Alkali halide surfaces near melting: Wetting and nanofriction properties

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Abstract

Alkali halide (1 0 0) crystal surfaces are poorly wetted by their own melt at the triple point. We carried out simulations for NaCl(1 0 0) within the well tested BMHFT model potential. Calculations of the solid–vapor, solid–liquid and liquid–vapor free energies showed that solid NaCl(1 0 0) is a non-melting surface, and explain its bad wetting in detail. The extreme stability of NaCl(1 0 0) is ideal for a study of the nanofriction in the high temperature regime, close to and even above the bulk melting temperature (T_M). Our simulations reveal in this regime two distinct and opposite phenomena for plowing and for grazing friction. We found a frictional drop close to T_M for deep ploughing and wear, but on the contrary a frictional rise for grazing, wearless sliding. For both phenomena we obtain a fresh microscopic understanding, relating the former to "skating" through a local liquid cloud, the latter to softening of the free substrate surface. It is argued that both phenomena, to be pursued experimentally, should be much more general than the specific NaCl surface case. Most metals in particular possessing one or more close packed non-melting surface, such as Pb, Al or Au(1 1 1), should behave quite similarly.
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1. Introduction

The high temperature surface properties of alkali halide crystals, particularly of NaCl, are very unusual as these solids are incompletely wetted by their own melt [1]. We investigated theoretically these surfaces and their uncommon behavior, with a multiple goal. The first goal was to uncover the physical reasons for the poor wetting. The second was to exploit the availability of the standard empirical potential parametrized long ago by Tosi and Fumi (BMHFT) for a first quantitative characterization of all the interfaces – and particularly their structure and their temperature dependent interface free energies – in a well defined solid–liquid–vapor system. Achieving this kind of goal is of particular interest in the general context of high temperature capillarity, a field where such a detailed understanding is usually unavailable. A third goal was to verify whether the solid NaCl(1 0 0) surface exhibits surface non-melting, as the partial

self-wetting would imply on thermodynamic grounds. A fourth goal was to study the NaCl liquid surface, extracting from its temperature dependent surface tension the surface entropy, and comparing it e.g., with the solid surface entropy at the melting point. Again, it seems that this comparison is generally unavailable. A fifth and more practical type of goal was finally to put to use the understanding obtained for the non-melting solid surface, in the field of nanofriction. In particular, our aim is to provide a first theory and simulation approach to both *ploughing* and *grazing* friction of hard nanotips on a solid surface near melting.

In the following we summarize the results of work that appeared in Refs. [2–5].

2. Partial wetting of NaCl by its own melt

Our classical molecular dynamics simulations with the Tosi–Fumi potentials confirm that in this model crystalline NaCl(1 0 0) is only partly wetted by a (nano) droplet of molten NaCl [2]. Moreover, as expected, solid NaCl(1 0 0) is confirmed to be a non-melting surface, stable without any precursor signals of melting up to the bulk melting point. In a metastable state, and in the absence of defects, it can even be overheated by as

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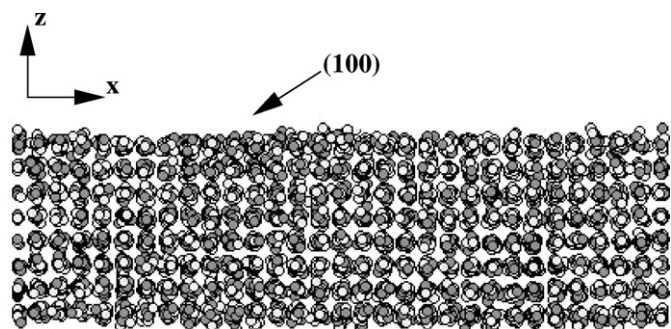
Fig. 1. Snapshot of a simulation of a NaCl(1 0 0) slab, at 1120 K $\simeq T_M + 50$ K (the calculated bulk melting temperature is $T_M = 1066$ K, in good agreement with experimental data). The (1 0 0) surface is normal to the z direction, indicated in the figure. In our simulations at 1120 K, NaCl(1 0 0) remains crystalline in a metastable state for at least 200 ps, confirming its non-melting nature. Upon increasing temperature, crystalline NaCl(1 0 0) persists up to a surface spinodal temperature $T_{ss} \simeq 1215$ K $\simeq T_M + 150$ K.

much as 100K above the melting temperature (Fig. 1). Extracting from the simulations the properties of the three interfaces – solid–vapor, liquid–vapor, and solid–liquid – we calculated and analyzed their free energies (Fig. 2) and found that the surface non-melting of NaCl(100) and the resulting partial self-wetting stem from three separate reasons:
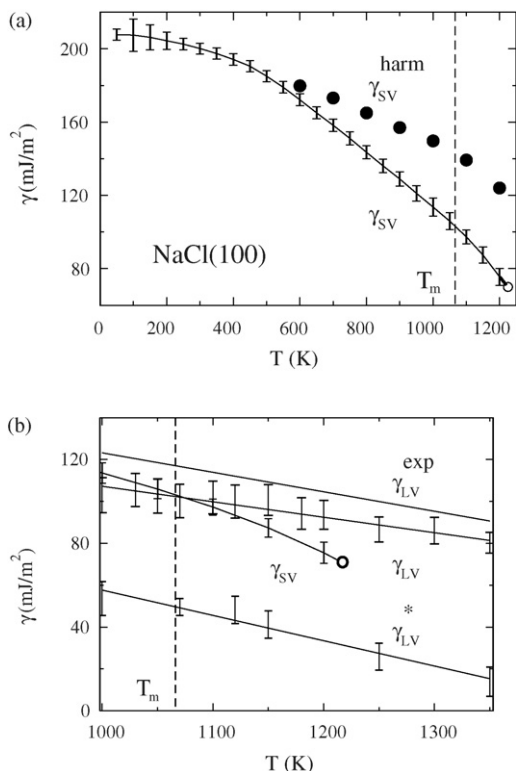

Fig. 2. (a) The solid surface free energy γ_{SV} from thermodynamic integration (solid line) and from the effective harmonic approximation (dots) [4]. (b) Liquid NaCl surface tension γ_{LV}, compared to the experimental value γ_{LV}^{exp}. The solid surface free energy γ_{SV} is reported in the same plot. γ_{LV}^{*} is the surface tension re-calculated by artificially removing the correlations between atoms at the outer surface. [3,4] Once surface molecular order is removed in this way, the surface entropy rises and the surface tension drops. Solid NaCl(1 0 0) would be completely wet by this artificial liquid.
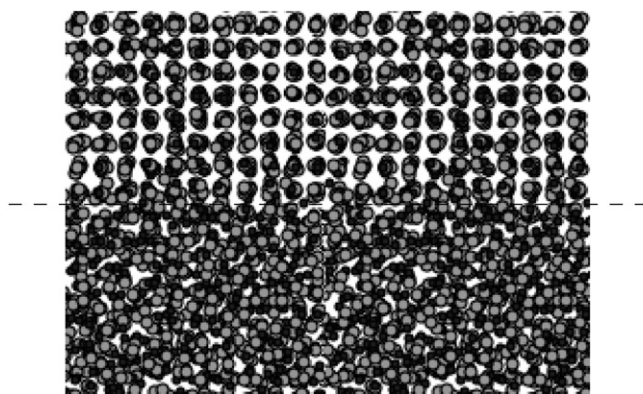

Fig. 3. Simulated NaCl(1 0 0) solid–liquid interface at the melting point. The interface is quite sharp. Its free energy is calculated to be $\gamma_{SL} = 36 \pm 5$ mJ/m^2.

(i) Solid NaCl(1 0 0) is an exceptionally stable solid surface (Fig. 1), with a strongly decreasing surface free energy at high temperature (Fig. 2). Stability in this regime is enhanced by extremely large anharmonicities. At the melting point T_M, we found $\gamma_{SV} = 103$ mJ/m^2.

(ii) The solid–liquid interface is spatially sharp (Fig. 3), and is energetically very expensive ($\gamma_{SL} \simeq 36$ mJ/m^2). This can be attributed to large structural differences between solid and liquid, in particular a 27% density difference between the two.

(iii) The liquid–vapor interface free energy (surface tension) is relatively high ($\gamma_{LV} \simeq 102$ mJ/m^2), actually almost identical to the solid–vapor free energy at the melting point. The reason for this high surface tension is traced to a surprising "deficit" of liquid surface entropy, which we calculate to
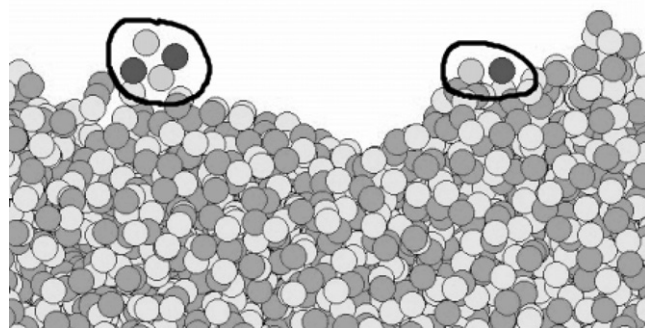

Fig. 4. Snapshot of a simulation of a liquid NaCl surface (liquid–vapor interface), at 1250 K well above the melting point and even above the surface spinodal temperature T_{ss}. Note the very pronounced fluctuations in the instantaneous surface profile. This picture, suggestive of a low surface tension, high entropy surface, is in apparent contradiction with the massive non-wetting of solid NaCl(1 0 0). Indeed, we found in simulation [3,4], an incipient molecular surface ordering which lowers the surface entropy by a factor $\simeq 2.5$. The origin of this molecular surface order is charge order, which, already important in bulk, plays an enhanced role at the molecular liquid surface. Analyzing the correlations between Na$^+$ and Cl$^-$ ions at the surface, one finds that the outermost layer is rich in NaCl monomers and dimers, as highlighted in the figure.