, Nature **467**, 190–194 (2010).
[12] A. V. Yakubovich, I. A. Solov'yov, A. V. Solov'yov, and W. Greiner, **52**, 25–32 (2009).
[13] A. Hussien, A. V. Yakubovich, A. V. Solov'yov, and W. Greiner, The European Physical Journal D **57**, 207–217 (2010).
[14] E. Surdutovich, a. V. Yakubovich, and a. V. Solov'yov, The European Physical Journal D **60**, 101–108 (2010).
[15] A. V. Yakubovich, I. A. Solov'yov, A. V. Solov'yov, and W. Greiner, **40**, 363–367 (2006).
[16] I. A. Solov'yov, A. V. Solov'yov, and W. Greiner, Int. J. Mod. Phys. E **13**, 697–736 (2003).
[17] O. I. Obolensky, I. A. Solov'yov, A. V. Solov'yov, and W. Greiner, Comp. Lett. **1**, 313–318 (2005).
[18] I. A.Solov'yov, A. V.Solov'yov, W.Greiner, A.Koshelev, and A.Shutovich, Phys. Rev. Lett. **90**, 053401–(1–4) (2003).
[19] I. A. Solov'yov, M. Mathew, A. V. Solov'yov, and W. Greiner, Phys. Rev. E **78**, 051601–(1–13) (2008).
[20] I. A.Solov'yov, A. V.Yakubovich, A. V.Solov'yov, and W.Greiner, Phys. Rev. E **75**, 051912–(1–9) (2007).
[21] A.V. Yakubovich, I.A. Solov'yov, A.V. Solov'yov, W. Greiner, Europhysics News **38**, p.10, (2007)
[22] J. Geng, I. A. Solov'yov, W. Zhou, A. V. Solov'yov, and B. F. G. Johnson, J. Phys. Chem. C **113**, 6390–6397 (2009).
[23] I. A. Solov'yov, J. Geng, A. V. Solov'yov, and B. F. G. Johnson, AIP Conf. Proc. **1197**, 89–102 (2009).
[24] I. A. Solov'yov, J. Geng, A. V. Solov'yov, and B. F. G. Johnson, Chem. Phys. Lett. **472**, 166–170 (2009).
[25] J. Geng, I. A. Solov'yov, D. G. Reid, P. Skelton, A. E. H. Wheatley, A. V. Solov'yov, and B. F. G. Johnson, Phys. Rev. B **81**, 214114–(1–13) (2010).
[26] V. V. Dick, I. A. Solov'yov, and A. V. Solov'yov, AIP Conf. Proc. **1197**, 76–88 (2009).
[27] V. V. Dick, I. A. Solov'yov, and A. V. Solov'yov, J. Phys.: Conf. Ser. **248**, 012025–(1–11) (2010).
[28] V. V. Dick, I. A. Solov'yov, and A. V. Solov'yov, Phys. Rev. B **84**, 115408–(1–14) (2011).
[29] V. V. Golovlev, S. L. Allman, W. R. Garrett, N. I. Taranenko, and C. H. Chen, Int. J. Mass Spectr. and Ion Proc. **169-170**, 69–78 (1997).
[30] A. V. Zinovev, I. V. Veryovkin, J. F. Moore, and M. J. Pellin, Analytical Chemistry **79**, 8232–8241 (2007).
[31] B.R.Brooks, R.E.Bruccoleri, B.D.Olafson, D.J.States, S.Swaminathan, and M.Karplus, J. Comp. Chem. **4**, 187–217 (1983).
[32] A. P. Sutton and J. Chen, Philos. Mag. Lett. **61**, 139 (1990).
[33] F. Mittendorfer and J. Hafner, **472**, 133–153 (2001).
[34] J. C.Phillips, RosemaryBraun, WeiWang, *et al*, **26**, 1781–1802 (2005).
[35] W.Humphrey, A.Dalke, and K.Schulten, J. Molec. Graphics **14**, 33–38 (1996).