The high temperature surface properties of alkali halide crystals are very unusual. Through molecular dynamics simulations based on Tosi-Fumi potentials, we predict that crystalline NaCl (100) should remain stable without any precursor signals of melting up to and even above the bulk melting point $T_m$. In a metastable state, it should even be possible to overheat NaCl (100) by at least 50 K. The reasons leading to this lack of surface self-wetting are investigated. We will briefly discuss the results of calculations of the solid-vapor and liquid-vapor interface free energies, showing that the former is unusually low and the latter unusually high, and explaining why. Due to that the mutual interaction among solid-liquid and liquid-vapor interfaces, otherwise unknown, must be strongly attractive at short distance, leading to the collapse of any liquid film attempting to nucleate at the solid surface. This scenario naturally explains the large incomplete wetting angle of a drop of melt on NaCl (100).

Keywords: Surface stress; Surface thermodynamics; Wetting; Alkali halides; Molten salt surfaces; Molecular dynamics simulation.

I. INTRODUCTION

Interest is increasing toward adhesion, the structure and physics of solid-liquid interfaces, and the structure of liquid surfaces, particularly of complex and molecular systems. In order to gain more insight into these problems, there is a strong need for good case studies, to use as well-understood starting points.

One of the easiest starting points may be to study the relationship and contact of a liquid with its own solid, a clear situation where there will be no ambiguity of physical description, no uncertainty in chemical composition, no segregation phenomena, all of them complications present in the study of adhesion between different substances.

Adhesion of a liquid onto the surface of its own solid usually materializes spontaneously with temperature. Most solid surfaces are known to wet
themselves spontaneously with an atomically thin film of melt, when their
temperature $T$ is brought close enough to the melting point $T_m$ of the
bulk solid. The phenomenon whereby the thickness $l(T)$ of the liquid film
diverges continuously and critically as $T \rightarrow T_m$ is commonly referred to
as (complete) surface melting\cite{1, 2}.

There are actually a number of exceptions to this behavior. Some solid
surfaces in particular remain fully crystalline as $T \rightarrow T_m$. This surface non-melting phenomenon, originally discovered in molecular dynamics simulations of Au(111)\cite{3} and independently observed experimentally
in Pb(111)\cite{4}, is known for the close-packed face of other metals too, such
as Al(111)\cite{5}.

Here we are concerned with the surface of alkali halides, crystals well
known for their unusually stable neutral (100) faces. Addressing a long
time ago the NaCl (100) surface, bubble experiments by Mutaftschiev and
coworkers revealed incomplete wetting of the solid surfaces by their own
melt\cite{6, 7}, moreover with an extraordinarily large partial wetting angle of
$48^\circ$. This kind of incomplete wetting, as is physically clear, and as was
demonstrated on metals surfaces\cite{2, 8}, is associated with non-melting of
the crystal surface.

In this paper we will review our recent theory work, where we showed
by direct simulation the surface non-melting of NaCl (100)\cite{9, 10}. The
reasons leading to this kind of surface non-melting are investigated. First,
we will show the solid surface free energy calculated by thermodynamic
integration, and see that at high temperature it drops due to a larger
anharmonicity than in most other solid surfaces. Next, we will examine
the surface tension of the liquid NaCl surface, we will find unusually large,
owing to a surface entropy deficit, connected with the local surface short
range molecular order. The solid-liquid interface free energy will finally be
argued to be large, due to a 26% density difference. We will also discuss
qualitatively -- were hypothetically the solid-vapor interface to split into a
pair of solid-liquid and liquid-vapor interfaces, with a thickness $l$ of liquid
in between -- the interaction free energy $V(l)$ expected between them. This
interaction is here strongly attractive at short range, leading to the collapse
of any liquid film attempting to nucleate at the solid-vapor interface, and
causing surface non-melting.

All quantitative results reviewed here were derived by means of molecular
dynamics simulations, carried out extensively for NaCl (100) slabs.
These simulations, as will be detailed below, are entirely based on inter-
atomic potentials that Mario Tosi refined and published, together with
Fausto Fumi, just over 40 years ago\cite{12}. It is a fitting tribute to Mario’s
scientific perseverance, thoroughness, and general dependability, that these
potentials still turn out to be so incredibly accurate, even well outside the
range of temperatures for which they were constructed and tested, such a
long time ago.
II. SIMULATIONS WITH TOSI-FUMI POTENTIALS

The high temperature properties of solid NaCl bulk and NaCl (100) slabs were studied by classical molecular dynamics (MD) simulations. NaCl was described with the potential of Tosi and Fumi who accurately parametrized a Born-Mayer-Huggins form. The Coulomb long-range interactions were treated by the standard three dimensional (3D) Ewald method applied to a geometry consisting of infinitely repeated identical crystal slabs. Simulated systems generally comprised about 2000–5000 molecular units, with a time-step of 1 fs, and a typical simulation time of 200 ps. Long-range forces severely limit size and time in these simulations by comparison with the order-of-magnitude larger sizes and longer times typically affordable for systems with short range forces. We took explicit care to ensure that all our results are not crucially affected by small sizes, and that full equilibration was achieved in all cases. We checked that 80 Å of vacuum between repeated slabs are sufficient to prevent the interaction of a liquid slab with its own replicas. Calculations were done at constant cell size and with periodic boundary conditions. Thermal expansion was taken care of by readjusting the \((x, y)\) size of the cell at each temperature so as to cancel the \((x, y)\) stress in the bulk solid. The theoretical thermal expansion was \(4.05 \times 10^{-5}\) \(\text{K}^{-1}\), compared with \(3.83 \times 10^{-5}\) \(\text{K}^{-1}\) in experiment. The theoretical bulk melting temperature \(T_M\) of NaCl was calculated by two phase coexistence to be \(1066 \pm 20\) K. Remarkably, this Tosi-Fumi melting temperature is extremely close to the experimental melting temperature of 1073.8 K. The volume expansion at melting is about \((27 \pm 2)\%\), also in excellent agreement with the experimental value of 26%.

Tab. I lists some of the calculated thermodynamical quantities at high temperature, close to the melting point. These results provide an independent confirmation of the outstanding quality of the Tosi-Fumi description of thermodynamics of NaCl, even at very high temperatures and as we shall see even at surfaces, where it was by no way guaranteed.

III. SURFACE FREE ENERGIES AND NON-MELTING OF NaCl(100)

High temperature simulations of crystalline NaCl(100) slabs directly showed the full stability of the dry, solid surface up to \(T_M\). Moreover, a well pronounced metastability of the slab solid faces above the melting point \(T_M\) indicated a clear surface non-melting behavior. We found that a much higher (“surface spinodal”) temperature \(T_S \approx T_M + 150\) K needs to be reached before the crystalline NaCl (100) surface spontaneously melts. \(T_S - T_M\) thus represents the maximum ideal overheating that a defect free NaCl (100) surface can theoretically sustain without becoming spontaneously unstable against melting. This large overheating is quite similar in magnitude to that predicted for, e.g., Au(111) and Al (111).
Simulation | Experiment
---|---
$T_M$ (K) | 1066±20 | 1074
$\Delta V$ | 27% | 26%
$L$ (eV/molecule) | 0.29 | 0.29
$\Delta S_m$ ($k_B$) | 6.32 | 6.38
dP/dT (kbar/K) | 0.0311 | 0.0357
RMDS (ave.) (Å) | 0.60 | 0.49
$\delta$ | 20–24% | 17–20% [11]

TABLE I: High temperature properties of NaCl. $T_M$ is the melting temperature; $\Delta V$ is the volume jump at the melting point; $L$ is the latent heat of melting; $\Delta S_m$ is the entropy variation at the melting point; dP/dT is the resulting Clausius-Clapeyron ratio at the melting point. RMSD is the averaged root mean square displacement of atoms at the melting point; $\delta$ is the RMSD over the Na–Cl distance, for the Lindemann melting criterion.

At any temperature between $T_M$ and $T_S$, bulk melting can only originate through nucleation. Even though nucleation of the melt is in reality likely to proceed from a localized surface droplet or defect, it is instructive to consider a very idealized nucleus consisting of a uniform liquid film of thickness $l$. As a function of temperature, there will be a critical nucleation thickness $l_{crit}$ decreasing from $\infty$ to zero between $T_M$ and $T_S$ [3, 13]. The free energy difference per unit area between a surface with a liquid film of thickness $l$ and the same surface in its full crystalline state is

$$G(l) = -\rho \lambda \left( \frac{T}{T_M} - 1 \right) + (\gamma_{SL} + \gamma_{LV} - \gamma_{SV}) + V(l)$$

(1)

The first term is the gain due to the melting of the solid at $T > T_M$. Here $\lambda$ is the latent heat per unit mass and $\rho$ is the liquid mass density. The second term $\Delta \gamma_{\infty} \equiv (\gamma_{SL} + \gamma_{LV} - \gamma_{SV})$, is the free energy imbalance caused by replacing the SV interface with the SL+LV pair of interfaces, supposed to be non-interacting. The last term $V(l)$ is an interface interaction, representing the correction to $\gamma_{SL} + \gamma_{LV}$ when the two interfaces are at close distance. This definition implies $V(+\infty) = 0$ and $V(0) = -\Delta \gamma_{\infty}$. At very large distance the interaction disappears. The solid-vapor crystal surface is instead recovered when the SL and LV interfaces collapse, and the liquid film disappears at $l = 0$. The non-melting condition $\gamma_{SL} + \gamma_{LV} > \gamma_{SV}$, or $\Delta \gamma_{\infty} > 0$ implies that here the interaction $V(l)$ is mainly attractive.

This formulation indicates three possible origins for non-melting: an exceptionally low free energy $\gamma_{SV}$ of the solid surface; an unusually large free energy $\gamma_{SL}$ of the solid-liquid interface; a relatively high surface tension $\gamma_{LV}$ of liquid NaCl. As detailed elsewhere [9, 10], all three mechanisms are actually relevant to NaCl(100).

The solid-vapor interface free energy at the melting point was calculated...
FIG. 1: The solid surface free energy of NaCl(100) calculated from thermodynamic integration (circles: effective harmonic approximation).

Through standard thermodynamic integration, using

\[
\left(\frac{\partial (F/T)}{\partial (1/T)}\right)_{N,V} = E, \tag{2}
\]

where \( E \) is the surface internal energy, extracted from simulation of the crystalline NaCl(100) slab and the corresponding bulk at increasing \( T \) from 50 K to 1200 K. The surface free energy in Fig. 1 shows a large drop at high temperatures, with an increasing deviation from an effective harmonic behavior above 600 K, indicating very strong surface anharmonicity in this regime. The main source of this anharmonicity is connected with large root mean square thermal fluctuations of the surface Cl and Na ions above 20% of the Na–Cl distance, largely exceeding the canonical Lindemann values. \[10\]

The liquid-vapor free energy, equal to the liquid surface tension, was evaluated from simulations of liquid NaCl slabs via the standard Kirkwood-Buff formula [14]. The first thing we note in the result, shown in Fig. 2, is that right at \( T_m \) the solid and liquid surface free energies are essentially identical, 103±4 and 104±8 mJ/m\(^2\) respectively. This is very unusual, and implies directly surface non-melting, because clearly \( \Delta \gamma_\infty = (\gamma_{SL} + \gamma_{LV} - \gamma_{SV}) > 0 \). In fact, even though we did not calculate \( \gamma_{SL} \), this interface free energy has no reason to be very small, owing to the large solid-liquid density difference. We independently estimated a lower bound for \( \gamma_{SL} \) to be 36±6 mJ/m\(^2\) [10].

The question that remains to be explained is therefore the physical reason why the liquid surface tension is so relatively high. The liquid surface density profile, in particular, is very smooth, with none of the layering phenomena displayed by the metal surfaces (see Fig. 3).
FIG. 2: The calculated liquid surface free energy calculated. The NaCl (100) surface free energy is also shown in the temperature range from 1000 K to 1250 K.

FIG. 3: Surface density profile of liquid NaCl, compared with that simulated for liquid Ar, and for two liquid metals. Note that NaCl does not show layering as the metals do, and has an even smoother profile than Ar.
An important clue is provided by surface entropy (per unit area) $S_{\text{surf}} = -d\gamma/dT$. The temperature dependence of two surface free energies of Fig. 2 shows a factor 2.6 lower surface entropy $S_{LV}$ of the liquid surface compared with that of the solid surface. This liquid surface entropy deficit (SED) strongly suggests some underlying surface short range order. Short range order can in turn also explain why the surface tension is here as high as the solid surface free energy. The surface profile indicates that the order is clearly not layering: so what is it instead?

The answer we find is that charge order, already very important in bulk, plays a newer and enhanced role at the molecular liquid surface. If surface thermal fluctuations are indeed very large, we find them revealing correlated. For a Na\(^+\) ion that instantaneously moves e.g., out of the surface, there is at least one accompanying Cl\(^-\), also moving out; and vice versa. So on one hand the large fluctuations smear the average liquid vapor density profile, bridging very gently between the liquid and essentially zero in the vapor, (Fig. 3). On the other hand the two body correlations, described e.g., by the the Na-Cl pair correlation function, or by its integral, the ion coordination number $N$, do not vanish identically in the vapor, but tend to a typical value corresponding to the NaCl molecule, (plus in fact a large concentration of dimers, Na\(_2\)Cl\(_2\)). The lack of freedom implied by the incipient molecular bond explains the entropy deficit, and the consequent large surface tension of the molten salt surface. To confirm if this is true, we recalculated $\gamma_{SL}$ modifying the forces in the Kirkwood-Buff formula by removing all contributions from surface ions whose coordination is between zero and 1.3, the average NaCl vapor value, which amounts to suppress the molecular order at the liquid-vapor interface. This construction, meant to provide a qualitative estimate of where would the surface tension drop if surface molecular order were absent, gives a surface tension of about 50 mJ/m\(^2\). With a surface tension this low, surface non-melting would in fact disappear, and wetting of the solid surface by the molten salt would be complete. Hence the high surface tension of liquid NaCl can indeed be ascribed to surface molecular short range order, ultimately due to charge neutrality. This result confirms an early surmise by Goodisman and Pastor.

**IV. INTERFACE INTERACTION**

In this short speculative section we further rationalize the results above within the phenomenological framework of Eq.(1), where besides the bare interface free energies just calculated, an interaction $V(l)$ appears. We will not present a calculation of $V(l)$, but simply discuss it on physical grounds, in the light of our new microscopic understanding gained through simulations, and calculations of interface free energies just reviewed. The definition of interface interaction $V(l)$ given earlier implied $V(+\infty) = 0$ and $V(0) = -\Delta\gamma_{\infty}$. At very large distance the interaction disappears. At the opposite limit, when the SL and LV interfaces approach each other
and merge at very close quarters, they will eventually yield the SV interface upon their collapse, when the liquid film disappears altogether at $l = 0$.

The non-melting condition $\gamma_{SL} + \gamma_{LV} > \gamma_{SV}$, or $\Delta \gamma_{\infty} > 0$ implies here that the interaction $V(l)$ is attractive at short range.

In non-melting metal surfaces, a source of finite-range attraction was described as the result of a constructive interference between two equal-period damped density oscillations, one entering the liquid film from the solid side, the other, due to surface layering, from the vacuum side. Here, one of the two oscillations, namely that on the vacuum side, is missing, because there is no layering at the molten salt surface. At large distance the main interaction between the SL and the LV NaCl interfaces will essentially be due to electrostatic forces and to dispersion forces. The latter in particular give rise to an additional long-range interface interaction $V_{\text{dis}}(l) = H l^{-2}$ which is dominant at large distances. Here $H$ is the Hamaker constant, that can be estimated through the formula $H = (\pi/12) C_6 (n_s - n_l)(n_l - n_v) = 0.00119 \text{ eV}$, where $C_6 = 72.5 \text{ eV} \text{Å}^6$ is the coefficient of the Lennard-Jones interaction between chlorine ions, $n_s$, $n_l$ and $n_v$ are the number of Cl$^-$ ions per unit volume respectively in the solid, liquid and vapor phase$[17]$. Since the liquid density is only about 79% that of the solid, this constant is positive which implies a long range repulsion of the SL and LV interfaces. A simple estimate indicates however that $V_{\text{dis}} < H/a^2 = 0.51 \text{ mJ/m}^2$, a value that makes it irrelevant in practice.

Therefore we expect the effective interaction $V(l)$ to be very weak in NaCl, everywhere except very close to zero range, $l \approx a$. Here it will suddenly turn strongly attractive, $V(0) \approx -\Delta \gamma_{\infty}$. The physics of this short range attraction has already been described, because it amounts to the free energy gained by replacing the two costly LV and SL interfaces, with the single and less costly SV interface.

V. CONCLUSIONS

Summarizing, the NaCl(100) surface is predicted to show non-melting and to sustain overheating up to a theoretical maximum of about 150 K above the bulk melting point. The thermodynamics of surface non-melting in alkali halides is shown to differ from that of metal surfaces, e.g. Al(111), Pb(111) or Au(111). Unlike metals, non-melting in alkali halides is not connected with liquid layering, but to molecular short range order raising the liquid surface tension, as well as to strong anharmonicity that lowers the free energy of the solid surface. It is argued moreover that the thermodynamical SL-LV interface interaction should consist mainly of a strong short-range attraction. Fresh microscopic experimental work, absent so far, is called for to check these predictions on the high temperature behavior of NaCl(100) and other alkali halide surfaces.
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