Abstract

Alkali halide (100) surfaces are anomalously poorly wetted by their own melt at the triple point. We carried out simulations for NaCl(100) within a simple (BMHFT) model potential. Calculations of the solid-vapor, solid-liquid and liquid-vapor free energies showed that solid NaCl(100) is a nonmelting surface, and that the incomplete wetting can be traced to the conspiracy of three factors: surface anharmonicities stabilizing the solid surface; a large density jump causing bad liquid-solid adhesion; incipient NaCl molecular correlations destabilizing the liquid surface, reducing in particular its entropy much below that of solid NaCl(100). Presently, we are making use of the nonmelting properties of this surface to conduct case study simulations of hard tips sliding on a hot stable crystal surface. Preliminary results reveal novel phenomena whose applicability is likely of greater generality.

Key words: Alkali halides, Wetting, Surface melting, Nanofriction

1 Introduction

Most liquids in nature are expected to wet very well the surface of their own solid at the melting point; and in fact they generally do. However, that is not always true and some examples of nonwetting do exist [1]. A striking case in
point is sodium chloride, where the NaCl(100) solid surface is badly wetted by its own melt, with an anomalously large partial contact angle of 48° (Fig. 1) [2]. How could one have predicted that, and what are the physical consequences? Moreover what applications, and what new phenomena, for instance in the field of friction, could this kind of non-self-wetting lead to? We addressed these questions using simple theory – basically surface thermodynamics and applied statistical mechanics – and computer simulation, in particular classical molecular dynamics (MD).

Fig. 1. The balance of the forces at the solid-liquid-vapor interface.

Consider a NaCl droplet deposited on NaCl(100). From Fig. 1, \( \gamma_{SV} = \gamma_{SL} \cos \theta_{SL} + \gamma_{LV} \cos \theta_{LV} \) and there will be partial wetting by the droplet if the three interface free energies satisfy \( \gamma_{SV} < \gamma_{SL} + \gamma_{LV} \) (\( \theta_{SL} \equiv 0 \) in our case). To obtain a microscopic theory, we must be able to calculate these three interface free energies. For the liquid surface, there is a well established method, the Kirkwood-Buff virial formula [3,4], that builds the surface stress (surface tension), equal to the interface free energy, from mechanical variables, \( i.e., \) from forces and coordinates that can in turn be extracted from MD simulations. Nothing so straightforward is available for the solid-vapor and for the solid-liquid interfaces. The problem is that the solid can support stress, so that the surface stress, which is mechanical and easily calculable, and the surface free energy are no longer the same. For the solid-vapor interface, the problem is solved by resorting to two parallel thermodynamic integrations carried out for two systems, identical in every respect, \( i.e., \) same number of particles, same crystal structure, same cell etc., except that one system is a bulk without surfaces, the other is a slab with two (identical) surfaces. Integration of \( \int_{1/T_i}^{1/T} E(T') d\left(\frac{1}{T'}\right) \) from some low temperature \( T_i \) up to \( T \) gives the free energies of the two systems. The surface free energy is obtained at each \( T \) as half their difference (the slab has two surfaces). For the solid-liquid interface finally, not even that works, because the interface is stable just at \( T = T_m \). Here, we circumvented the difficulty by turning so to speak experimentalists. We simulated a NaCl nanodroplet onto NaCl(100), let it settle, and extracted the contact angle \( \theta_{LV} \) [5]. Once \( \theta_{LV} \), \( \gamma_{SV} \) and \( \gamma_{LV} \) are known, then \( \gamma_{SL} \) can easily be obtained from Young’s force balance equation given above.
Fig. 2. Calculated NaCl surface free energies. a) Solid-vap or $\gamma_{SV}$. Note the metastability up to about 150 K above $T_m$. Dots: effective harmonic approximation. b) Liquid-vapor free energy: experimental and simulated values.

2 Calculations and Results

All results were produced using classical MD simulations, mostly in slab geometries. $\text{Na}^+$ and $\text{Cl}^-$ ions were assumed to interact via BMHFT potentials \cite{6}. These potentials are standard and well tested, but they have a long range Coulomb part. This reduces dramatically the sizes of systems we can simulate – we used between 1500 and 5000 NaCl molecular units – and the simulation times we could afford. Luckily, two hundred psec were usually more than enough to attain equilibrium configurations at our high temperatures. We ran a bulk simulation first, and extracted the bulk melting $T_m$ – the temperature where the BMHFT solid and liquid coexist – at 1066 K, extremely close to the experimental 1074 K of NaCl \cite{3,4}.

We then simulated solid NaCl(100), and found that it remained dry and crystalline up to 1210 K, well above the bulk $T_m$. This kind of nonmelting behavior, where the solid surface can survive in a metastable state even above $T_m$, is exactly what can be expected when the liquid does not wet the solid \cite{1}. The same slab system was then melted to generate a liquid slab – a liquid with two liquid-vapor interfaces. From these simulations, we extracted as explained earlier $\gamma_{SV}$ and $\gamma_{LV}$ shown in Fig.2. Here came three surprises. The first was the large decrease of $\gamma_{SV}$ with increasing $T$, strongly stabilizing the solid surface at high temperature. This is in part an anharmonic effect, and stems from the exceptional stability of long range Coulomb systems against large vibration amplitudes – even in bulk alkali halides largely exceeding the Lindemann melting criterion \cite{4}. The second surprise was to find $\gamma_{LV}$ so high – numerically equal to $\gamma_{SV}$ at $T_m$, when usually the solid surface is energetically much more expensive than the liquid one. The third surprise finally was that the surface entropy $-d\gamma/dT$ is a factor nearly three lower in the liquid than in the solid. This is strikingly contrary to our perception of a very disordered liquid surface (Fig.3) as opposed to an ordered solid surface. As it turns out these two last surprises are related to one another, and are related to incipient molecular NaCl pair bond formation in the outer layer of the liquid surface. A
Fig. 3. Snapshot of simulated liquid-vapor interface at $T_m$.

Fig. 4. Initial (a) and final (b) snapshots of NaCl droplet deposition on NaCl(100) at $T = T_m$. For the last 100 ps the drop remains in a metastable state forming a negligible internal contact angle $\theta_{SL}$, and an external contact $\theta_{LV}$ angle of 50$^\circ$.

way to assess quantitatively this effect was found by recalculating the surface tension after removing molecular correlations, and showing that when this is done both $\gamma_{LV}$ (see $\gamma_{LV}^\ast$ in Fig.2(b)) and the liquid surface entropy drop hugely [3,4].

Finally, we melted a small solid NaCl cube to form a nanodroplet, and deposited it on the solid NaCl(100) slab surface (Fig. 4). From this final simulation we extracted an external wetting angle $\theta_{LV}$ of 50$\pm$5$^\circ$, in good agreement with the experimental 48$^\circ$. When inserted in the force balance equation along with $\theta_{SL} \sim 0$, that finally yields $\gamma_{SL} = 36$ mJ/m$^2$, which is about 1/3 of $\gamma_{SV}$ and $\gamma_{LV}$. This relatively large value clearly demonstrates the poor adhesion of liquid NaCl to the solid, in turn reflecting the fact that they are very different – for example the liquid is 27% less dense than the solid. Nucleation studies [7,8] suggested even larger values of $\gamma_{SL}$ as large as 80 mJ/m$^2$ at $T \sim 800$ K.

In conclusion, three separate pieces of physics conspire to cause the poor wetting properties of NaCl(100) by its own melt. The first is the extreme anharmonic stability of the solid surface itself. The second is the poor adhesion of the liquid to the solid. The third is the high liquid surface tension caused by the unexpected but very real surface entropy deficit [3,4].
Fig. 5. Nanofriction simulation of a hard diamond tip ploughing into NaCl(100) near $T_m$. The substrate is solid, but despite that the furrow heals away and recrystallizes in a very short time of a few ps.

3 Nanofriction

The next class of problems we are presently addressing, is as important as it is unexplored, is the high temperature nanofriction of a hard sliding tip near $T_m$ for a nonmelting surface like NaCl(100). On a normal solid surface – one that is wetted by its own liquid – a thin liquid film will nucleate below $T_m$ causing a jump to contact with the approaching tip [9], and generally ruining it. A nonwetting surface like NaCl(100) will not do such thing. It is thus ideal, at least theoretically, to explore friction close to the melting point. Friction has been the subject of important simulation work [10,11]. High temperature friction is only recently beginning to receive some attention [12] and there is a clear need for more work. We intend precisely to explore and motivate future work in this extreme regime.

We conducted preliminary sliding friction simulations for hard tips on NaCl(100), exploring both the deep ploughing regime with a sharp tip (Fig. 5), and the gentle grazing regime with a flat tip. The tip was modeled to reproduce the interaction between rigid diamond and the NaCl surface[13,14]. For deep wear simulations we created a conical tip, composed of $\sim 400$ atoms. The diameter was around 13Å and the height $\sim 26$Å. On the contrary for light grazing wearless friction we use a completely blunt flat tip composed of $\sim 200$ atoms (not shown). The flat surface of the tip has a (111) plane of 13Å diameter roughly. In ploughing regime the tip was moving with a constant speed of 50 m/sec and the constant penetration depth of 6Å. The wear frictional force of Fig.6 shows that at high temperature there is a regime where friction drops, although the surface is still fully solid. The tip scratches the solid surface, leaving behind a furrow which in this regime heals out closing spontaneously on a very short time of 10 ps. Direct inspection shows that the tip is surrounded in this high temperature regime by a seemingly liquid cloud, moving along with
Fig. 6. The dependence of friction force on temperature shows a decrease of nanofriction on NaCl(100) close to the melting point, as in ice skating.

it and lubricating its motion. In this way, the tip effectively skates over the solid NaCl(100) surface. Discussions of skating near the melting point appear to exist so far only for ice [10].

Preliminary results show that under grazing conditions, the high temperature behavior of sliding friction is just the opposite [14]. The initially very low sliding friction of the flat tip over the cold surface rises with temperature, culminating in a frictional peak very close to the melting point. Here it appears that the large compliance of the (nearly unstable) hot NaCl surface lattice is responsible for the increased high temperature friction. There is to our knowledge no prior established mechanism of this kind for high temperature frictional increase.

These predicted nanofriction phenomena are currently under closer scrutiny for further physical characterization. It is hoped that experimental efforts could be started to investigate their existence, which we believe to be more general for all nonmelting surfaces, rather than specific to the NaCl(100) system studied here. A more detailed report of this part of the work is forthcoming [14].

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References

[1] U. Tartaglino, T. Zykova-Timan, F. Ercolessi, and E. Tosatti, Phys. Repts. 411, 291 (2005).

[2] G. Grange and B. Mutaftschiev, Surf. Sci. 47, 723 (1975).

[3] T. Zykova-Timan, D. Ceresoli, U. Tartaglino and E. Tosatti, Phys. Rev. Lett. 94, 176105 (2005).

[4] T. Zykova-Timan, D. Ceresoli, U. Tartaglino and E. Tosatti, J. Chem. Phys. 123, 164701 (2005).

[5] T. Zykova-Timan et al., Surf. Sci. 566/568, 794 (2004).

[6] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids 25, 45 (1964).

[7] E. R. Buckle and A. R. Ubbelohde, Proc. R. Soc. London, Ser. A 529, 325 (1960); 261, 197 (1961).

[8] C. Valeriani, E. Sanz and D. Frenkel, J. Chem. Phys. 122, 194501 (2005).

[9] L. Kuipers and J. W. M. Frenken, Phys. Rev. Lett. 70, 3907 (1993).

[10] Persson, B.N.J., Sliding friction: physical principles and applications, (Berlin, Springer-Verlag), 1998.

[11] B. Bhushan, J. N. Israelachvili and U. Landman, Nature 374, 607 (1995).

[12] S.Y. Krylov, K.B. Jinesh, H. Valk, M. Dienwiebel, J.W.M. Frenken, Phys. Rev. E 71, 065101 (2005).

[13] H. Tang et al., J. Chem. Phys. 108, 359 (1998).

[14] T. Zykova-Timan, D. Ceresoli and E. Tosatti, to be published.