Freezing point depression and freeze-thaw damage by nano-fluidic salt trapping

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Abstract

A remarkable variety of organisms and wet materials are able to endure temperatures far below the freezing point of bulk water. Cryotolerance in biology is usually attributed to “anti-freeze” proteins, and yet massive supercooling (≤ −40 °C) is also possible in porous media containing only simple aqueous electrolytes. For concrete pavements, the common wisdom is that freeze-thaw damage results from the expansion of water upon freezing, but this cannot explain the large pressures (> 10 MPa) required to damage concrete, the observed correlation between pavement damage and de-icing salts, or the damage of cement paste loaded with benzene (which contracts upon freezing). In this Letter, we propose a different mechanism – nanofluidic salt trapping – which can explain the observations, using simple mathematical models of dissolved ions confined to thin liquid films between growing ice and charged surfaces. Although trapped salt lowers the freezing point, ice nucleation in charged pores causes enormous disjoining pressures via the rejected ions, until their removal by precipitation or surface adsorption at a lower temperatures releases the pressure and allows complete freezing. The theory is able to predict the non-monotonic salt-concentration dependence of freeze-thaw damage in concrete and provides a general framework to understand the origins of cryo-tolerance.

Keywords

freezing, electrolyte, confined fluids, nanofluidics, freeze-thaw damage, cryo-tolerance

The durability of wet porous materials against freeze-thaw (FT) damage is critical in many areas of science and engineering. In biology, it is a matter of life and death. Living cells must somehow maintain a liquid state within the cellular membrane during winter4 while avoiding anoxia due to external ice encasement.3

As shown in Fig. 1, many forms of life manage to survive FT cycles, including various plants, reptiles, insects, bacteria, and even human embryos. Some of the simplest organisms can even recover from temperatures as low as −60°C. This incredible feat is normally attributed to solutes that are believed to dramatically lower the freezing point of water. Indeed, various anti-freeze proteins have been identified in cryo-tolerant animals, and cryo-protectant chemicals have been used for cryo-preservation and in...
Figure 1: Biological examples of supercooling and cryo-tolerance, compared with typical effects of nanofluidic salt trapping. The color bars indicate the predicted supercooling point of water containing trapped ions at different concentrations in a cylindrical pore of radius $R=5$ nm and surface charge density $\sigma = -1e/nm^2$, as illustrated in Fig.4 below.

**vitro fertilization** On the other hand, the remarkable bio-chemical and structural diversity of cryo-tolerant organisms shown in Figure 1 suggests that a more general, physical mechanism may also be involved.

The complex thermodynamics of supercooled water could play a role. Even in bulk water, deep supercooling can lead to multiple metastable disordered states. Phase transitions under nano-confinement can lead to exotic new phases, as well as modified ice nucleation, in both experiments and molecular simulations of water in nanopores.

The Gibbs-Thompson equation predicts modest freezing-point depression due to interfacial curvature, shown in Figure 1, and significant deviations have been observed in carbon nanotubes. None of these studies, however, have investigated FT damage or supercooling in more realistic, heterogeneous porous media.

In engineering, the most familiar example of FT damage is the fracture of concrete pavements during the winter, commonly attributed to the expansion of water transforming to ice within the pores. Despite the societal importance of this problem, a physics-based theory has not yet been developed that can predict the enormous pressures (>$10$ MPa) required to damage hardened cement paste. There is also the puzzling observation that FT damage occurs when cement is loaded with benzene, a normal liquid that shrinks upon freezing.

Recent experiments have challenged the prevailing hypothesis that FT damage is directly caused by solid phase transformations, not only ice formation, but also salt crystallization. Interestingly, there is strong correlation between FT damage and the use of de-icing salts on concrete pavements, which are often less durable than concrete structures without salt exposure in the same cold climates. Moreover, FT damage only occurs when the water saturation level exceeds a critical value.

In this Letter, we develop a predictive theory of freezing-point depression and FT damage in charged porous media, based a simple new mechanism sketched in Figure 2 nanofluidic salt trapping. It is well known in colloid science that, when two charged surfaces are separated
by a liquid electrolyte, the crowding of ions in solution results large repulsive forces whenever the electric double layers overlap, at the scale of the Debye screening length (1-100nm in water). This “disjoining pressure” is responsible for the stabilization of colloidal dispersions in aqueous electrolytes, surface forces in clays and other porous media, and the electrostatic properties of membranes. Disjoining pressure has been successfully modeled by the Poisson-Boltzmann mean-field theory for solutions of monovalent ions, and extensions are available to describe correlation effects involving multivalent ions. To our knowledge, it has not been recognized that the same theory, adapted for electrolyte freezing under confinement, can also predict large supercooling and FT damage in charged porous media, as we now explain.

**Physical Picture.** Consider a heterogeneous porous material saturated with liquid and gradually subjected to freezing temperatures. As in most organisms and construction materials, suppose that the pore surfaces and suspended materials are hydrophilic and charged, e.g. by the dissociation of surface functional groups or the adsorption of charged species. In many cases, the liquid is water, but the theory could also be applied to benzene or other non-aqueous solvents. Importantly, the liquid must contain dissolved salts, possibly at low concentration, as well as excess counter-ions to screen the pore surface charges and preserve overall electroneutrality. Ions in solution mediate surface forces, which play a crucial role in the mechanical properties of concrete and the function of biological systems. In most cases, the ions are assumed to have negligible solubility in the frozen solid, as is the case with pure ice.

Freezing begins in the larger “macropores” (> 100 nm), where bulk water easily transforms to ice, slightly below the thermodynamic melting point of the solution, which may be depressed from that of the pure solvent by the dissolved salt and any anti-freeze solutes. This bulk ice can form by homogeneous nucleation, spinodal decomposition, or (most likely) by heterogeneous nucleation on surface or bulk impurities. Regardless of its origin, the advancing ice rejects insoluble ions, causing the salt concentration to rise in the nearby, increasingly confined liquid electrolyte.

What happens next depends on the degree of supercooling, the pore structure and the surface charge. As shown in Figure 2(a), even after partial freezing, an individual pore may remain open, allowing ions and water molecules to exchange freely with a reservoir of bulk solution.
via a percolating liquid path to neighboring unfrozen pores or an external bath. In this scenario, the liquid electrolyte and any solid ice within the pore remain in quasi-equilibrium with the bulk reservoir at constant chemical potential. The connected path to the reservoir may pass through liquid-saturated pores, or partially frozen pores with sufficiently thick liquid films to allow unhindered transport.

As freezing proceeds, many ions and water molecules will inevitably be trapped out of global equilibrium, although still in local quasi-equilibrium within each nanoscale pore or liquid film. The simplest case is that of a bottleneck pore, sketched in Fig. 2(b), which may block solvated ions (with their water shells) from passing by steric hindrance or charge exclusion. Even if some ions and water molecules can diffuse through a given bottleneck, their electrokinetic transport rate may be too slow to allow many to escape prior to more complete freezing. Such slow ion transport may be enhanced by long, tortuous pathways through a series of bottlenecks and compounded by a large volume of micropores, effectively cut off from the macropores with insufficient time for salt release, in materials of low pore-space accessibility. Even in relatively open porous structures, nanofluidic salt trapping can also result from bottlenecks created by the advancing ice, as shown in Figure 2(c). Under nano-confinement, a supercooled liquid film often remains on nanopore surfaces prior to complete freezing. In biological cells, as shown in Figure 2(d), electrolytes are contained within the cell walls, and nanofluidic salt trapping is facilitated by the charged cytoskeleton and charged macromolecules (including cryo-resistant proteins). Internal salt concentrations are also actively maintained by ion channels and pumps in the cell membrane.

The supercooling of confined liquids can be greatly enhanced by the salt rejected by freezing, as the remaining solution becomes more concentrated between a charged solid surface and the bulk ice. Large disjoining pressures are then produced in the liquid film and transmitted to the solid matrix, potentially causing damage. For hard porous materials, the ice may also crack and temporarily release ions and water molecules, propelled by diffusio-osmosis.

At sufficiently low temperatures, salt-enhanced supercooling and freeze-thaw damage are relieved by the sudden removal of ions from the confined liquid, thus allowing complete freezing of the pores. Ions may be cleared by adsorption reactions on the pore surface, which regulate and neutralize the surface charge. At high rates of freezing, some trapped ions may also penetrate the ice, making it polycrystalline or amorphous.

**Theory.** The total free energy for a liquid electrolyte and its frozen solid confined to a charged pore can be described in the mean-field approximation by

$$F_{tot} = F_{liquid} + F_{solid} + F_{interface}$$

$$= \int_{V_s} dV \left( \mu_s - \mu_t - \frac{\epsilon_s}{2} \| \nabla \phi \|^2 \right) + \int_{V_l} dV \left[ g(\{c_i\}) + \rho \phi - \frac{\epsilon_l}{2} \| \nabla \phi \|^2 \right]$$

$$+ \sum_{j=s,l,sl} \int_{S_j} dS (\gamma_j + q_j \phi)$$

where the integrations are performed over volumes of solid ($V_s$) and liquid ($V_l$) with permittivities $\epsilon_s$ and $\epsilon_l$, respectively, and over surfaces of the solid-liquid interface ($S_{sl}$), the liquid-pore interface ($S_l$) and the solid-pore interface ($S_s$), with corresponding surface charge densities, $q_{sl}$, $q_l$ and $q_s$ and interfacial tensions, $\gamma_{sl}$, $\gamma_l$ and $\gamma_s$; $\mu_s - \mu_t$ is the bulk chemical potential difference between solid and liquid phases; $-\nabla \phi$ is the electric field; $g(\{c_i\})$ the non-electric part of homogeneous liquid electrolyte free energy; $c_i$ the concentration of ion species $i$ having charge $z_ie$; and $\rho = \sum_i z_ie c_i$ the net charge density, assumed to be negligible in the solid phase. We focus on situations of complete wetting by the liquid, $\gamma_s - \gamma_l \gg \gamma_{sl}$, in which case we can neglect $S_s$ and assume $S_l$ covers the entire pore surface.

Setting $\delta F_{tot}/\delta \phi = 0$ for bulk and surface variations, we obtain Poisson’s equation

$$\epsilon_l \nabla^2 \phi = -\rho \quad \text{in } V_l$$

$$\epsilon_s \nabla^2 \phi = 0 \quad \text{in } V_s$$
and electrostatic boundary conditions

\[ q_{sl} = (\varepsilon_s \vec{E}_s - \varepsilon_l \vec{E}_l) \cdot \hat{n}_{ls} \text{ on } S_{sl} \]
\[ q_i = \varepsilon_l \nabla \phi \cdot \hat{n}_l \text{ on } S_l \]  (3)

The equilibrium state of liquid-solid coexistence is found by minimizing the total free energy with respect to the position and shape of the solid-liquid interface, \( S_{sl} \), subject to electrochemical constraints. Here, we consider two cases: (1) an open pore where ions of species \( i \) exchange freely with a reservoir of concentration \( c_i^\infty \), or (2) a pore with trapped ions, whose total number is fixed by screening the pore surface charge in the liquid, prior to freezing, by the mechanisms shown in Fig. 2. Importantly, we neglect the effects of volume changes due to the water/ice transformation, under the assumption that liquid water molecules (of size \( \sim 3\AA \)) are mobile and small enough to escape the pore as freezing progresses, regardless of whether ions are trapped. The phenomenon of ion trapping in charged nanochannels, while water remains free to diffuse and flow to a nearby reservoir or larger pore, is well established in the field of nanofluidics and forms the basis for various devices, such as electrosymmetric micropumps,\(^6^9\) nano-fluidic diodes and bipolar transistors\(^6^3,6^6\), and nanofluidic ion separators\(^6^2\). In contrast to the common wisdom about freeze-thaw damage in pavements, this picture must also hold for well-connected hierarchical porous materials such as concrete.

The preceding thermodynamic framework for confined electrolyte phase transformations can be extended in various ways, e.g. to account for ion-ion correlations\(^3^9,6^8\) (especially involving multivalent ions), finite ion sizes\(^6^1\) and hydration surface forces\(^3^1,6^5,6^6\), but here we focus on the simplest Poisson-Boltzmann mean-field theory\(^2^9\), which suffices to predict the basics physics of freezing-point depression and material damage. The homogeneous free energy is then given by the ideal gas entropy for point-like ions, \( g_i = c_i [\ln (v_i c_i) - 1] \), and the electrostatic potential in the liquid electrolyte is then given by the Poisson-Boltzmann (PB) equation:

\[ -\varepsilon_l \nabla^2 \phi_l = \rho = \sum_i z_i c_i e^{-\beta z_i e \phi_l} \]  (4)

Since we focus on highly confined electrolyte liquid films, we set the relative permittivity, \( \varepsilon_l = 10\varepsilon_0 \), to that of water near dielectric saturation at high charge density\(^6^7,6^8\).

To assess the prevalence of nanofluidic salt trapping within Poisson-Boltzmann theory, the state of a bottleneck shown in Fig. 2 can be estimated by comparing the double layer thickness \( \lambda_D \) (or hydrated ion size \( a \)) inside with its radius \( R \): if \( \lambda_D \lesssim R \) (or \( a \gtrsim R \)) then the double layer(s) span across and the bottleneck is approximated as “closed” to ions, since freezing rate may exceed ion transport rate, given a high tortuosity of the pore network. If \( \lambda_D \ll R \) (or \( a \lesssim R \)), then the channel may be viewed as open to ion exchange. For an initial salt concentration of 0.1 mol/L in a binary monovalent electrolyte, (with \( \varepsilon_r \approx 10 \)), we find \( \lambda_D \sim \sqrt{\frac{4\varepsilon_r k_B T}{2e_0 e^2}} \sim 0.5 \text{ nm} \).

**Symmetric pores.** In order to obtain analytical results, we consider isotropic electrolyte freezing in \( d \) dimensions, where ice nucleates to form a plate \( (d = 1) \), cylinder \( (d = 2) \) or sphere \( (d = 3) \) of radius \( r \) within a pore of the same symmetry, whose surface is located at \( x = R \). The total pore volume is \( V(d)r^d \), and \( S(d)r^{d-1} \) the surface area of the ice core \( (x < r) \), surrounded by a liquid electrolyte shell \( (r < x < R) \). At thermodynamic equilibrium, the location \( r^* \) of the solid-liquid interface is determined by minimizing the total free energy w.r.t. \( r \):

\[ \delta F_{tot}/\delta r = 0; \]
\[ r^* = \text{argmin}_r F_{tot}(r) \]  (5)

which yields the equilibrium ice volume fraction, \( \chi = (r^*/R)^d \). Once \( r^* \) is found, mechanical equilibrium at the solid-liquid interface gives pressure of both phases, which is transmitted to the pore boundary

\[ P = -\left( \frac{\partial F_{solid}}{\partial r} \right)_{r=r^*} = \left( \frac{\partial F_{liquid}}{\partial r} \right)_{r=r^*} \]  (6)
The first equality describes the tendency to form more ice and hence expand its volume, while the second equality shows the free energy cost to squeeze the electrolyte, resisting the growth of ice.

For a symmetric pore, the total free energy of electrolyte and ice in a freezing pore can be partitioned as $F_{\text{tot}} = F_{\text{elec}} + F_{\text{ice}} + F_{\text{surface}}$, where the integrals in Eq. (11) take simpler forms. After freezing starts, the free energy of ice is given by

$$F_{\text{ice}} = (\mu_s - \mu_l) V(d)r^d,$$

where $(\mu_s - \mu_l)$ is the Gibbs free energy change for bulk water freezing, which can be calculated using the Gibbs-Helmholtz relation, as shown in the Supporting Information. In principle, the electric field energy of the ice core $(x < r)$ depends on its shape and the electrostatic boundary conditions, but vanishes here by symmetry. The interfacial energy is $F_{\text{surface}} = \gamma_{sl} S(s)r^{d-1}$, which gives rise to the Gibbs-Thomson effect of freezing point depression for confined pure water. The free energy of the electrolyte shell is given by

$$\frac{F_{\text{elec}}}{S(d)} = q_l \phi(R) R^{d-1} + \int_r^R x^{d-1} dx \left[ g(\{c_i\}) + \rho \phi - \frac{\epsilon_l}{2} \| \nabla \phi \|^2 \right],$$

where the first term is the electrostatic energy of surface charges, and the integrand takes the form given above for mean-field theory of point-like ions. The Poisson-Boltzmann equation, Eq. (4), must be then solved with the boundary conditions, $\phi'(r) = 0$ at the ice core and $\epsilon_r \phi'(R) = q_l$ at the charged pore wall.

**Free ions.** As freezing proceeds in an open pore, where all ions can escape to a reservoir, the surface charge is eventually screened in a thin liquid film containing only counter-ions, which corresponds to a one component plasma (OCP). In the limit of weak coupling (typically valid for monovalent ions), the mean-field approximation is valid, and the Poisson-Boltzmann equation for the OCP can be integrated for symmetric pore shapes (as shown in the Supporting Information) to obtain the mean electrostatic potential. For a slit pore

$$\Delta T = \frac{\Delta T}{\Delta c_p}$$

Figure 3: Electrolyte freezing and pressure generation in a parallel slit pore ($d = 1$) without effects of interfacial tension. For an open pore with free ions exchanging with a reservoir, the freezing point depression, $\Delta T \sim 0.1$ K, and disjoining pressure, $P \sim 0.1$ MPa, are quite small, even for a highly charged nanopore of radii $R = 5$ nm, in the limit of a one-component plasma of only counter-ions.

$$P \sim c_{\text{free}}$$

where $\phi_0$ is an (arbitrary) reference point of the potential and $l_G \sim \frac{4\pi q_l k_B T}{\epsilon_l}$ the Gouy-Chapman length. The parameter $\tilde{P}$ is the dimensionless disjoining pressure,

$$\tilde{P} = \frac{4\pi l_B^2 l_G^2}{k_B T} \left( \frac{Q}{T_0} - \Delta c_p \frac{\Delta T^2}{T_0} \right)$$

where $l_B = \frac{2^2 k_B T}{4\pi q_l k_B T}$ is the Bjerrum length, $Q$ the latent heat of bulk water freezing, $\Delta c_p$ the difference of heat capacity between water and ice, $T_0$ the bulk freezing point, and $\Delta T = T - T_0$ the freezing point depression. To determine $\Delta T$, we use the fact that $|\tilde{P}|$ satisfies

$$\sqrt{\frac{|\tilde{P}|}{2 l_G}} \tan \left( \sqrt{\frac{|\tilde{P}|}{2 l_G}} \right) = \frac{Z q_l^\beta e^2}{2\epsilon} = \frac{2\pi R}{l_G}$$

where $R$ is again the pore size.

Inserting typical values, we can estimate the
In contrast to Fig. 3, for a binary electrolyte with trapped ions, (a) freezing-point depression as large as $-40$ K can occur, and (b) large disjoining pressures up to $\sim 10$ MPa occur during the freezing process, below the temperature to start freezing, $T_f$, and above that of complete freezing of the pore $T_{ff}$, when ions are removed by precipitation.

Trapped ions. The situation is completely different in the opposite limit, where all ions in the original liquid binary electrolyte remain trapped within the pore during freezing. Total ion number conservation is then imposed on the PB equations, $\int R r c_i S(d) x^{-1} dx = N_i$, and significant freezing-point depression can be achieved. The mathematical details can be found in the Supporting Information, and here we focus on the physical predictions of the theory.

First we consider a binary 1:1 liquid electrolyte freezing in a parallel slit pore ($d = 1$), without any effects of solid-liquid interfacial tension. As shown in Fig. 2, the freezing point is substantially decreased by increasing the initial salt concentration $c_0$ in the confined liquid. After freezing starts at temperature $T_f$, due to the resistance of the electrolyte, the equilibrium ice volume fraction $\chi$ monotonically increases as temperature decreases. The freezing process continues until the trapped ions are suddenly removed from the thin liquid film at the temperature of freezing finished $T_{ff}$, when the salt solubility limit is reached, and $\chi$ suddenly jumps to 1. The pore is completely frozen now. Complete freezing may also occur if the trapped ions are adsorbed on the pore surface, thereby neutralizing the surface charge (as shown below).

As shown in Figure 4, significant disjoining pressures ($\sim 10$ MPa for $R = 5$ nm) can be generated by confined ions during the freezing process. The pressures at the freezing start temperature $T_f$ and the complete freezing tem-
perature $T_{ff}$ are labeled as $P_f$ and $P_{ff}$, respectively. The disjoining pressure varies approximately linearly with temperature between these values during the freezing process in a slit pore.

**Salt solubility limit and surface charge regulation**— As ice volume fraction increases, salt concentration goes up. At some point the concentrated electrolyte will become saturated and salt will crystallize. The volume of salt crystal precipitate is neglected. The solubility equilibrium for 1:1 electrolyte ($M^+ + B^-$) at saturation is $K_{eq} = \frac{[M^+][B^-]}{[MB]} = (c_0^{sat})^2$. Once saturated concentration $c_0^{sat}$ is reached the equilibrium position of ice front becomes thermodynamically unstable and all the liquid turned into solid phases of ice and salt crystal. In Fig.4 all the curves at some point reach the solubility limit and undergo sudden crystallization, when ice volume fraction discontinuously jumps from $\chi < 1$ to $\chi = 1$. The pressure at this point is denoted as $P_{ff}$ in Fig.5. As opposed to the concept of “crystallization pressure” that has been proposed to account for pressure and damage (under room temperature) in construction materials, here the pressure of the freezing pore is determined by thermodynamic equilibrium between freezing and precipitation, thus salt crystallization is merely a consequence, instead of the cause for pressure.

When the concentration of trapped ions is high enough, counter-ion recombination with the surface charge will reduce the double layer thickness and “opens” the bottlenecks, although large ion sizes can still render crowded and slow ion transport. This effect is calculated by a modified boundary condition for the PB equations (see SI).

**Application to Concrete**— The predictions of this theory are semi-quantitatively consistent with experimental observations FT damage in cement. Below critical degree of water saturation, plenty of large pores remain open transport pathways for ions during freezing, hence no significant damage observed. The volume expansion of water during freezing is irrelevant in this theory, so it can also explain qualitatively similar results observed in freeze-thaw experiments on cement samples.

![Figure 5](image-url)

Figure 5: (a) typical experiment protocol reproduced from. $T_f$ and $T_{ff}$ correspond to the temperature when ice formation initiates and solubility limit reached, as indicated in Fig.4. (b) shaded area shows the pressure range after freezing starts in a trapped pore. $P_f$ and $P_{ff}$ correspond to the pressure when ice formation initiates and solubility limit reached, as indicated in Fig.4. Dash line shows open pores with free ions. Data points show damage measured as acoustic energy accumulation in cement paste FT experiment, a non-monotonic function of salt concentration. Tensile strength of hardened cement paste is $\sim 3$ MPa.
loaded with benzene, which shrinks upon freezing. The non-monotonic dependence of damage on NaCl concentration can be explained by crossover from salt trapping to channel opening though charge regulation, as shown in Fig. A fully quantitative comparison requires the plasticity and fracture mechanics of the solid matrix due to these local high pressures, and the connectivity of the pores, which is currently a missing link. Also to quantify the transport timescales for ions as freezing proceeds, pore connectivity is key information. Nevertheless, to our knowledge this is the first theory that shows potential to encompass all these observations.

Conclusion.— In this Letter, we present a theory of the freezing of electrolytes in charged porous media. The key insight is that, if ions become trapped by advancing ice, large disjoining pressures can cause material damage, until further supercooling triggers salt precipitation and complete freezing. Freezing point depression, ice volume fraction and pressure are calculated using a simple mean-field theory.

Many extensions of the theory could be considered in future work. Ion correlations, including the strong-coupling limit, can be introduced via higher order terms in Eqn. resulting in modified PB equations. At larger length scales, models of interfacial instabilities leading to dendritic growth could be extended to account for electrokinetic phenomena in charged pores. Although the freezing conditions self-consistently assumed here \((T > 200 \, K, P < 100 \, MPa, d < 100 \, nm)\) are not so extreme that bulk Ih phase of ice is always formed, exotic phases of ice (non-Ih phase) are known to dominate under more extreme conditions. Salt ions can also affect the surface tension of ice-electrolyte interface, as well as other aspects of nucleation under confinement, described in a companion paper.

As a first application to material durability, our theory may explain complex trends of freeze-thaw damage in hardened cement paste. These predictions could influence industrial practices in road de-icing, pavement design, reservoir fracturing, and oil/gas extraction. The theory may also shed new light on the physics of cryo-tolerance and cryo-preservation in biological materials, which abound in electrolyte-soaked macromolecules, nanopores and membranes.

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Supporting Information Available

The following files are available free of charge.

1. details of the theoretical derivation.

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