Wetting to Non-wetting Transition in Sodium-Coated C\textsubscript{60}

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Based on \textit{ab initio} and density-functional theory calculations, an empirical potential is proposed to model the interaction between a fullerene molecule and many sodium atoms. This model predicts homogeneous coverage of C\textsubscript{60} below 8 Na atoms, and a progressive droplet formation above this size. The effects of ionization, temperature, and external electric field indicate that the various, and apparently contradictory, experimental results can indeed be put into agreement.

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Fullerene molecules are now commonly used as building blocks of complex materials having unusual physical and chemical properties \cite{1}. The possibilities offered by molecules such as C\textsubscript{60} or C\textsubscript{70} in terms of electric or optical devices have laid ground for the rapidly expanding nanotechnology area. The interaction between fullerenes and alkali atoms has attracted a lot of attention after the discovery of superconductivity in the K\textsubscript{2}C\textsubscript{60} solid \cite{5}. Sodium-C\textsubscript{60} compounds have also received much attention \cite{6,7}. More recently, several groups investigated experimentally the gas phase properties of exohedral alkali-C\textsubscript{60} compounds \cite{8,9,10,11}, to further predict the solid state of alkali-doped fullerite.

Using mass spectrometry, Martin and coworkers \cite{6} inferred from the most stable “magic numbers” that sodium covers the C\textsubscript{60} molecule in a continuous and homogeneous fashion, and that metallic bonding starts above 6 metal atoms. Palpant and coworkers \cite{7} deduced from photoelectron spectroscopy measurements that coating proceeds by trimers units rather than single atoms. They also estimated that metallic bonding only appears at n = 13 sodium atoms. Very recently, Dugourd and coworkers \cite{9} measured the electric polarizability of Na\textsubscript{n}C\textsubscript{60} clusters in the range 1 ≤ n ≤ 34. They concluded that a sodium droplet is formed on the surface of the fullerene. These apparent contradictory results are surprising, as far as they rely on similar experimental conditions but different interpretations.

The situation is in fact even more intricate due to the variety of theoretical conclusions on the very same systems \cite{1,2,3,4,5,6,7,8,9,10,11}. With the exception of the study by Rubio and coworkers \cite{11}, which assumes complete wetting of C\textsubscript{60} by sodium in a continuous two-shell jellium description, the electronic structure calculations by Hira and Ray \cite{5,6} and by Hamamoto et al. \cite{12} reach different conclusions as to whether the Na\textsubscript{n} molecule remains as a dimer or dissociates into atoms, which locate on opposite sides of C\textsubscript{60}. At the unrestricted Hartree-Fock level, Hira and Ray find that charge transfer is negligible in Na\textsubscript{n}C\textsubscript{60}, in apparent contradiction with experiments \cite{6,7}, and also that Na\textsubscript{2} remains as a dimer loosely bound to C\textsubscript{60}. On the other hand, the more realistic density-functional theory (DFT) calculations performed by Hamamoto and coworkers \cite{12} at the local density approximation level tend to favor regular coating, preferentially by trimers, in agreement with the picture of Palpant et al. \cite{7}. However, all these \textit{ab initio} investigations could only focus on very limited sets of chosen geometries, simply because global optimization on such complex energy landscapes is far beyond the current possibilities of fully quantum mechanical approaches. In addition, statistical and temperature effects still remain a major limitation in large scale simulations based on first principles.

To overcome the above difficulties, we have constructed an empirical, \textit{ab initio} based atomistic model allowing systematic static and dynamical investigations in a large size range. Briefly, given the geometry \textbf{R} = \{\textbf{r}_i, \textbf{r}_j\} of the Na\textsubscript{n}C\textsubscript{60} system, with \textbf{r}_i ∈ Na\textsubscript{n} and \textbf{r}_j ∈ C\textsubscript{60}, the total potential energy is written as

\begin{equation}
V(\textbf{R}) = V_{\text{Na}_n}(\textbf{r}_i) + V_{\text{C}_60}(\textbf{r}_j') + V_{\text{inter}}(\textbf{R}) + V_{\text{Coul}}(\textbf{R}),
\end{equation}

where \(V_{\text{Na}_n}\), \(V_{\text{C}_60}\), \(V_{\text{inter}}\), and \(V_{\text{Coul}}\) are the energies of sodium, C\textsubscript{60}, covalent interactions between Na and C\textsubscript{60}, and Coulomb interactions, respectively. Metallic forces in sodium are described by a simple many-body potential in the second-moment approximation of the electronic density of states in the tight-binding theory \cite{3}. Covalent forces in C\textsubscript{60} were most often neglected, as the temperatures of interest are low enough (< 300 K) to keep the fullerene rigid. We occasionally checked the rigidity of C\textsubscript{60} in some optimal structures with the Tersoff potential \cite{4}. The covalent interaction between sodium and carbon atoms was modelled as a pairwise repulsion term taken from \textit{ab initio} calculations of the â"Γ state of the NaC molecule, and expressed as \(V_{\text{Na}_n}^{\text{covalent}}(r) = D \exp(-\alpha r)\). To account for charge transfer, and to quantify the extent of ionic interaction in the system, fluctuating charges \(Q = \{q_i, q_j\}\), with \(q_i ∈ \text{Na}_n\) and \(q'_j ∈ \text{C}_60\), were added to all atoms in the system. For any geometry \textbf{R}, the charges are determined in order to minimize the global Coulomb interaction \(V_{\text{Coul}}\), which is equivalent to equalizing the ef-
effective electronegativities in the sense of Sanderson [15]:

\[
V_Q(R) = \sum_i \varepsilon_{Na} q_i + \frac{1}{2} H_{Na} q_i^2 + \sum_j \varepsilon_C q_j^2 + \frac{1}{2} H_C q_j^2 \\
+ \sum_{i<j} J_{ij} q_i q_j \sum_{j<j'} J_{jj'} q'_j q'_j \\
+ \sum_{i,j} J_{ij} q_i q_j' + \lambda \left( \sum_i q_i + \sum_j q'_j - Q \right)
\]

In this equation, \( i \) and \( j \) label sodium and carbon atoms, respectively. \( \varepsilon_{Na} \) and \( \varepsilon_C \) are the respective electronegativeties of sodium and carbon, \( H_{Na} \) and \( H_C \) their ‘hardnesses’, \( J_{ij} \) the Coulomb interactions. The hardnesses parameters correspond to the on-site repulsion in the Hubbard model. The latter quantities were extracted from ab initio calculations of the Coulomb integrals. Due to the finite delocalization of the electrons, \( J_{ij} \) does not diverge at short distances. We have used the simple expression \( J_{ij}(r) = \left(r^2 + H_{ij}^{-1} \exp(-\gamma r^2)\right)^{-1/2} \) to model the Coulomb parts of the Na–Na, C–C, and Na–C interactions. The hardnesses parameters \( H_{Na} \) and \( H_C \) are the \( r \to 0 \) limits of \( J_{Na–Na} = J_{C–C} \). Finally, the Lagrange multiplier \( \lambda \) in (2) ensures that the system carries a global charge \( Q \). This electrostatic model was further improved by including 90 fixed charges, 60 on each carbon site with value \( \delta q, 30 \) on the middle of each C=C bond with value \( -2\delta q \). This was previously used by Schelkacheva Tareyeva in a study of a bulk C_{60} [14].

The dynamical use of the full potential energy function is greatly facilitated by considering an extended Lagrangian where the fluctuating charges are treated as independent variables [17], in a way similar to the Car-Parrinello scheme [18]. This empirical model has 15 parameters, namely the 5 parameters of the SMA potential, the 2 parameters of the covalent Na–C interaction, the electronegativity difference \( \varepsilon_C - \varepsilon_{Na} \), the 6 parameters of the Coulomb interactions (including hardnesses), and the fixed charge \( \delta q \). These parameters were obtained by minimizing an error function \( \chi^2 \) to reproduce several properties independently evaluated by ab initio and DFT calculations [19] with the B3LYP nonlocal functional [20]. These properties are the charge transferred from sodium (0.87e) and the electric dipole (14.5 D) in NaC_{60}, the energy difference between the two Na_{2}C_{60} isomers with sodium atoms on adjacent or opposite hexagonal sites (\( \Delta E = -0.35 eV \)), and the binding energy and equilibrium distance in Na_{2} (resp. \( D_e = 0.73 eV \) and \( R_e = 3.08 \AA \)). It should be noticed that these theoretical values agree well with the experimental data available [8]. We also added to the error function a penalty term to reproduce the experimental electric polarizability of the C_{60} molecule (76.5 Å³ [21]).

The lowest energy structures of Na_{n}C_{60} clusters were determined using a variant of the basin-hopping, or Monte Carlo + minimization algorithm [22], in which each sodium atom is offered a probability to rotate freely over the C_{60} surface, in addition to the usual random displacements moves. Some of the optimal structures are represented in Fig. [1] for the sizes \( n = 4, 7, 8, 12, \) and 20.

![FIG. 1: Some optimal structures of Na_{n}C_{60} clusters. (a) \( n = 4 \); (b) \( n = 7 \); (c) \( n = 8 \); (d) \( n = 12 \); (e) \( n = 20 \). The lowest energy structure for Na_{30}C_{60} within an electric field \( E = 2.55 \times 10^8 \) V.m^{-1} if represented in (f).](image-url)
8, 12, and 20 as a function of \(1/T\) in an Arrhenius plot. These plots provide us with estimates of the corresponding activation barriers, for which we find \(A \approx 400\) K for all four sizes. At room temperature, sodium atoms thus show a significant mobility over the \(C_{60}\) surface. This agrees with the recent experimental findings on \(K_{C_{60}}\) [22]. To quantify the effect of temperature on the morphology in \(Na_nC_{60}\), we have calculated the average size of the largest sodium fragment. A fragment is here defined as a set of connected atoms, i.e. having at least one neighbor at a distance shorter than 8 bohr. The same geometrical observable was also computed at \(T = 0\) for neutral or singly charged molecules. In the case of charged systems, global optimization was carried out for each of the results without electric field and those with a homogeneous field of magnitude \(E = 2.55 \times 10^8\) V.m\(^{-1}\) relevant to the experiments of Dugourd et al. [8], and at zero temperature. The corresponding data were averaged on 30 different orientations of the field, relative to the \(C_{60}\) geometry. Global optimization was carried out for each of these orientations. The variations of the largest fragment size \(\langle N \rangle\) against the total number of sodium atoms \(n\) are plotted in Fig. 3. The rise of \(\langle N \rangle\) at the crossover size \(n^*\) marks the onset of droplet formation. As temperature increases, isolated atoms are more likely to meet either with each other or with the preexisting droplet. This lowers \(n^*\) by a visible amount. However, 300 K is a relatively high temperature for sodium clusters lying usually above their melting points [26]. Thus, external bonds are often broken in the course of the dynamics, which results in lowering \(\langle N \rangle\) at larger \(n\). Ionizing the cluster can also strongly affect the crossover size \(n^*\): negatively charged molecules are more stable in segregated form due to a much lower Coulomb repulsion of the alkali atoms, and positively charged molecules are less stable and remain homogeneously coated up to \(n = 10\).

At the experimental value, a finite electric field disfavors regular location of the charges over the nearly spherical \(C_{60}\) surface. This yields more frequent metallic bonds. In addition, the lowest energy structures found for all field directions can also change significantly. For instance, as seen in Fig. 4, two sodium atoms get closer to one another, yet they still do not form a bond at 0 K.

Electric susceptibilities \(\chi\) have been estimated with the present model using the high-temperature approximation to the Langevin theory for rigid dipoles undergoing orientational thermal fluctuations: \(\chi = \alpha + \mu^2/3k_B T\). In this formula \(\alpha\) is the static polarizability, \(k_B\) is the Boltzmann constant, and \(\mu\) the electric dipole. The variations of \(\chi\) with cluster size \(n\) are shown in Fig. 4. They qualitatively resemble the experimental data of Dugourd et al. [8], but lie somewhat lower than the actual measured

![FIG. 2: Arrhenius plots of the diffusion constants of some Na\(_n\)C\(_{60}\) clusters, for \(n = 4, 8, 12, 20\) (no field), and 6 within an electric field.](Image)

![FIG. 3: Size of the largest fragment of sodium atoms in Na\(_n\)C\(_{60}\) clusters in various conditions, and for neutral or charged molecules.](Image)

![FIG. 4: Electric susceptibilities at 300 K. Inset: electric dipole moment and comparison with DFT calculations.](Image)
values. This may first come from the parameterization. We tested this hypothesis by comparing the predictions of the present empirical model to single-point DFT calculations performed at the same geometry. The electric dipoles given in the inset of Fig. 4 show good agreement between the empirical and electronic structure estimates. We also note that the strong variations in the dipole reflect the changes in the molecular symmetry. It is also worth pointing out that the model predicts an energetic ordering of the isomers essentially similar to that found by Hamamoto et al. [12] for the very restricted set of structures considered by these authors. Therefore, the quantitative difference between our results and the experimental data more likely comes from the Langevin formula, strictly valid for rigid dipoles. This approximation may be insufficient to describe the dipole fluctuations associated with the floppy character of the metal droplet. However, regarding the difference between the present results and the data obtained in Ref. 3 adding several isolated atoms on the opposite side of the growing droplet decreases the dipole moment, hence the susceptibility. A fully dynamical simulation would probably be required to get a more quantitative agreement.

The present investigation shows that the appearance of metallic bonding corresponds to seeding a droplet, which progressively grows and captures remaining isolated atoms. This picture partly reconciles the apparently contradictory experimental interpretations [3][5][6][8][11]. The empirical potential was fitted to reproduce electronic structure calculations as well as some experimental data. By allowing large scale simulations and structural sampling unaccessible to quantum mechanical studies, we could estimate the crossover size between wetted and nonwetted morphologies to be located near 8 atoms. This is also the size range where the metallic transition can be estimated to occur. We have also been able to investigate how the crossover size depends on various effects such as charge or temperature.

The current limitations of the present empirical model are mostly due to the lack of an explicit account of electronic structure. Even though Coulomb repulsion should play an important role when only few sodium atoms are effectively charged but close to each other, shell closing can enhance stability in a local way. In particular, this could help in explaining why charged trimers remain stable. Such quantum effects are obviously beyond the fluctuating charges model, especially with its current training on purely neutral molecules. A next step could be a simple quantum tight-binding approach, which would include both covalent and charge transfer effects. However, a realistic tight-binding Hamiltonian for the Na$_n$C$_{60}$ system would require 240 + n electronic states (4 s + p electrons for each carbon atom, 1 s valence for each sodium atom). This is still too heavy for exhaustive sampling and large scale simulations. In addition, precise quantum effects are essentially expected at small sizes, and the role of a single charge on the structure and stability should decrease as the sodium droplet grows.

For large sizes, it would be interesting to study in more details how the physical and chemical properties of the sodium droplet are modified by the interaction with the C$_{60}$ molecule. The influence of the C$_{60}$ deformation and vibration on the metal cluster dynamics could also be an important issue. Use of the present model to treat other metals could help in understanding the differences observed in the experiments [3][5][6][7]. Further extensions, including the treatment of endohedral or exohedral fullerenes, nanotubes or surfaces with materials possibly other than metals [28][29], could also be carried out.

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