Invited Lecture

Interfacial potentials in crystallization: nucleation-resistant surfaces and focused crystallization fronts

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The process of crystal nucleation can be facilitated by the presence of nucleation centres in solution (pre-existing particulate material) or compliant surfaces that lead to lower interfacial tension of a crystal nucleus formed at the surface than that generated in solution. Heterogeneous nucleation can pose significant problems in the form of pipe scaling, but also pathological crystallization of blood vessels (cardiovascular calcification) or vascular grafts. In this context, it is important to explore how to create nucleation-resistant surfaces. In our work we focus especially on the adverse crystallization events in biological context, although the same principles might be used also to design nucleation-suppressing surfaces for engineering applications. We explore the properties of the surfaces that preclude crystal nucleation by preventing ionic precursors of crystals from approaching the surface, and create an extensive layer of interfacial water that remains depleted in ions.

We use hydrogels as our model surfaces that, in terms of structure (porosity) and functional groups ($-COO^-$ and $-OSO_3^-$), resemble properties of glycocalyx – a gel-like lining of blood vessels. We show that the concentration and chemical identity of functional groups as well as pore size determine the exclusion of ions (potential crystal precursors), but also of colloidal particles (possible nucleation centres) to tens of micrometers from the surface [1]. Even in contact with supersaturated ionic solution crystals are formed only in a bulk solution and do not approach the surface (Fig.1). We show that it is possible to adjust the exclusion distance with the use of physiologically-relevant stimuli, CO_2 (respiratory gas), KH_2PO_4 (cell metabolite) or infrared (IR) – metabolic heat. The exclusion is the result of the emergence of an electric field normal to the surface due to the separation of ionic charges diffusing toward/out of the surface with different speeds and creating liquid junction potential. We argue that the ability of vascular lining to support/generate charge separation (voltage) contributes to prevention of calcification of healthy vessels and to maintenance of frictionless blood flow focused in the centre of the vessel lumen. In particular, our findings indicate that CO_2 (dissociating into H^+ and HCO_3^-) gradient across the vessel wall together with high $-OSO_3^-$ (accompanied by mobile H^+) content of glycocalyx and of heparin might create interfacial water layer depleted in ions, plasma solutes and cells (corresponding to the recognized cell-free layer in capillaries). Interfacial voltage excludes solutes and particles from the surface, but also promotes their enrichment/focusing at the depleted region/bulk interface. We discuss how interfacial charge separation can be generated also at the surface of a protein molecule and show how its manipulation may contribute to protein self-assembly. Specifically, we use IR radiation to support the expansion of protein interfacial water layer that separates protein-fixed charges from their mobile counterions. The interfacial water aligned in this self-generated electric field i) prevents non-specific contact formation (protein aggregation), but ii) supports mutual attraction in solution (focused, but mobile charges enable induced dipoles formation) and iii) promotes crystal nucleation by increasing entropy gain on releasing water molecules [2].

In summary, suppression of surface nucleation might be achieved by creating conditions supporting the emergence of liquid junction potential at the interface. The latter is generated by ions that separate in space in aqueous solution when moving in a specific direction, toward or out of the surface. Directional movement is prompted by non-equilibrium conditions that may result from imposing a gradient of ions across the interface or placing a surface (or a biomacromolecule) with ionizable functional groups in the environment promoting groups dissociation and release/exchange of mobile counterions.

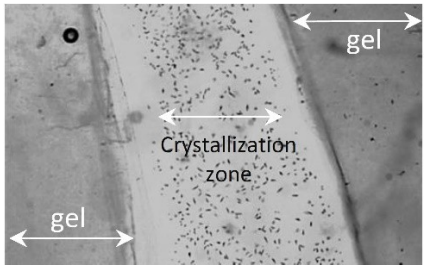

Figure 1. Crystallization-free zones next to the gel surfaces and crystallization front in the centre

[1] Kowacz, M., Niestępski, S., Withanage S. (2023) Soft Matter, 39,7528-7540

[2] Kowacz M., Marchel M., Juknaite L., Esperança J. M. S. S., Romão M. J., Carvalho A. L., Rebelo L. P. N. (2017) J. Crystal Growth, 457, 362.

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