

**LIQUID NANODROPLETS THAT DO NOT WET THEIR OWN SOLID:  
CONTRASTING NaCl AGAINST METALS**

E. Tosatti(\*)  
SISSA, ICTP, and INFN Democritos  
Trieste, Italy

A liquid droplet deposited on the surface of its own solid at a temperature below but very close to the bulk melting point  $T_m$  will generally spread on the solid surface, due to complete wetting of the solid by the liquid. Notable exceptions are predicted to occur for some close packed metal surfaces like Au(111) or Al(111),[1] and also for ionic crystal surfaces like NaCl(100).[2] These are solid surfaces that do not undergo surface melting, and are therefore only partially wetted by their own melt at the triple point. In these cases, liquid nanodroplets delicately deposited on their own crystal surface in full equilibrium near  $T_m$  should not spread, but settle in a metastable but long lived configuration with a nonzero partial wetting angle.

It would be interesting to check if that is indeed the case experimentally, and if that could be put to use e.g., to build controlled asperities on otherwise flat terraces.

Here I will concentrate on the basic theory and describe first of all molecular dynamics simulations that demonstrate the phenomenon in Al(111) and NaCl(100). As a by product of simulations one also obtains partial wetting angles that agree well with the macroscopic angle when experimentally known, such as in NaCl where its magnitude is as large as 48 degrees.[3]

Subsequently, I will address the underlying microscopic physics, stressing a common aspect, but otherwise contrasting the generally different mechanisms preventing complete wetting for metals and for alkali halides respectively. The main common aspect is that the liquid surface is in both cases unusually low in internal energy, and correspondingly poor in entropy. In metals that is due to surface layering, causing the outermost liquid layer to be better packed, more ordered, less fluctuating, and altogether closer to a solid layer than to any layer in the liquid interior at the same temperature.[4] In alkali halides, by contrast, there is no such layering. The NaCl liquid surface at the melting point is not solid-like at all, and its profile in fact exhibits huge thermal fluctuations. Despite that, direct calculation of the surface tension and of its temperature derivative yields a liquid surface entropy falling way short of that of the solid surface, the latter independently obtained by thermodynamic integration up to  $T_m$ . [5]

I tentatively attribute this surprising entropy deficit to charge neutrality, which suppresses surface fluctuations involving single atoms, while permitting only milder fluctuations with a molecular character.

#### References

(+) Work sponsored by the Italian Ministry of University and Research, through COFIN03, FIRB RBAU01LX5H, and FIRB RBAU017S8R; and by INFN, through PRA NANORUB

- (\*) In collaboration with T. Zykova-Timan, U. Tartaglino, and D. Ceresoli
- [1] F.D. Di Tolla, F. Ercolessi, and E. Tosatti, *Phys.Rev. Lett.* 74,3201 (1995).
  - [2] T. Zykova-Timan, U. Tartaglino, D. Ceresoli, W. Sekkal-Zaoui, and E. Tosatti, to appear on *Surf. Sci.* (2004)
  - [3] G. Grange and B. Mutaftschiev, *Surf. Sci.* 47, 723 (1975)
  - [4] F. Celestini, F. Ercolessi, and E. Tosatti, *Phys. Rev. Lett.* 78, 3153 (1997).
  - [5] T. Zykova-Timan, U. Tartaglino, D. Ceresoli, and E. Tosatti, in preparation (2004)