

【Review Paper】

Some Biological Hints on the Control of Heat and Mass Transfer*

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Abstract

This review paper explores the possibilities of the control of heat and mass transfer associated with drought tolerance and freeze tolerance. The accumulation of some metabolites, such as proline and trehalose, are effective for drought tolerance. The special microstructures on the surfaces of some plants and insects in deserts are effective for collecting moisture in the air. Methods of preserving crops will be improved by the mimetic of the drought tolerance. Calcium ions and a protein are effective for the retrieval of damaged cell membrane due to ice formation. Ice crystal growth is inhibited by some substances such as antifreeze proteins. The cryopreservation of foods and organs will be improved by the mimetic of the freeze tolerance.

Key words: Defense Reactions, Biomimetics, Drought Tolerance, Freeze Tolerance, Metabolites, Antifreeze Protein

1. Introduction

The purpose of studying heat transfer is to understand basic concepts concerning thermal insulation, heat transfer enhancement and temperature control⁽¹⁾. Heat transfer enhancement clearly contributes to energy-saving and environmental preservation. Therefore, energy-saving and environmental preservation are the purposes of studying heat transfer.

Many methods and techniques for the enhancement and control of heat transfer have been investigated. In particular, methods of enhancing convection have been widely proposed, designed and utilized. These methods were classified based on the mechanism in some reviews^(2,3). The control of heat transfer was also referred to in these reviews. The present author extends the classification. Table 1 shows our new review. The categories are: passive methods, active methods, destabilization methods, multiphase methods and control methods.

In the passive methods, the heat transfer surfaces are modified, while the fluid flows are unchanged. Thus, the terms in the governing equations of momentum and energy are the same as those in the case without such methods. The boundary condition is modified. Examples of the methods are as follows: the fin effect of the extended heat transfer surface, a discontinuous surface to attenuate the development of boundary layers such as offset-fin arrays, the artificial cavities of high-performance boiling surfaces for the purpose of maintaining bubble nuclei, and so on.

In the active methods, the flow field is modified. Thus, the convection terms in the governing equations are different from those in the case without such methods. Examples of the methods are as follows: the insertion of cylinder in flow, the attachment of vortex generators on heat transfer surface, and so on.

In the destabilization methods, flow oscillations or vortices are generated. The unsteady terms in the governing equations are significant. Examples of the methods are as follows: vortex streets generated by an obstacle located near the heat transfer surfaces, oscillating plates near the surfaces, and so on.

In the multiphase methods, an immiscible substance is added to the fluid flow. The interaction between the substance (dispersed phase) and carrier fluid (continuous phase) flow enhances heat transfer. The external-force terms in the governing equations associated with the phase interaction are significant. Examples of the methods are as follows: bubbles or immiscible droplets are mixed into liquid flow, particles made of magnetic substances are mixed into gas flow, and so on.

In the control methods, the external forces, which are controllable, are added to the flow field. The external-force terms in the governing equations are significant. Examples of the methods are as follows: the imposition of a magnetic field or an electric field (by using electro-hydro dynamic effects) on the flow, and so on.

In order to establish a sustainable society, further energy-saving and environmental preservation are required. In such a situation, it is not enough to improve the methods mentioned above. Furthermore, almost all the methods are not directly applicable to newly-emerging heat transfer problems, such as micro-scale and nano-scale heat transfer, and so on. It should be noted that the methods mentioned above are also not applicable to the temperature control, which is crucial for chemical reaction in manufacturing and food engineering. The creation of new methods based on the new paradigms and viewpoints are necessary and would be indispensable. We can obtain some hints for the creation from animals and plants because micro-scale heat transfer and temperature control is common in both.

2. Biomimetics

For three decades, studies have been carried out on the features and functions of creatures in order to achieve new, more appropriate materials and functions, which work similar to or better than the functions of creatures⁽⁴⁾. This is called biomimetics⁽⁵⁾. Recently, the concept of biomimetics has been extended to designs and processes in vivo. Studies on the new concept are named bio-mimicry. Typical examples of products or prototypes based on biomimetics or bio-mimicry are shown in Table 2. Many other examples are shown in Ref. (4).

As far as the present author knows, products and prototypes concerning the biomimetics of heat transfer have not yet been developed. In Ref. (4), the modeling of transport phenomena in the human body, such as thermal mannequins, blood-vessel systems, and respiratory systems, are described in detail. Measurements and analyses on the blood flows and cells in human bodies are also explained. These studies have been made necessary by medical science and air-conditioner manufacturers. However, a human body is a highly complicated system. It is not easy to obtain hints about biomimetics associated with heat and mass transfer from human bodies. It is expected that we will be able to focus on the heat and mass transfer of creatures with simpler systems.

3. Existence of creatures

The earth is a miraculous planet with an average temperature of approximately 18 degrees near its surface a year. This is because the earth is covered with air and water whose thermal capacities are high enough. The cells of creatures are able to retain their structure at this temperature. Various organs composed of many cells are able to exhibit their functions. A lot of vital mechanisms for the cells, the tissues, the organs, and the organ groups are governed by the control systems⁽⁶⁾. Thus, the creatures are able to exist.

Table 1 Typical classification for the control of heat transfer

Classification	Mechanism	Application example
Passive method	Modification of surface	Discontinuous heat-transfer plate High-performance boiling surfaces
Active method	Modification of flow field	Insertion of column and a thin plate Vortex generators on surface
Destabilization method	Flow oscillation	Oscillating plates Vortex street
Multiphase method	Adding immiscible substance to flow	Bubbles, Droplets, Magnetic particles
Control method	Adding external forces to flow field	Electric field (EHD) Supersonic wave

Table 2 Examples of biomimetic products

	Products	Origins
Practical use	Hook-and-loop fasteners Adhesive tape Hydrophobic, stain-free paint Oil-stain-free tile Flexible optical fiber Wing of fan Design of airplane wing Automobile design Ventilation of office building complexes Ceramic processing technology	Seeds of burdock Gecko feet Lotus leaves Shell of snail Sponge Snail Whale's shape Boxfish Termite mounds Shell of abalone
Experimental stage	Smart clothes Shape-changeable wing	Ramentum of pine Bird's wing

The cells are composed of proteins, carbohydrates, lipids, inorganic salts and water. The major element of these substances is water, regardless of the organs or species of creature. All the other substances, except for the lipids, are soluble in water. Thus, water contributes to the transport of the other substances in vivo in the physical point of view, and contributes to the field of chemical reactions in vivo in the chemical point of view. In addition, the specific heat, the latent heat and the phase change temperature of water are higher than those of other liquids whose molecular weight and molecular configuration are similar to water. These peculiar characteristics depend on the hydrogen bond of water molecules. They suppress a rapid change in temperature, support the mechanisms of the cells, tissues and organs, and are extremely effective for creatures. Therefore, the existence of a creature depends to a large degree on the miraculous substance of water.

4. Stressors

Creatures do not usually exhibit their abilities clearly except for at times when the environment changes from its state of equilibrium. When a creature suffers due to an external stimulus, it will be in a state of stress. The external stimuli are called stressors. Various stressors have been studied⁽⁷⁾. The present author classifies these stressors into (i) physical aspect, a chemical aspect or a biological aspect, and for each aspect, (ii) a cell level, an immobile level such as plants and small insects and a mobile level such as animals. Table 3 shows typical stressors in each of the categories. The creatures are threatened when the quality or quantity of the stressors exceeds a threshold. In particular, the stressors of a low temperature and dryness deprive creatures of the miraculous characteristics of water mentioned above. Thus, these stressors are fatal. The function

and the material of creatures related to heat and mass transfer appear in the defense reactions of the creatures when escaping from such fatal situations. In the following, examples of defense reactions and the possibility of the biomimetic control of heat and mass transfer are shown with reference to drought tolerance and freeze tolerance.

5. Drought tolerance

5.1 Metabolites

Some metabolites, which adjust the osmotic pressure of cells, have recently been paid attention to in relation to drought tolerance. One of the metabolites is proline, which is an amino acid. Enzymes for synthesizing proline are increased by drought stress. At the same time, enzymes for decomposing proline decrease. It is considered that a large amount of prolines are stored in cells as a result, and that they adjust the osmotic pressure of cells ⁽⁸⁾.

Some other metabolites, such as trehalose and raffinose, also contribute to drought tolerance. These oligosaccharides do not inhibit the activities of other metabolites and enzymes, even if they are accumulated in cells. Trehalose is thought to prevent cell membrane and intracellular proteins from dehydrating by inducing the glass transition of water. This is because the concentration of trehalose becomes higher when some plants and insects suffer from drought stress.

Mammals do not have trehalose in their cells, but have glucose, which does not act as a drought-tolerant substance. Thus, the insertion of trehalose into mammals' cells has been attempted ^(9, 10).

5.2 Functional surfaces

It is not expected that creatures living in deserts will harvest water from the ground or underground. Nevertheless, some insects and plants can survive. This is because they have special devices to collect moisture from the air. Some species of the plant genus *Tillandsia* have thick and internally curving leaves. The leaves are covered with microstructures called trichomes. These leaves gather moisture in the air. Note that these species of *Tillandsia* have no roots.

The tenebrionid beetle living in the Namib Desert collects drinking water from early-morning fog by using its special surface ⁽¹¹⁾. The elytra of the beetle are covered with an array of bumps. The peaks of the bumps are smooth and hydrophilic. The fog water droplets settle on the peaks, forming drops. Other areas, including the sides of the bumps, are covered by a microstructure coated in wax. These areas are hydrophobic. The fog water droplets are blown from near these areas to the hydrophilic peak regions. Eventually, the drops at the peaks are detached and roll down the tilted surface of elytra to the beetle's mouth.

Table 3 Various stressors

	Cell level	Immobile level	Mobile level
Physics	Temperature Dryness Pressure Ultraviolet rays	Temperature Dryness Flame Ultraviolet rays	Temperature Dryness Flame Sound, Electric current
Chemistry	Ion concentration Oxygen concentration Medicine	ph Oxygen concentration Heavy metal	Medicine Toxin Oxygen concentration
Biology	Bacillus Virus	Bacillus Harmful insect	Bacillus Virus

The biomimetic potential of the structure is referred to in the references (11): a water-trapping tent, water condensers and engines. Zhai et al. mimicked the structure by creating a hydrophilic surface with superhydrophobic coatings⁽¹²⁾. They referred the potential applications of such surfaces to a controlled drug release coating and lab-on-chip devices. The surface of the plant leaves covered with trichomes and the tailor-made structure of the beetle elytra are similar to the extended heat transfer surface or high-performance boiling surface, which belongs to the passive methods for heat transfer enhancement.

6. Freeze tolerance

6.1 Cell membrane retrieval

Since the volume of intracellular water increases through its freezing, the structure of cells is destroyed. When extracellular water freezes, dehydration inside cells and cell membrane destruction occur. The following hypothesis has been proposed⁽¹³⁾: the calcium ion and a certain kind of protein enter into cells from the damaged part of the membrane and contribute to membrane retrieval.

6.2 Freeze-tolerant insects

Many insects are freeze-tolerant. This is because they contain a large amount of glycerol in their bodies⁽¹⁴⁾. Glycerol lowers not only the freezing point but also the supercooling temperature. The glycerol concentration in some insects increases in autumn, and decreases in spring. Glycerol is added to the samples of human or bull sperm when they are kept frozen and remain viable. Some other insects have ice-nucleating agents in order to avoid a rapid growth of ice.

6.3 Antifreeze protein

Fish are freeze-intolerant. The concentration of antifreeze substances rapidly increases when some fish living in a cold sea are subjected to temperature which is lower than the freezing point of their body fluid. The substances inhibit the growth of ice crystals in capillary vessels and cells. As a result, a fatal situation, in which the blood vessels are obstructed by ice crystals, is avoided.

Only the small, unusual shapes of ice crystals are observed in the solution of antifreeze compounds under a thermal equilibrium state at sub-zero degrees (For instance, a bi-pyramidal shape in the case of the antifreeze protein type I from winter flounder⁽¹⁵⁾). The following hypothesis of the antifreeze mechanism for this protein has been accepted: the hydrogen atoms of the hydrophilic residues of the protein are bonded to the oxygen atoms of water on the surface of the ice crystal⁽¹⁶⁾. Consequently, many hydrophobic residues orient themselves away from the ice surface, and interfere with the approach of water molecules towards the surface⁽¹⁷⁾. However, the following counterexamples have been discovered: the solutions of mutant protein, in which the threonine residues are replaced with hydrophobic valine residues, show a similar antifreeze effect, while the solutions of other mutant protein, in which the threonine residues are replaced with more hydrophilic serine residues, show a low antifreeze effect⁽¹⁸⁾.

The present author carried out a molecular dynamics analysis on a mixture of supercooled water, a hexagonal ice crystal and segments of winter flounder antifreeze protein⁽¹⁹⁾. The segment has a helical structure, and consists of nine alanine residues (Ala25, Ala26, Ala28, Ala29, Ala30, Ala31, Ala32, Ala33 and Ala34), two threonine residues (Thr24 and Thr35) and one asparagine residue (Asn27). Mutant segments were also used. The models were arranged so that their helical axes were parallel to the z-axis in Fig. 1 at the initial instant. Thr24 was located at the lowest point. The z-component of the zenith angle of the segment increased as time proceeded, and then fluctuated around its

average value of 14 degrees. Some hydrophilic sites of Thr24 and Asn27 (indicated with an arrow in Fig. 1) were close to the ice surface. This is due to the hydrogen bond between the hydrophilic sites of these residues and the water molecules, and the hydrogen bond between these water molecules and the water molecules on the ice surface. The valine and serine residues in the mutant segments do not approach the prism face of the ice crystal compared with the threonine residue located near the asparagine residue.

Five segments were placed side by side (See Fig. 2) near the ice surface in order to examine the effects of the aggregated state of the proteins on the motion of the segments. The helical axes of these segments were parallel to the z-axis at the initial instant. The z-component of the zenith angle of the segments fluctuated around its average value of 5 degrees⁽¹⁹⁾. Thus, the motion of each segment was attenuated. This is because of the gathering of water molecules caused by hydrophobic hydration, not only around alanine residues but also around the methyl sites of threonine residues.

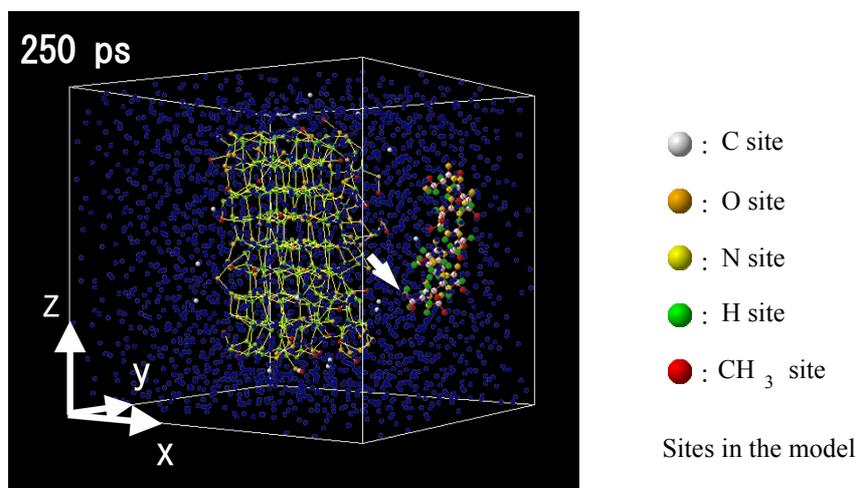


Fig.1 Snapshot of a twelve-residue segment of antifreeze protein type I and a hexagonal ice crystal in supercooled water (yellow lines represent the possibility of hydrogen bond among water molecules in ice).

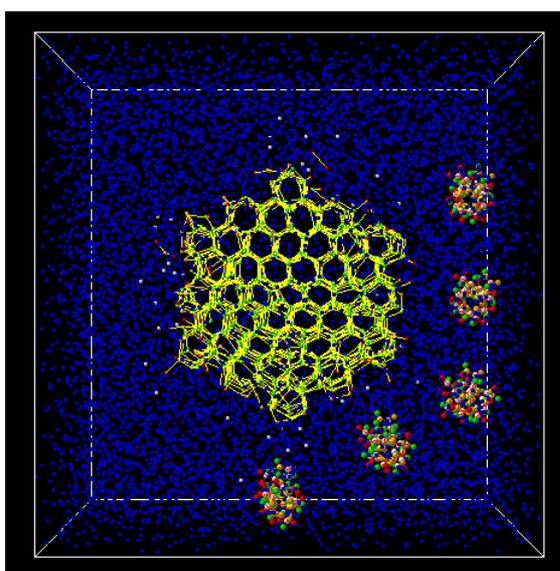
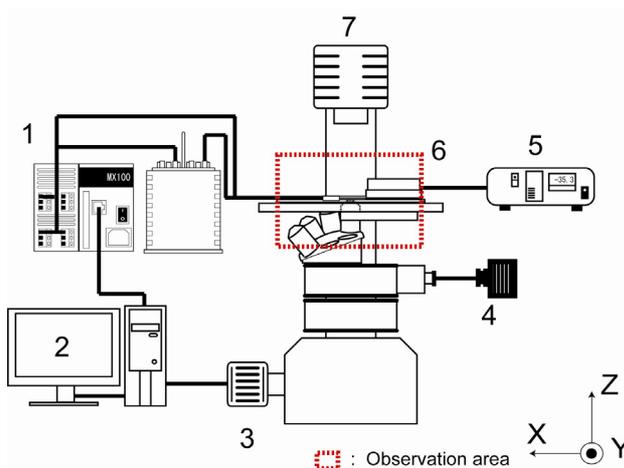


Fig.2 Snapshot of five segments of antifreeze protein type I and a hexagonal ice crystal in supercooled water (yellow lines represent the possibility of hydrogen bond among water molecules in ice).



1: Data logger, 2: PCs, 3: Video camera, 4: Mercury lamp, 5: Thermal controller, 6: Electrical cooling device, 7: Halogen lamp

Fig. 3 Schematic diagram of apparatus.

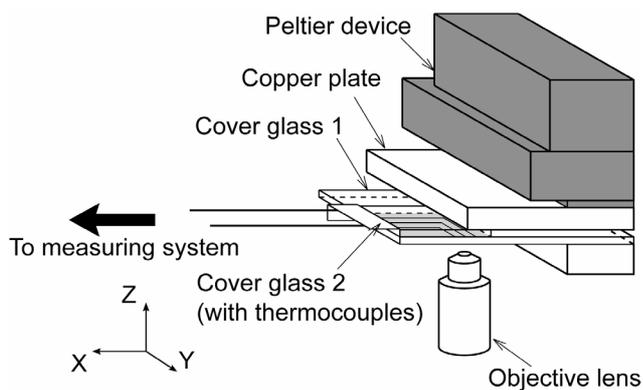


Fig. 4 Details of the observation section on the bench of the microscope.

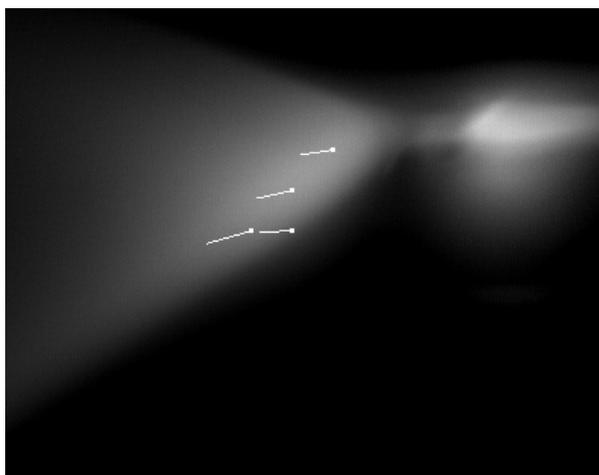


Fig.5 Velocities of the movement of protein concentration distribution near a growing ice obtained with a fluorescence intensity correlation method

The present author also conducted experiments on the gradual, one-directional freezing procedure of a solution of winter flounder antifreeze protein ⁽²⁰⁾. Figure 3 shows the apparatus, which consists of an inverted microscope, a data logger for temperature measurement, a PC, a CCD video camera, an electrical cooling device, and a thermal controller for the cooling device. The dilute solution of winter flounder antifreeze protein was kept in a narrow space between the two parallel cover glasses (See Cover glass 1 and 2 in Fig. 4). Cover glass 2 was in contact with the edge of the lower surface of the heat-transfer plate. This plate was cooled by the electrical cooling device.

Time change in the temperature of the solution was measured with Ni-Cr thin film thermocouples fabricated on the inner surface of the upper cover glass (Cover glass 2). These thermocouples can minimize disturbance in a temperature field.

In order to measure the concentration of the proteins, the amino-base side chain of lysine residue and that of the aspartate end residue in the protein were tagged with fluorescence-emitting molecules (fluorescein isothiocyanate).

Figure 5 exhibits a typical image with the interface of the ice and the protein solution. The black areas show the ice. In the ice, no protein exists because of solute displacement through the solidification process. The white area, which is similar to the cross section of a funnel, shows the solution region. Generally, the brightness increases with the concentration of fluorescence molecules. Thus, the brighter a local white area is, the higher the protein concentration is in the area. The brightest area is in the right-hand side of the figure. This area results in a high concentration region in a long, narrow liquid domain. The next brightest region is near the inclined interface where the displaced protein is accumulated.

We estimated the velocities of the movement of protein concentration distribution by applying a fluorescence intensity correlation method to a series of images. The velocity vectors are shown by white pin-like shapes in the figure. The head of the 'pin' represents the center of interrogation window ($9.0\mu\text{m}\times 9.0\mu\text{m}$) on the image a minute before the image in the figure, while the tail of the pin represents the corresponding window in a search region in the figure. The threshold for the correlation is 0.8. These vectors were different from the vector for the growing speed of ice. Thus, the protein concentration distribution moves relative to the surface. This suggests that the diffusion and aggregation of the protein can be related to the antifreeze effect of the protein.

If the inhibition mechanism of ice crystals due to the protein is clarified, great progress is expected in developing freeze-resistant fish for aquaculture, or producing cold-hardy varieties of plants for agriculture ⁽²¹⁾, and improving the cryopreservation of organs which are to be transplanted ⁽²²⁾. The insertions of antifreeze protein type I into salmon roe and a rat heart are reported in these references. Also, the organs and crops can be stored easily by maintaining the temperature between the freezing point and melting point. This saves energy. Furthermore, the mechanism will contribute to the production of micro ice slurry, which will be useful for cooling of the heart and brain during cardiac arrest. Note that Inada and Lu ⁽²³⁾ examine polyvinyl alcohol (PVA) as an alternative substance of the protein.

7. Concluding remarks

The special microstructures on the surfaces of some plants and insects in deserts are effective for collecting moisture in the air. These structures are similar to the heat transfer surface in the passive method of heat transfer enhancement. The inhibitors of ice crystal growth, such as antifreeze protein, modify the process of water freezing. This is effective for the control of temperature and heat transfer. If the mechanisms of drought- and freeze-tolerance due to some metabolites are clarified, they are promising for developing new methods of heat and mass transfer enhancement based on biomimetics.

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