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Sodium dimers on the surface of liquid ^{4}He

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We have studied the structure of a sodium dimer interacting with liquid ^{4}He. We calculated the equilibrium configuration and binding energy of a Na$_2$ molecule solvated in a bulk liquid ^{4}He "bubble" and near the liquid-vapor interface "dimple" by using a density-functional approach. We find that the solvated molecule is a metastable state, while the the lowest energy bound state occurs when the molecule lies flat on the surface of the liquid. The binding energy for the "erect" dimer is only ~ 1 K higher than the flat dimer, with no potential energy barrier between the two orientations, implying relatively free rotations of the molecule on the surface. The small effects of the liquid environment on the vibrational properties of the dimer are investigated.

The interaction of a helium atom with alkali-metal atoms is extremely weak, even weaker than that between two helium atoms.[1] The hard-core repulsion arising from the very diffuse electron charge surrounding the alkali atom core keeps the He atom relatively far from it, in a region where the rapidly decaying Van der Waals attractive interaction is very small. A surprising consequence of the weakness of these interactions is that ^{4}He does not wet the surface of Cs and Rb metals.[2–4] A related "nonwetting" phenomenon arises when isolated alkali atoms interact with the surface of liquid ^{4}He, i.e., they prefer to adsorb on the surface of the liquid rather than solvating into it.[5,6]

The absorption of atomic and molecular foreign species by liquid ^{4}He clusters has recently become the subject of extensive experimental[7–10] and theoretical[5,11,6,13] studies. This interest is motivated by the possibility of using impurities as sensitive probes to detect possible superfluid behavior of ^{4}He clusters. Among others, alkalis impurities (monomers and simple molecules) are ideal experimental probes[9] because of their relatively simple electronic structure and because their spectroscopic and optical properties are accurately known.

We extend here our previous calculations on the adsorption of alkali monomers on the surface of liquid ^{4}He (Ref. 6) to the case of alkali dimers and consider explicitly the case of a Na$_2$ molecule. Unlike in Ref. 6, we include in our calculations the valence electronic structure of the dimer: this allows us to study possible changes of the dimer properties, like the vibrational frequencies and the dimer bond length, due to the presence of the liquid. Similar to the case of alkali atom impurities,[5] we find that a Na$_2$ dimer in bulk liquid has a positive value for the solvation energy, corresponding to an unstable state, whereas stable states occur when the molecule is adsorbed on the surface of the liquid. This confirms that in experiments with helium clusters beams, after the pickup, the alkali dimers will reside on the surface of the clusters.[9] The surface states are stable for any orientation of the molecule axis with respect to the surface plane. The "flat" dimer geometry, however, has a slightly higher binding energy with respect to other orientations ("erect" and 45° tilted). No energy barrier is found to separate the extreme configurations in which the molecule axis is either parallel or perpendicular to the surface plane, indicating a relative facility for the dimer to rotate on the surface even at very low temperatures. We analyze the change in the helium-vacuum interface structure in proximity of the dimer adsorption site. Similar to the case of monomer adsorption, the surface binding energy is enhanced by the formation of a "dimple" in the liquid just below the adsorbed molecule.

We finally point out the very small effect of helium on the dimer vibrational energies and on the interatomic equilibrium distance. Our findings are consistent with the experimental observation that the low-energy vibrational levels of Na$_2$ on the surface of large ^{4}He clusters are not shifted with respect to the free molecule.[9,10] When the molecule is embedded in the liquid, a very small blue shift in the frequency is predicted, which should be observable using spectroscopic techniques, possibly allowing one to discriminate in experiments between solvated (metastable) and surface (stable) states.

In our calculations liquid ^{4}He is described by a phenomenological density functional[14] which gives a good description of the $T=0$ equation of state, of the static density-density response function of the bulk liquid and of the properties of the free surface of liquid ^{4}He. The energy functional has the following form:

$$E_{\mathrm{He}}[\rho(\mathbf{r})]=\frac{\hbar^2}{2M}\int[\nabla\rho^{1/2}(\mathbf{r})]^2d\mathbf{r}+\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')V_\ell(|\mathbf{r}-\mathbf{r}'|)+\frac{c}{2}\int\rho(\mathbf{r})(\bar{\rho}_{\mathbf{r}})^{1+\gamma}d\mathbf{r}, \tag{1}$$

where $\rho(\mathbf{r})$ is the density of the liquid and M is the ^{4}He atomic mass. The first term is the quantum kinetic energy term, the second term contains a two-body ^{4}He-^{4}He pair potential $V_\ell(r)$ screened at distances shorter than a characteristic length h_ℓ, while the third term, which contains the average of the density over a sphere of radius h_ℓ, $\bar{\rho}_r$, accounts for the internal kinetic energy and for the increasing contribution of the hard-core He-He repulsion when the density is increased. The three free parameters h_ℓ, c, and γ are adjusted in order to reproduce the experimental values of the

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energy per atom for liquid ^{4}He, the compressibility of bulk liquid at the saturation density, and the surface tension σ. The above functional has been used recently in a variety of calculations, including the study of impurities[5] and electrons[12] in bulk ^{4}He, alkali atom adsorption on the surface of liquid ^{4}He (Ref. 6) and wetting phenomena on alkali-covered substrates.[15]

Accurate *ab initio* results for the two-body interaction potential of a Na_2 molecule with a He atom are available.[16] In order to estimate the energetics of adsorption and the distortion of the liquid-vacuum interface in response to the adsorbed molecule it would be sufficient to incorporate this *ab initio* interaction potential in the density-functional description for He, as done for instance in Ref. 5 in the case of atomic impurities in liquid ^{4}He. A complete neglect of the electronic structure of the molecule is however a limitation, since it does not allow one to calculate the variations in the properties of the dimer itself due to the presence of the nearby liquid. For instance, one may wonder what changes the helium environment induces in the vibrational constants of the immersed molecule. These are quantities that can be measured experimentally with very high accuracy,[9,10] even if a very small effect is expected in the present case due to the small amount of interaction energy involved in alkali-He interaction.

In order to properly include the dimer electronic structure, Na_2 is described by a density-functional (DF) scheme where the two valence electrons in the molecule are represented by a one-particle (doubly occupied) orbital $\Psi(\mathbf{r})$ interacting with the frozen Na ion cores via *ab initio* pseudopotentials.[17] Within the DF formalism, the total energy of the molecule (in vacuum) is given by

$$E_e[\Psi]=\frac{\hbar^2}{2m}\int|\nabla\Psi(\vec{r})|^2 d\vec{r}+E_{\rm ion}(d)+\int V_{ps}(\mathbf{r})\rho_e(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{\rho_e(\mathbf{r})\rho_e(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{\rm xc}[\rho_e(\mathbf{r})]. \qquad (2)$$

Here $\rho_e(\mathbf{r})=|\Psi(\mathbf{r})|^2$ is the valence electron charge density, $E_{\rm ion}(d)$ is the Coulomb repulsion between the two Na ionic cores at a distance d, $V_{ps}(\mathbf{r})$ is a norm-conserving, angular-momentum-dependent pseudopotential[18] describing the interaction between the two valence electrons and the ionic cores. The fourth term is the Hartree electron-electron interaction and the last term is the many-body exchange-correlation contribution, which is evaluated in the usual local-density (LD) approximation, i.e., $E_{\rm xc}[\rho_e(\mathbf{r})]=\int\epsilon_{\rm xc}[\rho_e(\mathbf{r})]\rho_e(\mathbf{r})d\mathbf{r}$, where $\epsilon_{\rm xc}[\rho_e(\mathbf{r})]$ is the exchange-correlation energy density of a homogeneous electron gas of density $\rho_e(\mathbf{r})$. The nonlinear core correction to the exchange-correlation energy is included in evaluating $E_{\rm xc}$.[19] This correction is necessary in order to describe accurately the electronic properties of alkali atoms and molecules. In particular, the neglect of such correction leads to a serious underestimate of the dimer bond length and an overestimate of the vibrational frequency.

We tested the LD approximation (2) by calculating a few properties of the Na_2 dimer in vacuum and comparing them with available experimental data. We find for the equilibrium Na-Na distance $d_{\rm eq}=3.02$ Å and for the vibrational frequency $\omega_v=159.6$ cm^{-1}. The corresponding experimental values are $d_{\rm eq}=3.08$ Å and $\omega_v=159$ cm^{-1}, respectively.[20]

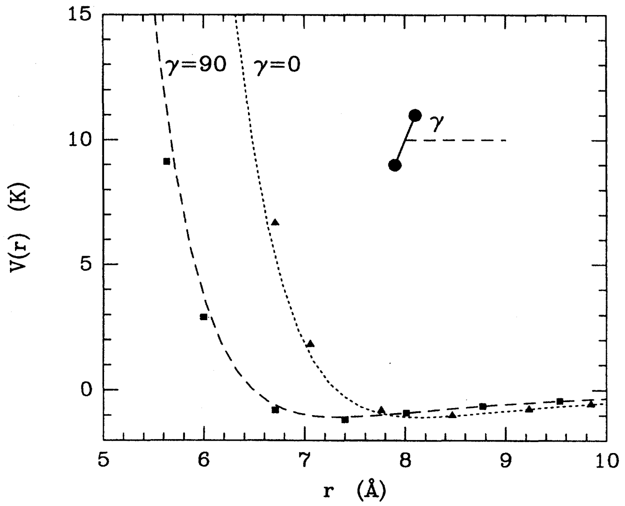

FIG. 1. Na_2-^{4}He interaction potential. Squares and triangles: calculated as described in the text; dashed and dotted lines: *ab initio* calculations from Ref. 16.

To include the interaction between the molecule and the ^{4}He system, we add to the functional $E_e+E_{\rm He}$ for the noninteracting system the term

$$E_{e-{\rm He}}[\rho,\Psi]=\int\int\rho(\mathbf{r})|\Psi(\mathbf{r}')|^2 w(\mathbf{r}-\mathbf{r}')d\mathbf{r}d\mathbf{r}'+\int\rho(\mathbf{r})w_c(|\mathbf{r}-\mathbf{r}_c|,\gamma)d\mathbf{r}. \qquad (3)$$

Here $w(\mathbf{r})$ is a short-range repulsive term due to the overlap of the helium and Na_2 electronic wave functions. Following Ref. 21, we take $w(\mathbf{r})=\alpha\delta(\mathbf{r})$, where α is a constant. This approximation becomes exact in the case of alkali atom-^{4}He interaction.[21] We choose $\alpha=564$ eV a_0^3 to fit the repulsive part of the two-body interaction potential between a ^{4}He atom and a Na_2 molecule, as calculated in Ref. 16 using accurate *ab initio* methods. The term $w_c(|\mathbf{r}-\mathbf{r}_c|,\gamma)$ accounts for the anisotropic dipole-dipole dispersion attraction $\propto|\mathbf{r}-\mathbf{r}_c|^{-6}$. Here $\mathbf{r}_c$ is the coordinate of the dimer center of mass, while γ is the angle between $\mathbf{r}-\mathbf{r}_c$ and the axis of the molecule. We take for $w_c(|\mathbf{r}-\mathbf{r}_c|,\gamma)$ the *ab initio* result of Ref. 16. Our calculated ^{4}He-Na_2 potential energy curves are shown in Fig. 1. Although both the position and the depth of the potential wells are close to the results of Ref. 16, a discrepancy in the repulsive part of the potential, due to the approximate form used for $w(r)$, results in a slight overestimate of the overall anisotropy of the interaction potential.

We used in our calculations a supercell geometry, with periodic boundary conditions imposed on the electron wave function $\Psi(\mathbf{r})$ and on the ^{4}He density $\rho(\mathbf{r})$. These are expanded in plane waves, whose maximum number is chosen such as to give converged values for the total energy of the system. The minimization of the total-energy functional of the interacting system $E=E_e+E_{\rm He}+E_{e-{\rm He}}$ with respect to

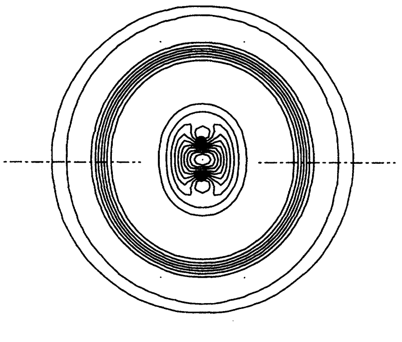

FIG. 2. Na_2 molecule in bulk liquid ^{4}He. Contour plots of the electron and helium densities in a plane passing through the Na_2 ion cores. The electron charge-density distribution is visible in the center of the cavity. The dots indicate the Na cores positions.

ρ and Ψ, subject to the constraints of a constant number of ^{4}He atoms in the supercell, $\int \rho(\mathbf{r}) d\mathbf{r} = N$, and of the correct normalization of the electronic wave function $\int |\Psi(\mathbf{r})|^2 d\mathbf{r} = 2$, yields two coupled Euler-Lagrange equations whose self-consistent solutions provide the extremal electronic wave function Ψ and the ^{4}He density profile ρ. The computational method used for the functional minimization of the total energy E is described in Ref. 12, to which the reader is referred for further details.

We have studied first the case of Na_2 in bulk-liquid ^{4}He at the saturation density $\rho_0 = 0.0218$ Å^{-3}. The minimum energy electron and ^{4}He densities are shown in Fig. 2. The dimer resides in an ellipsoidal cavity with an average radius $R_b \sim 6$ Å and eccentricity $\epsilon = 0.87$ (measured on the surface of constant density $\rho = \rho_0/2$). Figure 3 shows the ^{4}He density profile along the direction shown in Fig. 2 with dash-dot lines. Note the presence of oscillations due to the close proximity of the Na cores and also the sharp liquid-bubble interface. The latter can be characterized by its $10-90$ % width, which is only ~ 1.2 Å (for comparison, the calculated t_{10-90} width for the free He surface is ~ 5.8 Å).

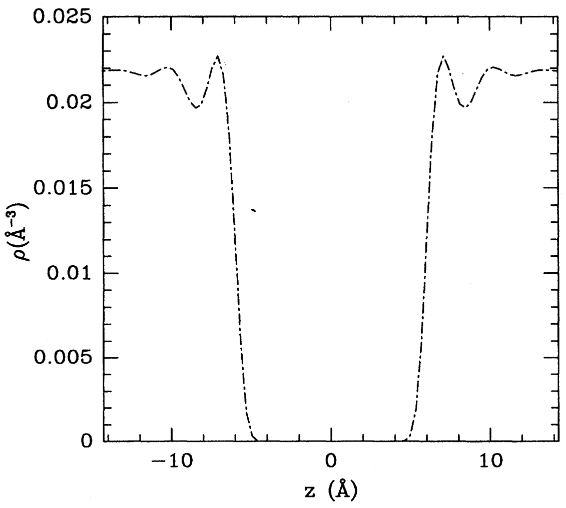

FIG. 3. ^{4}He density profile along the direction shown in Fig. 2 with dash-dot lines.

We have calculated the chemical potential μ of the dimer by comparing the total energies of the (fully relaxed) ^{4}He-dimer system, $E[Na_2 + He]$, and that of the isolated Na_2 and ^{4}He systems:

$$\mu = E[Na_2 + He] - N\epsilon_0 - E[Na_2].$$

Here $\epsilon_0 = -7.18$ K is the energy of a ^{4}He atom in a uniform liquid at density ρ_0. We find a positive value $\mu = +85.7$ K, indicating that the state shown in Fig. 2 is a metastable state. This is similar to the case of a Na monomer, where a positive chemical potential $\mu = +49$ K was found.[5]

Having established that a Na_2 dimer is not stable in bulk liquid ^{4}He, we look for possible stable states of the molecule on the surface of the liquid. In typical experiments, alkali atoms or molecules are captured by ^{4}He clusters.[9,10] We consider here instead the interaction of a dimer with a flat surface, which is computationally more convenient. Our results, however, should be representative of the behavior of dimer adsorption on the surface of big clusters, such as those usually produced in experiments ($N \sim 10^5 - 10^6$ atoms). To include in our calculations the presence of a free surface, we used a periodically repeated supercell containing a thin slab of liquid ^{4}He delimited by two planar surfaces (parallel to the x-y plane) plus a vacuum region to decouple the slab from its repeated images along the direction (z) normal to the surface.

For a given orientation of the molecule with respect to the substrate, we optimized in our calculations both the equilibrium bond length and the dimer-surface distance. We consider three possible orientations: parallel, perpendicular, and 45° tilted with respect to the surface plane. We calculated for each orientation the chemical potential $\mu = E[Na_2 + He] - E[He] - E[Na_2]$, the equilibrium dimer-surface distance and the Na-Na bond length. Here $E[He]$ is the total energy of the helium slab in the absence of the adsorbed dimer. We find in each case negative chemical potentials, indicating stable binding states at the surface. The lowest binding energy $E_b \equiv -\mu = 13.4$ K is found when the molecule is adsorbed with its axis parallel to the surface plane ("flat" dimer), while in the "erect" dimer geometry the binding energy is $E_b = 12.7$ K. When the molecule is 45° tilted with respect to the surface its binding energy is $E_b = 13.3$ K, i.e., almost the same of the flat dimer. We have checked that no energy barrier exists between these orientations, suggesting that the molecule should be relatively free to rotate on the surface of the liquid ^{4}He even at very low temperatures.

Figure 4 shows the ^{4}He and electron densities for the flat dimer. Note the "dimple" which develops on the surface of the liquid below the dimer. Figure 5 shows the ^{4}He density profiles directly below the dimer and far from the adsorption site. Close to the dimer the surface profile shows a steep liquid-vacuum interface and an oscillating behavior (dotted

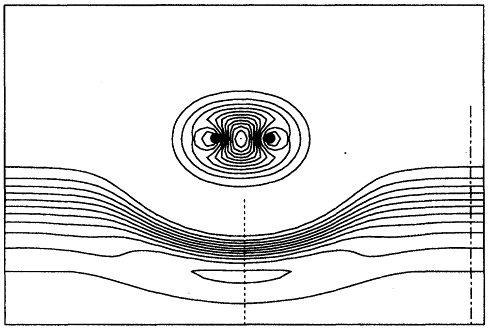

FIG. 4. Na_2 molecule on the surface of liquid ^4He. Contour plots of the electron and helium densities in a plane passing through the Na_2 cores and perpendicular to the He surface plane. The dots indicate the Na cores positions.

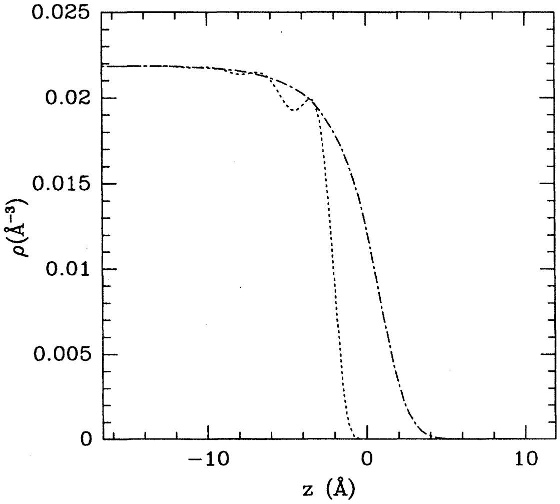

FIG. 5. ^4He density profiles along the directions shown with dash-dot and dotted lines in Fig. 4. The origin of the horizontal axis is taken at the Gibbs dividing surface position of the unperturbed surface.

line), whereas far from the dimer the smoother profile of the free ^4He surface is recovered (dash-dot line). The equilibrium dimer-surface distance is $Z \equiv z_{cm} - z_G = 4.11$ Å, z_{cm} being the position of the center of the molecule. Z is measured from the position of the Gibbs dividing surface $z_G = [\rho_0^{-1} \int z(d\tilde{\rho}/dz)dz]$ of the unperturbed surface, i.e., $\tilde{\rho}$ is the density profile shown with a dash-dot line in Fig. 5. The maximum distortion of the liquid-vacuum interface due to the adsorbed dimer (dimple depth) is $\xi \equiv z_G - z'_G = -2.41$ Å. Here z'_G is computed using the profile $\tilde{\rho}$ shown with a dotted line in Fig. 5.

The intersection of the surface of constant He density corresponding to $\rho = \rho_0/2$ with the plane parallel to the surface at the position of the unperturbed surface, $z = z_G$, is an ellipsis with semi-axis R_{par} and R_{perp}, parallel and perpendicular to the dimer axis, respectively. The in-plane anisotropy of the dimple structure can be characterized by $(R_{\text{par}} - R_{\text{perp}})/R_{\text{par}} \sim 0.13$. However, since the characteristic temperature for the molecule rotation $T_r = \hbar^2/2I_{Na_2}k_B \sim 0.2$ K, this small anisotropy is expected to be averaged out[13] even at the very low temperatures, $T \sim 0.5$ K, of typical experiments.[8,9]

In our calculations we varied the Na-Na interatomic distance in the dimer to find the minimum energy bond length, both in bulk liquid and on the surface. As expected from the weakness of the alkali-^4He interaction, the variations in the Na-Na equilibrium distance d_{eq} (with respect to its value in the vacuum) due to the presence of the nearby liquid are extremely small. We find $d_{\text{eq}} = 3.012$ Å when the dimer is inside the bulk, while at the surface the equilibrium distance is the same as in the vacuum, $d_{\text{eq}} = 3.015$ Å.

To evaluate the variations in the vibrational frequencies of the dimer due to the presence of the liquid, we calculated the Na-Na potential energy curve when the dimer bond is stretched (or compressed) with respect to its equilibrium value by a small amount δr. From a numerical fit of the calculated total-energy variations $\Delta E = a\,\delta r^2 + b\,\delta r^3 + c\,\delta r^4$ we estimate the effect of ^4He environment on the zero-point frequencies of the dimer either in bulk liquid or at the surface. We assume that the dimer motion does not couple with the collective vibrational modes of the surrounding liquid, i.e., the ^4He density is frozen in its lowest energy equilibrium configuration when the dimer bond length is varied. This is justified since the natural frequencies of the bubble cavity are much smaller than the vibrational frequencies of the embedded molecule. Compressional (breathing) vibrations of a spherical bubble cavity of radius R_b in ^4He have a characteristic frequency[22] $\omega_s = (8\sigma/M\rho_0 R_b^3)^{1/2}$. Here σ is the surface tension of the liquid-bubble interface. Higher energy modes of the cavity are surface vibrations with quadrupole distortions, with a characteristic frequency $\omega_q = \pi\omega_s/\sqrt{2}$. If we take for R_b the average radius of the elliptical cavity in Fig. 2, $R_b \sim 6$ Å, and for σ its experimental value for a free surface, $\sigma = 0.36$ dyn/cm, we find $\omega_s \sim 3 \times 10^{11}\ s^{-1}$, i.e., much smaller than the Na_2 lowest vibrational frequency $\omega_v \sim 3 \times 10^{13}\ s^{-1}$.

The zero-point energies of Na_2 are readily estimated from the coefficients of the fit to ΔE by treating the cubic and quartic anharmonic terms b and c in the potential energy curve by second and first order perturbation theory, respectively. We find $\hbar\omega/2 = 80.08\ cm^{-1}$ for the dimer inside the bulk and $\hbar\omega/2 = 79.70\ cm^{-1}$ at the surface. For comparison, the zero-point energy in vacuum is found to be $79.81 cm^{-1}$. Although extremely small, such variations are within the experimental resolution of state-of-the-art spectroscopy measurements like those reported in Refs. 10 and 9. The vibrational constants of highly excited Na dimers attached to the surface of large ^4He clusters have been measured to a high degree of accuracy[9,10] and found to be essentially those of the free molecules. The experimental determination of the vibrational constants of the electronic ground state of Na_2, with which our results should be compared, has not been possible due to low signal-to-noise ratio in the experimental data.[10]

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