

Breaking Barriers: Molding Thermodynamics by Geometry of Nanostructures

Marina Simović Pavlović^{1,2*}, Maja Pagnacco³, Bojana Bokić¹, Darko Vasiljević¹,
Marija Radmilović-Radenović¹, Branislav Radenović¹ and Branko Kolarić^{1,4}

¹Photonics Center, Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

²Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11120 Belgrade, Serbia

³Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia

⁴Micro- and Nanophotonic Materials Group, University of Mons, Place du Parc 20, 7000 Mons, Belgium

*Tel: (00381) 604273777, e-mail: simovicmarina99@gmail.com

ABSTRACT

Convective, conductive, and radiative mechanisms of thermal and optical management are essential for life, and they are often interwoven with geometry in Nature. Nanostructured materials have properties that depend on size and shape, are entirely different from their bulk counterpart, and very often exhibit size-dependent physical responses. In this study, we reveal the effect of corrugation and geometry on thermodynamic properties, i.e., heat capacity. The presented results highlight that the multifaceted geometry of natural photonic structures strongly shapes the thermodynamic response of the composite system, and, in some extreme cases, exhibits negative heat capacity. Besides the fundamental importance of revealing the geometrical constraints responsible for unusual thermodynamic response, the presented study offers the concept of shaping heat capacity on command by controlling the geometry of the system without changing its chemistry.

Keywords: nanomaterials, heat capacity, natural photonics, thermodynamics, optics.

1. INTRODUCTION

Thermodynamics is the best example of phenomenological science, where development starts from observations and proceeds by induction and conjectures to general laws, often improperly called "principles" because these conjectures are not fundamental [1]. However, thermodynamics is ultimately connected with the development of atomic and quantum theory, even though thermodynamics keeps a distance from assumptions about the "ultimate" nature of things [2].

On the other hand, photonics, as part of optics, is not ultimately related to thermodynamics. However, in a broader sense, photonics is linked with the structuring of matter. Controlling the structuring affects optical properties, offering passive and active control of light and surface properties, i.e., wetting.

In a simple sense, the energy and entropy of a composite system, such as nanostructures, are additive over the constituent subsystems and do not depend on the system's size. The presence of an interface (a real, not ideal Gibbs interface) causes, in some cases, the appearance of discontinuity and size-dependent behavior.

In the study, we reveal the effect of corrugation on thermal management for the first time to our knowledge. The presented results highlight that the multifaceted geometry of natural photonic structures with rich and complex interfaces powerfully shapes the thermodynamic response of the composite system, and, in some extreme cases, the composite system exhibits a nonreciprocal response [3] or even a decrease in heat capacity that highlights the appearance of highly effective cooling properties.

2. EXPERIMENTAL METHODS

Specimens of *Morimus asper funereus* and *Euchroma giganteum* are air-dried and obtained as a gift from the collection of the Nanophotonics Lab, Institute of Physics, University of Belgrade. No further sample preparation was necessary for the described measurements apart from electron microscopy observation. All analyses are performed using the insects' wings. The schematic view of the setup used for measuring the temperature gradient is shown in Figure 1.

3. DISCUSSION

In this article, we reveal that natural photonic structures with complex geometries and multifaceted interfaces strongly affect thermodynamic properties of matter that, in extreme cases, lead to a system that exhibits significant decreases of heat capacity in some temperature ranges. The natural photonic structures [4, 5] have already been studied for active and passive control of light and various material applications. In this study, we recorded the thermodynamic response of natural photonic structures by measuring heat capacity as a function of temperature and using a thermal camera to monitor the distribution of thermal gradient after irradiating beetle elytra with a

laser. The natural photonic structures of insects, mainly composed of polysaccharide chitin, are not broadly studied from a thermodynamic perspective, especially with the goal of exposing the effect of corrugations on thermodynamic response. First, we present DSC measurements of two beetle species (Fig. 2), namely *M. funereus* and *E. giganteum* that show the effect of the micro-architectures on the heat capacity as a function of temperature.

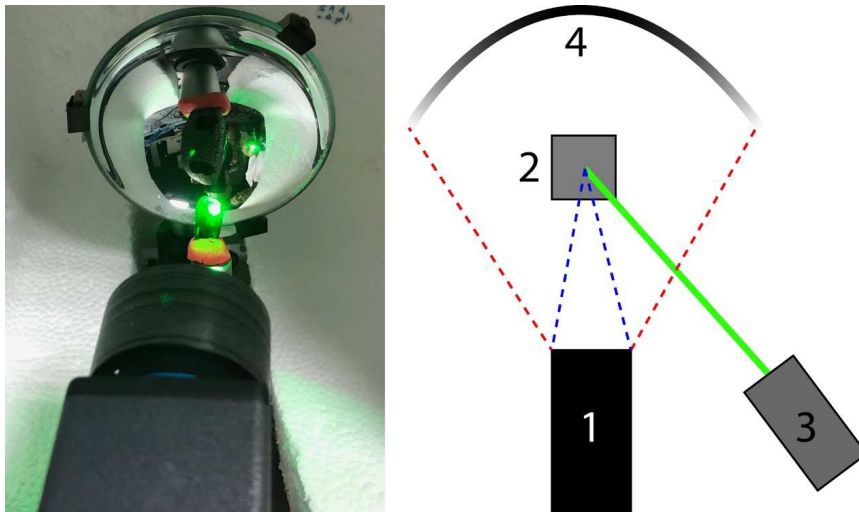


Figure 1. Setup for measuring the temperature gradient at elytra after irradiation with laser: (left) setup in the laboratory during the experiment, (right) scheme of the setup (1 - FLIR camera; 2 - aluminum mount with the sample; 3 - laser pointer at 532nm; 4 - spherical mirror).

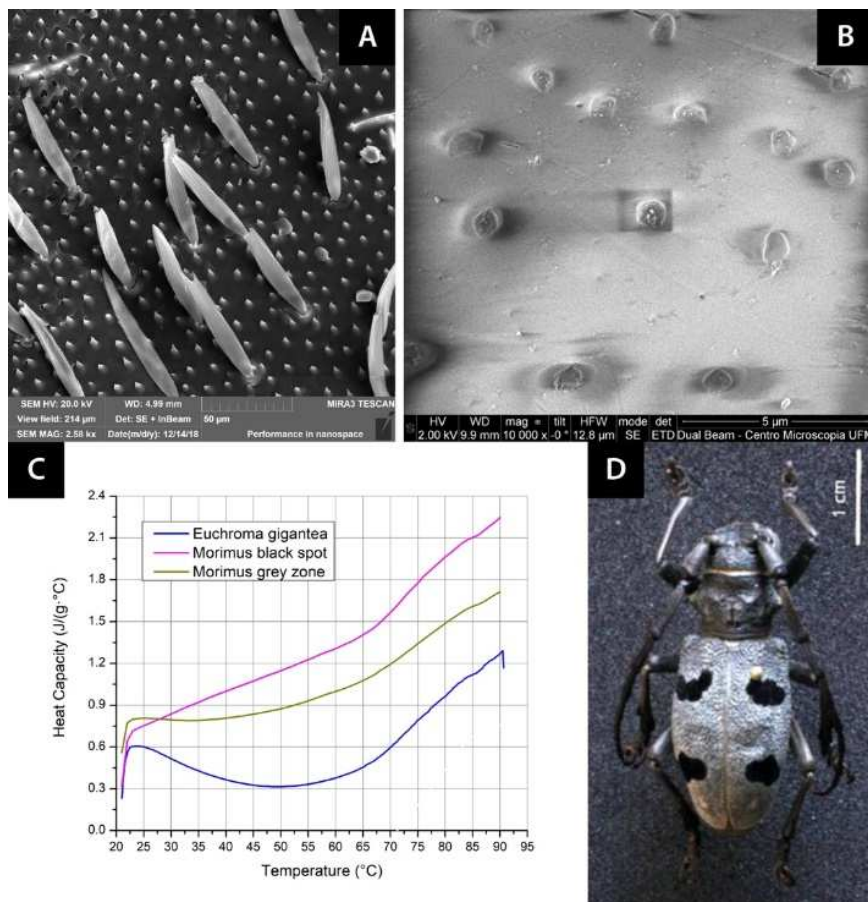


Figure 2. The microstructures occurring on (A) the elytra of *Morimus asper funereus*, and (B) *Euchroma giganteum* beetles observed by SEM. The heat capacity as a function of temperature is measured in the range of 20°C-90°C (C). An image of *Morimus asper funereus* (D). Figure (B) was reproduced from, Figure (D) was reproduced from [7].

Additionally, the *M. funereus* has a composite elytra consisting of a grey part with four black patches. In a previous study by co-authors of this article, it is shown that nanostructures occurring in the elytra of *M. funereus* manage heat transport [7] in an unusual way. In this account, the heat capacity of the black spots is independently investigated. In many systems, the increase in temperature causes the heat capacity to increase, and for many planar films, the observed dependence is linear or almost linear. The divergence of the heat capacity as a function of temperature from linearity indicates the effects of nano/micro-corrugation on heat management. Particularly in the case of *E. giganteum*, the functional dependence noticeably diverges from linearity: it exhibits a parabolic profile between 25 and 60°C (Fig. 3).

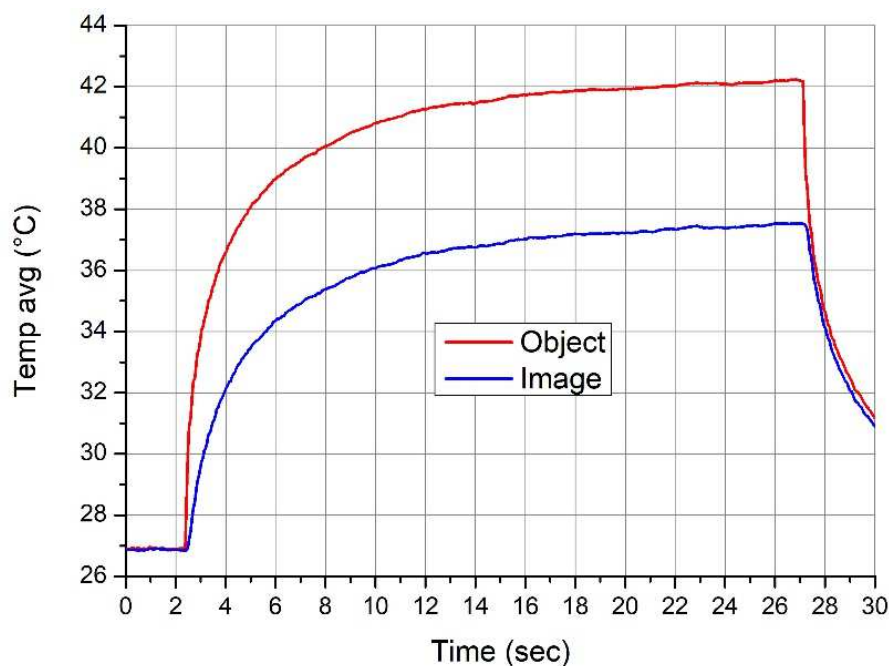


Figure 3. Average temperature differences of the outer (object) and inner (image) side of elytra illuminated by laser pointer at 650 nm.

The decrease of the heat capacity as a function of temperature perfectly matches the results obtained by irradiating elytra by laser. We did not expect to have any thermal gradient for such thin samples as elytra, but the results show highly effective cooling caused by the corrugation/nanostructures of elytra. Additionally, we perform image analysis using two-dimensional fast Fourier transformation (2D FFT), implemented in the Gwyddion software package for scanning probe microscopy data visualization and analysis.

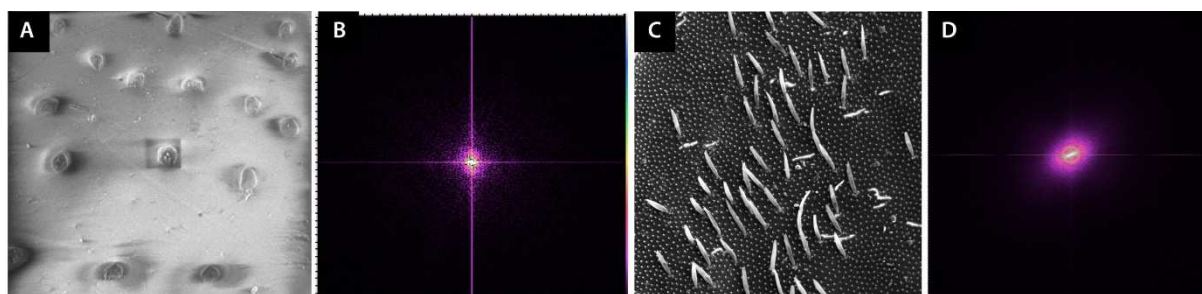


Figure 4. *Euchroma giganteum* – (A) SEM image of the elytra [6], (B) 2D FFT of Fig.4A image; *Morimus asper funereus* – (C) SEM image of the elytra, (D) 2D FFT of Fig.4C image.

The image analysis (Fig. 4) shows the effect of geometry on 2D FFT. When unusual heat management is observed (decrease of the heat capacity as a function of heating), the 2D FFT image shows that the periodicity is dominantly manifested in one direction (a linear form of the 2D FFT spectra). In contrast, in the case of well-expected thermal behavior, the 2D FFT images of the structure are almost circular, which means that two mutually normal directions are equally periodic.

4. CONCLUSIONS

However, our experimental results and theoretical analysis show that condensed systems with complex geometry and multiple interfaces shaped heat propagation in an unprecedented way and, in extreme cases, could cause a significant decrease in heat capacity values. The discovery of dependence between heat capacity and geometry in natural photonic structures offers the possibility to mimic these complex geometries for the development of highly energy-efficient materials. Additionally, the presented results show that Wolfgang Pauli was not entirely right in describing surface/interface as the devil's creation [8]. The presence of surface/interface indeed brings a lot of challenging tasks in the physical description of the system, but it also brings a plethora of new effects that could lead to new breakthroughs in material science and technology. Furthermore, the given article extends the power of photonics in the field of thermodynamics and offers the possibility of using the structuring of interfaces (not chemical modifications) to mold heat capacity and thermodynamic properties of materials.

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