Dear Mrs. Catherine Werner,

I would like to present a Final Report on the exchange grant

"Rupture of the flexible molecular chain from adhesive surface"

Reference number: **715**

in frame of which my research visit to Technische Universität Berlin, Institut für Mechanik, D - 10623 Berlin, Germany (group of Prof. V. Popov) for two months in November-December, 2005 is supported.

Sincerely yours,
A. Filippov

Final report

to the exchange grant

"Rupture of the flexible molecular chain from adhesive surface"

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The grant has been awarded for a financial support of the research visit of Prof. A. E. Filippov (Ukraine) to Technische Universität Berlin, Institut für Mechanik, D - 10623 Berlin, Germany (group of Prof. V. Popov) for two months in November-December, 2005

During the visit we studied an artificial structure of a plate with elastic fibers interacting with rough fractal surface by Van der Waals forces. This structure has been simulated numerically to find an optimal relation between the system parameters.

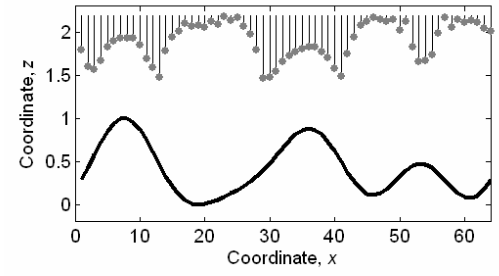
These numerical experiments were stimulated by a great attention which has been paid to dry adhesion at nano-scales which is relevant for some biological objects. It was found in particular, that a foot of the Gecko is covered by a layer of hair (fibers). Each of these fibers branches out into about 10^3 thinner ones. These smaller fibers end with a thin (5 − 10 nm) leaf-like plates. The latter structures are already small enough to be able to follow the surface roughness profile at almost molecular scale. As a rule, the synthetic systems still do not have properties comparable to natural ones, but very recent novel artificial structures which are based on relatively hard materials like carbon nano-tubes or micro-electromechanically produced 'organorods' show very good adhesive properties.

In this context, our goal during the visit was to simulate numerically such a structure of elastic fibers contacting with a rough fractal surface by Van der Waals forces to elucidate a nature of optimal relation between the system parameters. We show that there is an optimal elasticity to provide maximum adhesion force and that to have a high efficiency the artificial adhesives **must be made from stiff enough polymers**.

The force balance equations are solved numerically for different values of elastic constant and variable surface roughness. An optimal elasticity is found to provide maximum cohesion force between the plate and surface. It is shown that high flexibility of the fibers is not always good to efficiency of the system. If the elasticity is close to an optimum, the force is almost constant at a wide interval of the surface roughness. It is desirable to make system adaptive to wide spectrum of applications.

To simplify the preliminary model we restricted the motion by the z-direction (which is orthogonal to the mean positions of two contacting plates) only. An effective elasticity of the fibers in this case can be treated as a combination of bending of the hairs with their extension under Van der Waals force $K_{eff} \equiv K$. Conceptual structure of the simplified model takes a form shown in Fig1. Black line here presents a *small fragment* of fractal rough surface. The surface is generated numerically according to the standard definition: $z_0(x) = (2\pi)^{-1} \int dq\, c(q) \cos(qx + \zeta(x))$; where $c(q) = c_0 q^{\alpha}$ and $\zeta(x)$ is random phase $\langle \zeta(x) \zeta(x') \rangle = \delta(x-x')$. Gray lines in Fig.1 show schematically elastic bonds. Generally speaking, second surface, to which the bonds are attached, can be nonuniform too. However, from mathematical point of view, one can include all the inhomogeneity to one of the surfaces, without lose of generality.

The potential connecting each sole bond with the surface combines Van der Waals and elastic interactions: $U_{VdW} = (2/z^6 - 1/z^{12})/12$; $U_{elastic} = K(z-z_0)^2/2$. Corresponding forces are equal to $F_{VdW} = -\partial U_w/\partial z$ and $F_{elastic} = -\partial U_{elastic}/\partial z$ respectively. Total potential is shown in Fig.2 at different values of the distance $A=z_0$ (Fig.2a) and elastic constant (Fig.2b).



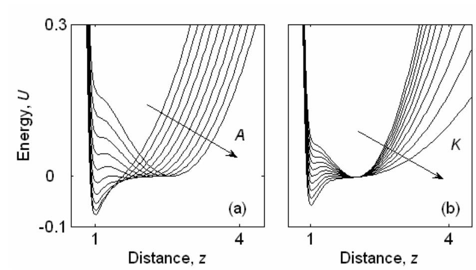


Fig1. **Fig2.**

It is seen directly that in both cases there are some regions of the parameters at which the potential has two valleys with comparable depth. *Here and below we measure all the energies, noise intensity and space scales in the units of Van der Waals potential* $U_{VdW} = (2/z^6 - 1/z^{12})/12$.

Due to general reasons of physical kinetics one can expect that at fluctuating parameters two comparable energy valleys can cause jumps between alternative states of the system. The randomness here is caused by the fractal surface $z = z_0(x)$, fiber dynamics (transferred down to the nano-scales from macro- and meso- motions of the system). It can be caused also by temperature fluctuations which are important in molecular scales.

Actual surface $z_0(x)$ is semi-fractal, it has some limited spectrum of wave vectors and it standard deviation is limited too: $<(z_0(x)-<z_0(x)>)^2>^{1/2} \sim A$, where A is "roughness". The fiber positions are distributed as well. It causes a distribution of the equilibrium forces too. In zero approximation, one can neglect an interaction between the bonds. The equilibrium in this case is given by the balance of the elastic and Van der Waals forces: $F_{VdW} = F_{elastic}$ For the fractal surface one has to solve this equation numerically. The solution is presented in Fig3.

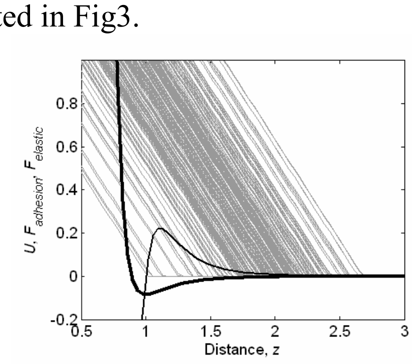


Fig3.

Gray lines show elastic forces for the family $z_0 = z_0(x)$. Bold and ordinary black lines correspond to Van der Waals potential and force respectively. The equilibrium forces and instant positions of each bond correspond to the intersections of the gray lines with the thin black one. One can integrate over these data arrays to find a dependence of the sticking force on the elastic constant at given roughness.

This procedure has been performed for different distances between the surfaces. An equilibrium distance between the surfaces is determined by the variation of the fractal structure and equal approximately to the constant A. Each value of A determines a family of the relations between the sticking force and elastic constant. The result is shown in Fig4.

Each force here has a maximum corresponding to an "optimal elasticity". These points are marked by the gray circles. Fig.5 presents how the optimal adhesive force F_{opt} and elastic constant K_{opt} depend on the amplitude A. The subplots (a) and (b) in this figure show K_{opt} in linear and logarithmic scales respectively. Optimal force F_{opt} is shown in the subplot (c). Despite of the fast asymptotics $1/z^6$ of the Van der Waals force, the optimal elasticity is found to go down (with growth of surface roughness A) much slower: $K_{opt} \sim 1/A^{1.18}$. Moreover, if the elasticity is chosen close to the optimal one the resulting **adhesive force does not go to zero even at formally infinite roughness: $A\to\infty$.**

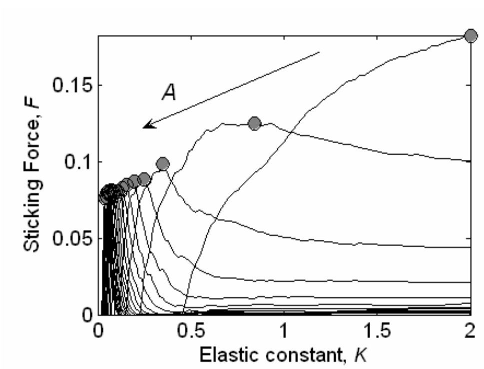


Fig4.

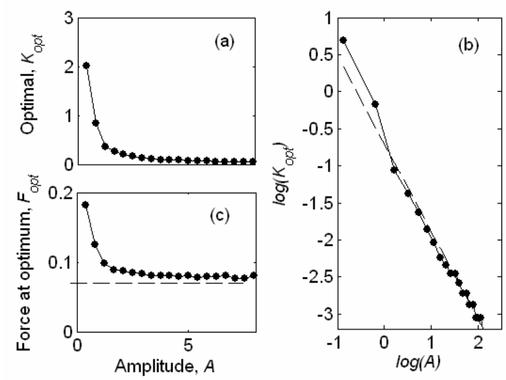


Fig5.

Even at slow dependence $K_{opt} \sim 1/A^{1.18}$ the elasticity can not be chosen optimal for all the surfaces at once. In reality adhesive force should fall down for variable roughness. However, there are many natural surfaces which have (at least) the same fractal structure at levels close to the molecular scale. So, it seems possible to choose the structure and elasticity of the "foot" quite close to the optimal one. In its turn, the existence of real Gecko foot, which is adaptive to wide variety of the surfaces, gives an '*a posteriori'* support to the statement that such **an optimization is possible.**

One aspect of the results shown in Figs.4 and 5 looks even contradictory to the intuitive expectations. The optimal elasticity is close to unit when $A\approx 1$. It leads to the highest sticking force of the same order. In the units of problem it corresponds to a characteristic distance and energy of the Van der Waals forces (see Fig.2 and note to the Eq.2). In other words, to fit well to the very smooth "slippery" surface and to create strong adhesion, it is good to have rather stiff enough fibers than very soft ones. Certainly, the ideal case $A\approx 1$ corresponds to extremely small roughness, which is comparable to the atomic scales and may not exist in the reality. However, the final fibers of Gecko's foot reach the scales close to 10 Nm, where it is really true. Very likely, artificial system has to combine both features: **soft tissues on relatively high scales** (to adapt preliminary large-scale part of the surface structure) and **hard short fibers to fit very last micro- and nano- scales.**

To complete the study, we simulated above system in dynamical approach. The equations of motion can be written as follows:

$$\partial^2 z_j / \partial t^2 = - \gamma\, \partial z_j / \partial t + F_{VdW} + F_{elastic} + \xi(z_j;t); \qquad (1)$$

Here we include random source $\xi(z_j;t)$ and dissipation $\gamma\ \partial z_j/\partial t$ which simulate together thermal and dynamic impacts to the system with an effective temperature T_{eff} :

$$< \xi(z;t)\ \xi(z';t')> = D\ \delta(z-z')\ \delta(t-t'); \qquad D = 2\gamma\ kT_{eff}\,. \qquad (2)$$

When the parameters are close to the optimum total potential has two close minimums. Dynamic chaos and randomness cause chaotic exchange of the bond states between the minimums. This effective "exchange interaction" results, in fact, in the strongest attraction between two surfaces. If the elastic constant is too large, all the bonds are mainly attracted to the upper plate and does not fit properly the rough surface. In opposite limit they can fit the surface "ideally". But, in this case they do not attract well the upper surface (due to weakness of the "springs"). Besides, one needs in a too long extension of the bonds to detach them from the down surface.

Typical instant configuration of the z-coordinate and time-averaged histogram $P(z)/P_{max}(z)$ for the probability distribution at optimal relation between the interactions are shown in left and right subplots of Fig.6 respectively.

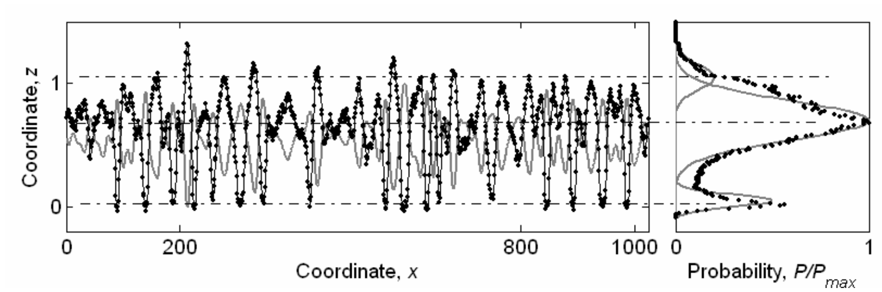


Fig6.

The numerical experiment has been repeated at different roughness of the surface (resulting in particular in different distances between the plates Δz), and for three different elastic constants: $K<K_{opt}$, $K\approx K_{opt}$ and $K>K_{opt}$. The results of the simulations are summarized in the Fig7.

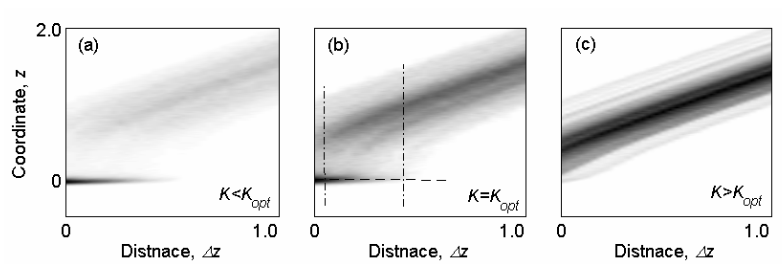


Fig7.

Each vertical cross-section in the gray scale maps corresponds to a particular histogram $P(z)/P_{max}(z)$ analogous to the shown in the Fig6. Dark gray depicts higher probability $P(z)$. The subplots (a), (b) and (c) correspond to $K<K_{opt}$, $K\approx K_{opt}$ and $K>K_{opt}$ respectively.

We expect that the performed research will stimulate new efforts to optimize elasticity and construction of artificial adhesives mimicking gecko foot-hairs. The results of this study are summarized in an article which we plan to publish in one of the internationally recognized physical journal.

Propositions for further collaboration

<u>The main result of the performed project sounds as follows</u>: artificial system has to combine both features: **soft tissues on relatively high scales** (to adapt preliminary large-scale part of the surface structure) and **hard short fibers to fit very last micro- and nano- scales.**

However, if the flexibility in direction orthogonal to the average surface is limited, additional degrees of freedom in other directions become important. To advance the study we already constructed the basic model and performed some preliminary simulations. It includes following elements: flexible soft tissue; relatively hard (but anyway, still flexible) fibers, attached to the tissue; adhesive surface which attracts the ends of the fibers by Van der Waals potential; randomness (temperature and other noise with dissipation); external force with arbitrary orientation (which can be applied to any part of the tissue).

General structure of the model is illustrated in Fig.8. Adhesive hard surface is shown by red line, flexible "foot" tissue is presented by blue line. The fibers are thin black lines attached to this tissue. In equilibrium each fiber forms some angle with the tissue. Van der Waals attraction to the surface (as well as repulsion from the bulk) bends the fibers. They find a compromise position, in which the fibers are bended and/or extended and attached to different points of the upper surface. In dynamics the distance is not fixed and fibers attract the tissue. As result, majority of the fibers fit better to the surface at arbitrary angles. This process leads to very fine fitting which seems to be very important for the practical use.

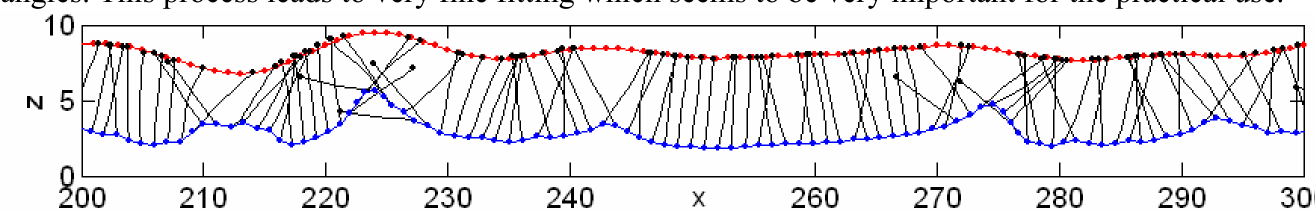


Fig.8

We plan to vary different features of this process (starting distances; surface roughness, fiber stiffness, so on) and to apply external force with different angles. Such a force should simulate a foot "closing" by real Gecko, which it applies to separate the fibers from the surface. From our previous study we expect different universal classes of behavior, corresponding to different regimes of peeling in the Fig.9.

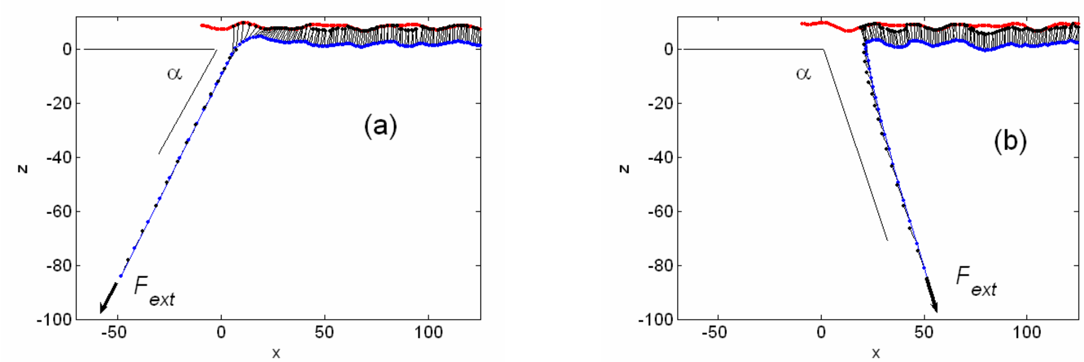


Fig.9.

Simultaneously to this report we submit next proposal to ESF**:**

"Flexible tissue with fibers interacting with adhesive surface"

We expect the proposed research will stimulate the development of new theoretical and experimental methods in a study and creation of the artificial adhesive systems at nano-scales, which is one of the main issues of the ESF program Nanotribology (NATRIBO)".