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Matters of Free Energy and a Tesseract

Introduction

Life on earth depends critically on the energy coming in from the sun, as well as on the materials existing in our biosphere. The latter may be considered a very large and open physical system with visco-elastic materials and many mobile molecules, including the essential and abundant water in our atmosphere and the oceans.

Matters of activity in such a physical system can be ascribed to its *free energy*, *F*, which means that part of the *inner energy U* of the system that can potentially be converted into physical work. In 1882, Hermann von Helmholtz contributed to the Königlich Preußische Akademie der Wissenschaften and coined the term *freie Energie*, with similar work carried out around that time by James Clark Maxwell and Josiah Willard Gibbs in England. This stimulated major research into the various forms of energy, including mechanical, electrical, chemical, or thermal energy, and their interconversions. Moreover, it coincided with major technological developments, which revolutionized various industries, particularly by exploiting electricity and chemistry.

The difference between the *inner* and the *free energy*, meaning the remaining energy *U minus F*, finally ends up in *thermal energy*, producing global warming in the long run, increasing the system's temperature *T* times its entropy *S*. Remarkably, the temperature allows to quantify precisely the *average* thermal energy of a single particle in the system, k_B *T*, with k_B being the Boltzmann constant. On the other hand, the entropy *S* is a measure of the disorder, i. e., a lack of precise information about a large system. More exactly, it characterizes the number of possible microscopic states of the individual particles of a system that comply with its macroscopic state.

Coming back to the particularly valuable free energy, the activities of nature on earth are largely determined by our environment, particularly temperature and humidity, but also light and carbon dioxide. As a consequence, there are circadian and annual cycles. For example, the optimum temperature for elongation growth in tulip petals differs for the upper and lower side of the mesophyll by 10° Celsisus, resulting in the blossoms' opening in the morning and closure in the evening.[1] On the other hand, materials such as papers based on partially hydrophilic fibers may keep their shape at low humidity levels but swell and therefore buckle at elevated ones.

In the following, we illustrate how the free energy of water molecules may be used to act precisely and exclusively at inner interfaces of materials. As an example, we focus on graphene, a two-dimensional material, on top of a cleaved natural layered

1 W. G. van Doorn and C. Kamdee, "Flower Opening and Closure: An Update," *Journal of Experimental Botany*, 65 (2014), 5749 – 57.

 https://doi.org/10.1515/9783110714883-019

crystal, mica. The internal interface between these two materials is employed to pull in selectively only water from a humid environment, thereby demonstrating its activity for *filtering molecules.* The intervening water also acts as a knife, *cutting* the tightly bonded materials at the interface. Moreover, wetting the interface with different molecules such as water and ethanol allows to control the formation of nanostructured two-dimensional molecular systems at internal interfaces. This controls the mechanical properties of the system: water *lubricates* better than ethanol, and—much to our surprise—heavy water with deuterium replacing the hydrogen lubricates an order of magnitude better than normal hydrogenated water.

The underlying activities for all these effects—cutting, filtering, and lubrication—are due to many-body effects, and therefore due to temperature and thermal energy, as well as entropy. This allows for very precise predictions of the behavior of large systems such as materials, the human body, or the Earth's atmosphere, without the need to know all details: a few degrees Kelvin—out of about 300 K on earth—determines whether an individual human or even mankind may survive. The concept of temperature allows predicting quite precisely what happens with a complex system such as a material, a biological organism, or an ecological system, even without precise knowledge of the microscopic details.

We therefore decided to expand our previously investigated metamodel for the established fundamental theories of physics for few-body systems, the Cube of Physics[2] into a four-dimensional Tesseract, the Hypercube of Physics for large many-body systems. Working practically with a model in 4D space is challenging, and we aim to accomplish this with a movie of a rotating 3D perspective of the 4D object in time.

Activities of Interfaces: Filtering and Cutting

Our work on filtering and cutting with interfaces started with an accidental observation about a decade ago.[3] Nikolai Severin from our group had deposited single layers of graphene, a two-dimensional version of graphite, onto a freshly cleaved piece of mica. Graphite and mica are naturally occurring layered minerals and were obtained as macroscopic pieces that can be easily cleaved, providing atomically smooth surfaces over macroscopic areas, up to many square centimeters. Much to our delight—and to some surprise—the deposited graphene pieces were atomically flat over large areas, which could be examined with optical microscopy and on the atomic scale with atomic force microscopy, where a scanning tip, tapping at high eigenmodes, can reliably image

2 Cube of Physics, https://cube-of-physics.org/.

3 Nikolai Severin, Philipp Lange, Igor M. Sokolov, and Jürgen P. Rabe, "Reversible Dewetting of a Molecularly Thin Fluid Water Film in a Soft Graphene-Mica Slit Pore," *Nano Letters* 12 (2012): 774–79, https://doi.org/10.1021/nl2037358.

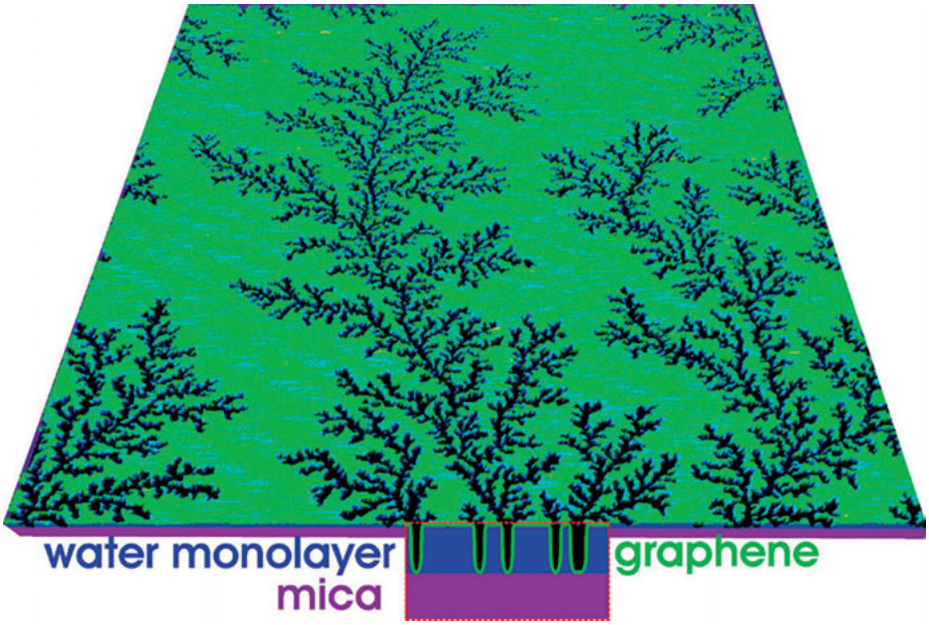

Fig. 1: Fractals in ultrathin films of water at the interface between mica and graphene in dry air during winter. The lateral and vertical dimensions are on scale of a few microns and less than a nanometer, respectively. Nikolai Severin, Philipp Lange, Igor M. Sokolov, and Jürgen P. Rabe, "Reversible Dewetting of a Molecularly Thin Fluid Water Film in a Soft Graphene-mica Slit Pore," *Nano Letters* 12 (2012): 774 – 79, doi:10.1021/nl2037358.

surface structures with atomic precision.[4] This effect went on during the summer, but when the winter came, some fractals were observed that we had not seen before. It did not take long until we realized that the flat graphene in summer may not have been in direct contact with the mica, but instead deposited on a very thin layer of water absorbed from the humid air onto the hydrophilic mica surface. During the deposition of the graphene onto the mica surface, almost all absorbed water molecules were removed, except a tightly bound first layer. In winter, however, when the ambient humidity was lower, some of the water molecules escaped the graphene-mica interface at the graphene edges, and this caused holes in the two-dimensional water layer, which became larger with time. Interestingly, the growth proceeded through fractal shapes (fig. 1), which allowed for systematic investigation and thereby for a better understanding of the underlying growth process.

Similarly, other hydrophilic molecules, such as ethanol, can wet and de-wet the interface, and mixtures between the two of them lead to interesting new phases at the

4 Nikolai Severin et al., "Atomic resolution with high-eigenmode tapping mode atomic force microscopy," *Physical Review Research* 4 (2022), 023149. https://doi.org/10.1103/PhysRevResearch.4.023149.

interface between mica and graphene (fig. 2).[5] [6] Other 2D materials such as MoS_2 and similar transition metal dichalcogenides have been employed,[7] providing a toolbox for shaping surfaces and interfaces of 2D materials on mica with intercalating water and ethanol.[8]

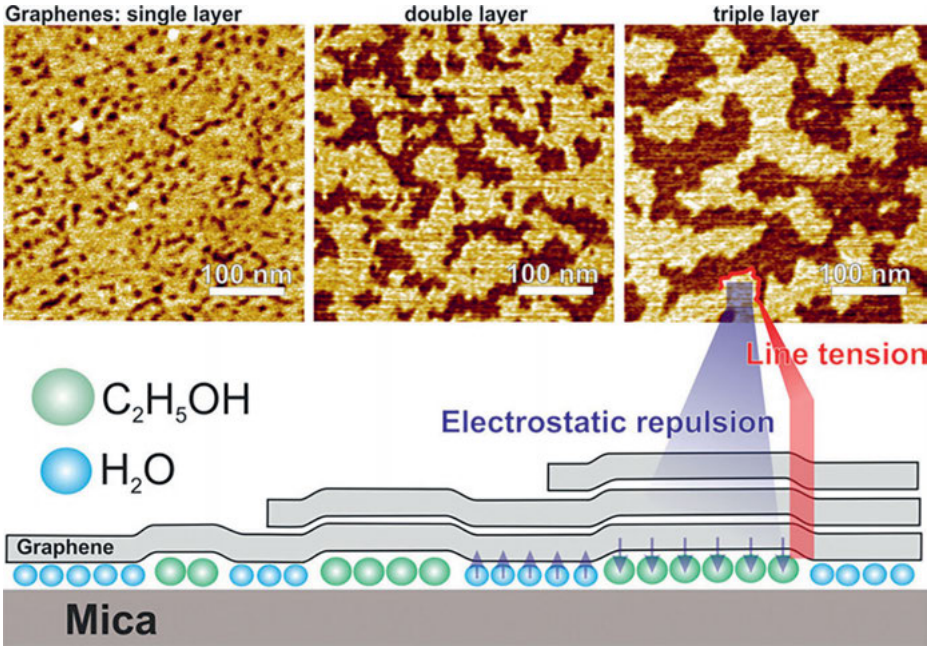

Fig. 2: Water and ethanol mix well in bulk liquids. At the interface between mica and graphene they phase separate on the nanoscale. Nikolai Severin, Jonas Gienger, Vitalij Scenev, Philipp Lange, Igor M. Sokolov, and Jürgen P. Rabe, "Nanophase Separation in Monomolecularly Thin Water-ethanol Films Controlled by Graphene," *Nano Letters* 15 (2015): 1171–76, doi:10.1021/nl5042484.

5 Nikolai Severin, Igor M. Sokolov, and Jürgen P. Rabe, "Dynamics of Ethanol and Water Mixtures Observed in a Self-Adjusting Molecularly Thin Slit Pore," *Langmuir* 30 (2014): 3455–59, https://doi.org/10.1021/la404818a.

6 Nikolai Severin et al., "Nanophase Separation in Monomolecularly Thin Water-Ethanol Films Controlled by Graphene," *Nano Letters* 15 (2015): 1171–76, https://doi.org/10.1021/nl5042484.

7 Abdul Rauf et al., "Non-Monotonous Wetting of Graphene-Mica and MoS2-Mica Interfaces with a Molecular Water Layer," *Langmuir* 34 (2018): 15228–37, https://doi.org/10.1021/acs.langmuir.8b03182.

8 Abdul Rauf et al., "Shaping Surfaces and Interfaces of 2D Materials on Mica with Intercalating Water and Ethanol," *Molecular Physics* 119 (2021): e1947534, https://doi.org/10.1080/00268976.2021.1947534.

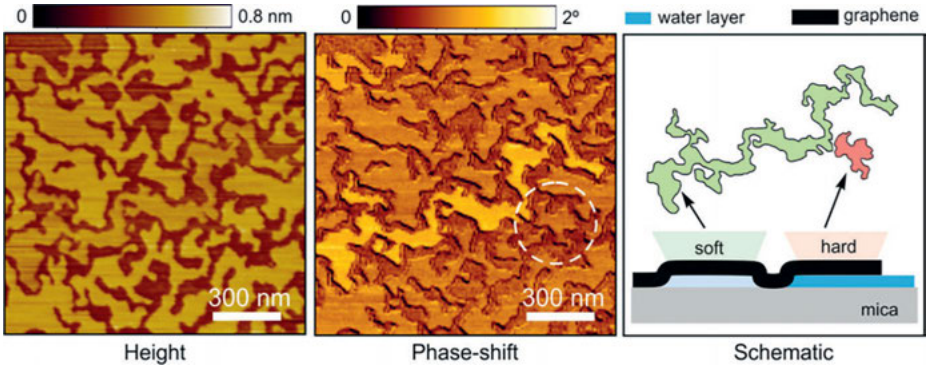

Fig. 3: Non-monotonous wetting of interfaces between mica and MoS_2 with water. Nikolai Severin, Jonas Gienger, Vitalij Scenev, Philipp Lange, Igor M. Sokolov, and Jürgen P. Rabe, "Nanophase Separation in Monomolecularly Thin Water-ethanol Films Controlled by Graphene," *Nano Letters* 15 (2015): 1171–76, doi:10.1021/nl5042484.

Interfacial Lubrication

The discovery of the easy control of ultraflat but dissimilar interfaces with small molecules, provided at atmospheric pressures and temperatures, raised the question: how to use this to control matters of materials' activities? We focused on two key interfacial materials properties: lubrication and electronic properties.

In order to investigate lubrication, we considered the graphene and MoS_2 on a mica sample as a beam, which can be bent (fig. 4) by putting it on two knife-edges and pushing on the ends of the slab with two screws. From the geometry of a thick mica slab and a monolayer of graphene or MoS_2 on top, one expects that the 2D materials would stretch upon bending the whole piece. If a 2D material sticks firmly to the mica, its bond lengths should be stretched, and if it slides, they should not. In order to monitor the bond lengths, we used Raman spectroscopy and photoluminescence, respectively, which are highly sensitive in these particular cases.[9]

Fig. 5 displays the result: for the *dry* interface without any intervening water (fig. 4B), one finds a stick-slip behavior, i. e., no sliding, while for the *hydrated* interface the 2D material is initially stretched upon a quick bend and then relaxes on a time scale of several minutes. This characterizes the lubrication due to the monolayer of water, which made its way from the ambient into the interface.

9 Hu Lin et al., "Influence of Interface Hydration on Sliding of Graphene and Molybdenum-Disulfide Single-Layers," *Journal of Colloid and Interface Science* 540 (2019): 142–47, https://doi.org/10.1016/j.jcis.2018.12.089.

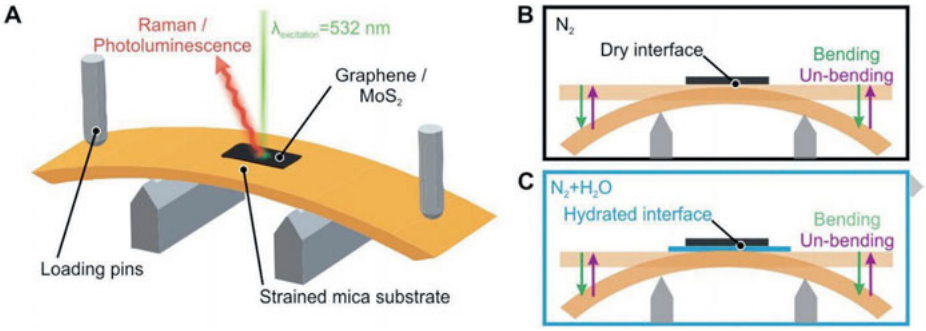

Fig. 4: Experimental set-up for the investigation of interfacial lubrication. Hu Lin, Abdul Rauf, Nikolai Severin, Igor M. Sokolov, and Jürgen P. Rabe, "Influence of Interface Hydration on Sliding of Graphene and Molybdenum-disulfide Single-layers," *Journal of Colloid and Interface Science* 540 (2019): 142 – 47, doi:10.1016/j.jcis.2018.12.089.

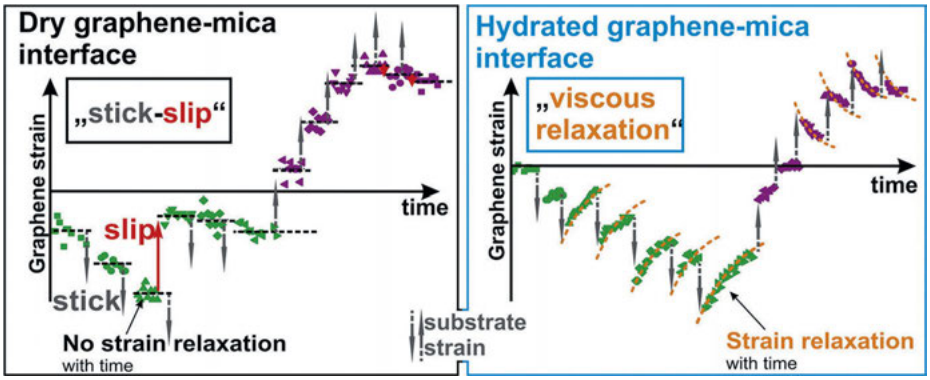

Fig. 5: Influence of interface hydration on sliding of graphene and molybdenum-disulfide single layers. Hu Lin, Abdul Rauf, Nikolai Severin, Igor M. Sokolov, and Jürgen P. Rabe, "Influence of Interface Hydration on Sliding of Graphene and Molybdenum-disulfide Single-layers," *Journal of Colloid and Interface Science* 540 (2019): 142 – 147, doi:10.1016/j.jcis.2018.12.089.

Of course, the lubricating activities depend on both the interfaces and the lubricants. The described setup allows for the investigation of the lubricating activities of a broad range of materials, both with regard to the solids and the lubricants.

Thin Film Electronics

When Herbert Kroemer, in his Nobel Prize lecture in 2000, coined the provocative phrase "the interface is the device," he referred to the revolutionary development of information technologies based on thin film semiconductors. Today, understanding and controlling charge transfer through molecular nanostructures at interfaces is

still of paramount importance, particularly for electronic devices and contact electrification as well as bioelectronics.

We investigated the influence of intercalation and exchange of molecularly thin layers of small molecules (water, ethanol, 2-propanol, and acetone) on charge transfer at the well-defined interface between an insulator (muscovite mica) and a conductor (graphene). Raman spectroscopy has been used to probe the charge carriers in graphene. While a molecular layer of water blocks charge transfer between mica and graphene, a layer of the organic molecules allows for it. The exchange of molecular water layers with ethanol layers switches the charge transfer very efficiently from off to on and back. We proposed a charge transfer model between occupied mica trap states and electronic states of graphene, offset by the electrostatic potentials produced by the molecular dipole layers, as supported by molecular dynamics simulations. Our work demonstrates how the intercalation of molecules of volatile liquids can reversibly affect charge transfer at interfaces. This implies its strong impact on the function of hybrid inorganic–organic electronic devices in different ambients and potential applications, including sensors and actuators.

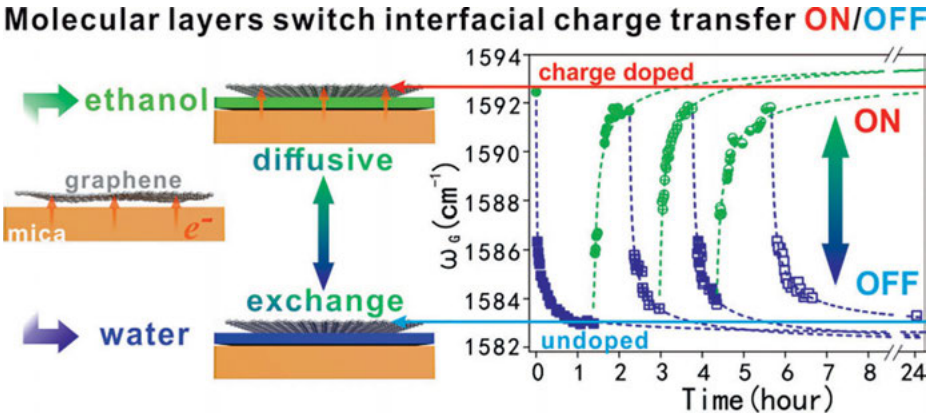

Fig. 6: Molecular layers switch interfacial charge transfer ON/OFF. Hu Lin, José D. Cojal González, Nikolai Severin, Igor M. Sokolov, and Jürgen P. Rabe, "Reversible Switching of Charge Transfer at the Graphene-mica Interface with Intercalating Molecules," *ACS Nano* 14 (2020): 11594 – 11604, doi:10.1021/acsnano.0c04144.

The Cube of Physics and the Hypercube

Towards the end of the twentieth century, the standard model of physics has been shown to encompass the current knowledge of physics. It describes all known elementary particles and the interactions between them. It even predicted phenomena such as the Higgs-Boson, which was discovered only decades later, when giant particle accelerators had become available. Nevertheless, the model exhibits a major deficiency: grav-

ity does not fit into the picture. For more than fifty years, physics did not manage to integrate gravity into the theoretical quantum-mechanical framework. As a consequence of this theoretical deficiency, events such as the big bang or the interior of black holes can still not be explained convincingly.

The Cube of Physics (fig. 7) is a spatial model of physics. The idea to establish a map of physics based on the natural constants G, c, and h goes back to the Russian physicist Matwei Bronstein in 1933.

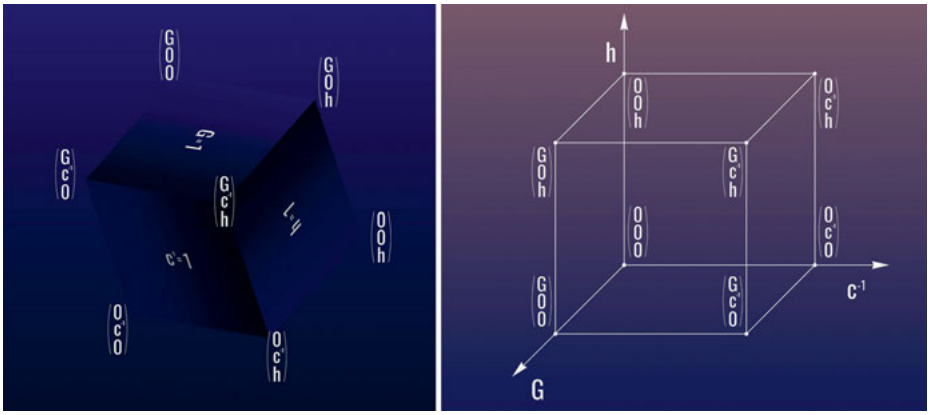

Fig. 7: The Cube of Physics 2022, https://cube-of-physics.org.

The gravitational constant G determines the force between two separate masses. Implicitly, this was measured for the first time at the end of the eighteenth century by determining the density of the earth. Also, the bending of space-time in general relativity is connected to G. The speed of light c is the natural constant known for the longest time. Its value is fixed exactly in the meantime. Firstly, it was determined in the second half of the seventeenth century based on astronomical observations. All electromagnetic and gravitational waves travel at speed c. In quantum mechanics, Planck's quantum of action h describes the ratio of energy and frequency of a photon. Max Planck discovered it at the end of the nineteenth century.

However, the Cube of Physics does not include Boltzmann's constant k_B, which Max Planck had introduced explicitly into physics in his seminal lecture on the temperature-dependent radiation of a black body.[10] Indeed, the three-dimensional Cube of Physics does not assign any distinct space to thermodynamics and statistical physics, and this calls for a novel metamodel of physics with four axes: the analog of the Cube of Physics in four-dimensional space, i. e., a tesseract (fig. 8), or the Hypercube of Physics.

10 Max Planck, "Zur Theorie des Gesetzes der Energieverteilung im Normalspectrum," *Verhandlungen der Deutschen Physikalischen Gesellschaft* 2 (1900): 237–45.

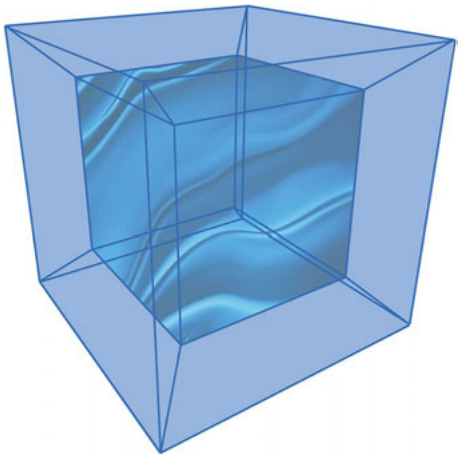

Fig. 8: 2D image of the 4D hypercube (tesseract).

Mathematically, a tesseract is the 4D analog to the 3D cube and the 2D square. However, while we know how to display a 3D object in a 2D plane by employing a perspective view, we are not used to displaying a 4D object in a 2D plane. One can achieve this upon employing time: a movie displaying sequential images of perspective drawings of the 4D Cube allows one to experience the structure and the symmetries of the tesseract.[11]

Concluding Comments

In large physical systems, such as the materials in our biosphere, *matters of activity* can be ascribed to their *free energy*, i. e., that part of the *inner energy U* of the system, which potentially can be converted into physical work. Temperature is a single key parameter, which can control its activity independent of the exact system size. Internal interfaces of materials are typical structural elements, which permit one to employ the free energy of, for instance, water in our atmosphere to drive processes such as filtering and cutting of materials: the water may act as a *sensing knife* for heterogeneous materials, being first filtered from the ambient and then used to cut internal interfaces of the materials. Moreover, water may act there as a lubricant, or it may work as the active element of an electronic device.

The key to all these processes is the temperature of the system, which explains why we should take good care of it. Our biosphere has established a rather stable average annual temperature over thousands of years, with only moderate fluctuations dur-

11 "Tesserakt," Wikipedia, https://de.wikipedia.org/wiki/Tesserakt, and https://de.wikipedia.org/wiki/Tesserakt#/media/Datei:Tesseract.gif. The "snapshot" in fig. 8 may be irritating, as it suggests an inequivalence of the eight 3D cubes, notabene a smaller inner and a larger outer cube, as well as six quadratic pyramids. The "Tesserakt" video, however, displays their equivalence.

ing ice ages and warm times. However, physical processes inadvertently also produce thermal energy, which has heated our atmosphere significantly during global industrialization: the average annual temperature changed on the order of a percent, i. e., a few degrees, since the late nineteenth century. As globalization continues, the consequences may become dramatic rather soon, if we do not counteract—for example, by smartly employing free and thermal energy.

Acknowledgments:
This work is based on the interaction with many individuals over the past years, including particularly José D. Cojal González, M. Fardin Gholami, Carlos-Andres Palma, Christian Kassung, and Matthias Staudacher from Matters of Activity, Hu Lin, Abdul Rauf, Bita Rezania, Nikolai Severin, and Stefan Kirstein of my research group, and Igor Sokolov in the Department of Physics.