Alkali Dimers on the Surface of Liquid Helium

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A recent paper by Ancilotto et al. (Zeitschrift für Physik B, in press), presented calculations of adsorption energies and the geometry of a surface dimple for alkali atoms bound to the surfaces of quantum liquids ($^4$He, $^3$He, $^2$H). Here we present a study of the adsorption of two alkali dimers ($\text{Li}_2$, $\text{Na}_2$) on the surface of liquid helium. The calculations employ a model of an abrupt interface formulated by Ancilotto et al. as well as one using a diffuse interface. Our conclusion is that the dimers are bound to the surface more strongly than their respective monomers. In the case of dimers there is an additional degree of freedom—the orientation of the molecular axis relative to the surface. We study the influence of molecular anisotropy on adsorption by comparing the cases of “erect” and “spinning flat” orientations and conclude that the latter is energetically favored.

1. INTRODUCTION

Helium atoms are the most inert atoms in the periodic table. One might therefore conclude that helium is more strongly attracted to any atom other than to itself. There is a flaw in this argument, however, as demonstrated by the recently established fact that $^4$He does not wet the surface of Cs and Rb metals.\(^1\)\(^1\)\(^-\)\(^3\) The flaw is due to the fact that the helium atom’s interaction with alkali atoms and surfaces is even weaker than that between two helium atoms\(^2\) (see Table in Ref. 2 for the relevant interactions between atoms and between atoms and surfaces) because of \(^1\)The isotope $^3$He is believed to wet all surfaces at low $T$,\(^4\) while $^3$He–$^4$He mixtures are known to exhibit re-entrant wetting behavior.\(^5\)

\(^2\)For example, the well-depth of the He–He potential is 11 K while that of He–Cs is about 1.2 K.\(^6\)\(^7\)
the large hard core repulsion arising from the diffuse electron cloud surrounding the alkali metal. An analogous non-wetting phenomenon arises when alkali atoms are placed near the surface of liquid He. Because of the inertness of their interactions, an alkali metal atom is expected to prefer to adsorb on the surface rather than solvating within the bulk liquid (The large positive energy of a solvated alkali in $^4$He was calculated by Dalfovo). $^8,9$

Recent experiments have probed the state of alkali species in the presence of helium clusters. $^{10}$ There is qualitative consistency between the spectra and the model of a surface state of the alkali metal chromophore. To date, there have appeared no detailed predictions of these spectra (although there have been for the metastable bulk state of such alkali atoms$^{11,12}$). One of the difficulties inherent in such a prediction is the need to treat the cluster dynamics in the presence of the alkali adatom. This is complicated by the tendency of the atom to distort the cluster by forming a shallow dimple beneath it.

The present paper discusses the adsorbed state of alkali metal dimers on liquid helium. This represents in part an extension of the work, called I henceforth, of Ancilotto et al. on alkali metal monomers. In Sect. 1, the problem was treated with two alternative models. One was a simplified "abrupt interface" model in which the distortion was characterized only by the spatial variation of the fluid's boundary due to the presence of the atom. The alternative was a more realistic density functional model, which allows more flexible density variation to minimize the energy (within functional forms in the model). In the present study of dimers, we use the former approach, as well, as an alternative "diffuse interface" model. This latter method allows us to perform relatively simple model calculations which have, presumably, reliability intermediate between that of the two other models.$^9$

The outline of this paper is the following. In the next section, we present the model and develop the equation which describes the shape of this interface in the presence of an admolecule. This equation depends on the pair potential between helium and the molecule. In Sect. 3, we outline different approximations to this potential. In Sect. 4, we display numerical solutions for several cases of adsorbed monomers and dimers. Section 5 summarizes our results.

2. MODEL OF AN INTERFACE FOR THE PROBLEM OF PHYSICAL ADSORPTION

In Sect. 1, there was presented an analysis of the dimple structure formed at the surface of a quantum fluid ($^3$He, $^4$He, or H$_2$) upon which was