Local supersolidity of ^{4}He around a charged molecular impurity

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Impurities in liquid helium are powerful probes of superfluidity and have greatly shaped our understanding of superfluid behavior [1, 2, 3]. In particular spectroscopic studies of various molecular impurities embedded in small helium clusters have shed light on the onset of superfluidity in small quantum clusters showing that even small clusters composed of a few ^{4}He atoms exhibit signs of superfluidity at the molecular scale [4, 5]. Charged impurities usually interact strongly with the surrounding helium resulting in a significant perturbation of the solvent. In the case of most cations, the helium gets strongly compressed leading to the creation of a solid core around the impurity [1, 6, 7, 8, 11, 12]. This effect, usually referred to as snowball effect [6], has been studied both theoretically [6, 7, 8] and experimentally [11, 12] in the case of atomic cations, and has been linked to a local disappearance of superfluidity within the frozen ^{4}He atoms of the snowball due to their strong spatial localization [7, 8].
We will present here the results of bosonic path integral simulations [9, 10] of a charged molecular impurity, namely protonated methane, embedded in helium clusters of up to 60 ^{4}He atoms at ultralow temperature. These simulations reveal that a similar snowball effect appears around molecular cations, such as CH_5^+, featuring a highly structured, solid-like, first helium solvation shell. Moreover, these highly localized ^{4}He atoms still participate in vivid bosonic exchange that is induced by the fast ro-vibrational motion of CH_5^+. This combination of strong ^{4}He localization with pronounced bosonic exchange, leading to an intense superfluid response, thus indicates manifestations of local supersolid behavior of ^{4}He, in the first solvation shell around CH_5^+. We expect this impurity induced local supersolidity to appear around most positively charged molecular impurities featuring a strong interaction with the quantum solvent coupled with fast ro-vibrational motion. Hopefully, this effect can be experimentally confirmed maybe through spectroscopic studies of molecular cations in small bosonic clusters in a way similar to the ground-breaking experiments that revealed the existence of molecular scale superfluidity [4, 5].

[1] Toennies, J. P., Vilesov, A. F. *Annu. Rev. Phys. Chem.* **49** 1 (1998).
[2] Toennies J. P., Vilesov A. F. *Angew. Chem., Int. Ed.* **43** 2622 (2004)
[3] Borghesani, A. F, *Electrons and Ions in Liquid Helium* Oxford University Press (2007).
[4] Grebenev, S., Toennies, J. P., Vilesov, A. F. *Science* **279** 2083 (1998).
[5] Tang, J., Xu, Y., McKellar A. R. W., Jäger, W. *Science* **297** 2030 (2002).
[6] Atkins, K. R. *Phys. Rev.* **116** 1339 (1959).
[7] Nakayama, A., Yamashita, K. *J. Chem. Phys.* **112** 10966 (2000).
[8] Galli D. E., Ceperley D. M., Reatto, L. *J. Phys. Chem. A* **115** 7300 (2011).
[9] Walewski L., Forbert H., Marx D. *Comput. Phys. Commun.* **185** 884 (2014).
[10] Brieuc F., Schran C., Uhl F., Forbert H., Marx D. *J. Chem. Phys.* **152** 210901 (2020).
[11] Müller, S., Mudrich, M., Stienkemeier, F. *J. Chem. Phys.* **131** 004319 (2011).
[12] Bartl, P., Leidlmaire, C., Denifl, S., Scheier, P. *J. Phys. Chem. A* **118** 8050 (2014).