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Electrophobic interaction induced impurity clustering in metals

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ABSTRACT

We introduce the concept of electrophobic interaction, analogous to hydrophobic interaction, for describing the behavior of impurity atoms in a metal, a “solvent of electrons”. We demonstrate that there exists a form of electrophobic interaction between impurities with closed electron shell structure, which governs their dissolution behavior in a metal. Using He, Be and Ar as examples, we predict by first-principles calculations that the electrophobic interaction drives He, Be or Ar to form a close-packed cluster with a clustering energy that follows a universal power-law scaling with the number of atoms (N) dissolved in a free electron gas, as well as W or Al lattice, as $E_c \propto (N^{2/3}-N)$. This new concept unifies the explanation for a series of experimental observations of close-packed inert-gas bubble formation in metals, and significantly advances our fundamental understanding and capacity to predict the solute behavior of impurities in metals, a useful contribution to be considered in future material design of metals for nuclear, metallurgical, and energy applications.

1. Introduction

Hydrophobic interaction is one of the most important concepts in understanding many natural phenomena. Water is arguably the most common solvent in life and industry for a variety of technological processes. The dissolution behavior of solutes in water is governed by their hydrophobicity. It is well known that the hydrophobic interaction between hydrophobic solutes, such as waxes and fats, resulting from their repulsion of water molecules is responsible for their segregation in water; while hydrophilic solutes, such as sugar and salt, disperse uniformly in water as they form ionic or hydrogen bonds with water molecules. Hydrophobic interaction is attractive in nature so that hydrophobic particles will segregate and form clusters spontaneously in water [1,2]. The super-hydrophobic engineering materials were designed based on hydrophobic interaction [3,4]. Hydrophobic effects also play an important role in protein macromolecular synthesis and biological stability, and have been extensively investigated [5–7].

An analogy to hydrophobicity is the concept of electrophobicity that has been used to describe whether molecules like or dislike electrons [8,9], but only in a limited context of describing the affinity for electrons amongst individual molecular groups in a chemical reaction. Hence, the possibility of an electrophobic interaction has never been discussed in this context, since hardly one would dissolve molecules in a “solvent” of electrons like dissolving molecules in water. However, it is important to realize that a metal made of a large number of free electrons, where metallic-like bonding is commonly treated by a jellium model [10,11], can be approximated as a solvent of electrons. Then the dissolution of impurity atoms in metal, which is a topic of great scientific and technological significance, could possibly be related to the electrophobicity of dissolved atoms (solutes). Most importantly, a form of electrophobic interaction can exist between the “electronic solutes” in metal, analogous to the hydrophobic interaction between

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solutes in water, which fundamentally governs the dissolution behavior of impurity atoms in metals. Yet, to the best of our knowledge, the concept of "electrophobic interaction" has never been discussed before.

An atom may dislike/like electrons depending on its electron shell structure. If an atom has a closed shell, i.e. He with a closed 1*s* shell or Be with a closed 2*s* shell, it dislikes electrons; if an atom has an open electron shell, it likes electrons. In fact, the degree of an atom dislikes/likes electrons can be roughly quantified by its electron affinity (see Supplementary Fig. S1) [12]: those with a positive affinity dislike electrons, while those with a negative affinity like electrons. Therefore, one can naturally extend the concept of electrophobicity to atoms dissolved in an electron gas. In fact, the embedding energy of an atom in an electron gas is the basis for the well-developed effective medium [13,14] and embedded atom computational methods [15]. Here, we demonstrate that this extension has a significant implication in achieving a new level of fundamental understanding of impurity atoms in metals, by revealing a form of electrophobic interaction between electrophobic solutes (impurity atoms) in a solvent of "electrons" (metal), in a perfect analogy with the important hydrophobic interactions associated with water.

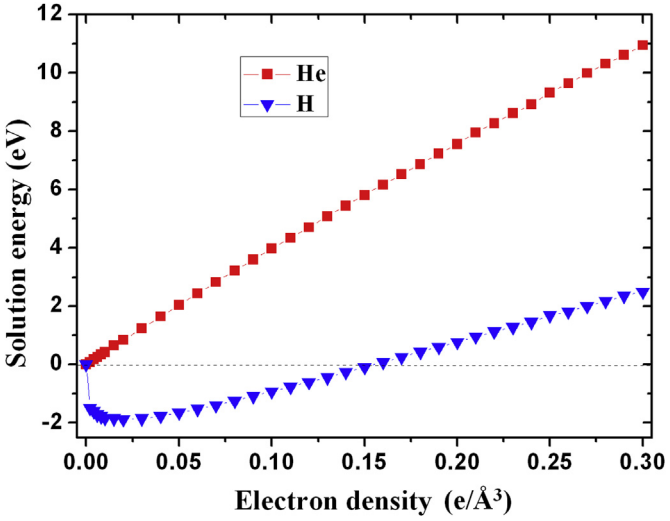

Fig. 1. The plot shows the solution energy of a He atom and a H atom in a homogeneous electron gas as a function of the electron density.

2. Methods

2.1. DFT calculations

Our calculations were performed using the pseudopotential plane-wave method as implemented in the VASP code [16,17] based on the density functional theory (DFT). We used the generalized gradient approximation of Perdew and Wang [18] and projected augmented wave potentials [19], with a plane wave energy cutoff of 500 eV. The bcc supercell of 128 atoms was used and its Brillouin zone was sampled with $(3 \times 3 \times 3)$ k-points by the Monkhorst-Pack scheme [20]. The energy minimization is continued until the forces on all the atoms are converged to less than 10^{-3} eV/Å. To possibly better account for dispersive interaction between the closed-shell atoms, test calculations are also done for He dimers in vacuum and electron gas with Van der Waals exchange-correlation functional, which made no significant difference.

2.2. Calculation of He and H solution energy in a homogeneous electron gas as a function of the electron density

The dissolution of He and H in a homogeneous electron gas with different electron density is simulated by adding electrons in an empty box with a compensating uniform positive charge background. First, we constructed a vacuum cubic supercell with fixed volume. Then, a given number of electrons is added for a given electron density along with the same density of uniform positive charge background. Next, He/H is added in the supercell at different electron density, and the He and H solution energy is calculated, as shown in Fig. 1.

2.3. Calculation of the He-induced deformation energy and electron density at defect sites

In order to get the He-induced deformation energy, He is first placed at a given defect site (TIS, OIS or SS), and both the atomic positions and supercell size are relaxed by energy minimization. Then, He is removed, and the atomic positions and the supercell size are fixed to account for the deformation induced by He, namely the difference between the total energy of the distorted lattice and that of the equilibrium induced by He. The electron density at the defect site is also calculated with both the supercell size and the atomic coordinates fixed.

2.4. Irradiation experiments and electron microscopy

Effects of inert-gas bubble formation in materials were performed through a series of jointly coupled irradiation and subsequent high resolution (scanning) transmission electron microscopy (S/TEM) studies. Resolving the effects of Xe clustering in metals, Al metal targets were selected. Al metal was targeted with a single 250 keV Xe ion beam at room temperature.

3. Results and discussion

We first illustrate the concept of an electrophobic solute (a closed-shell impurity) vs. an electrophilic solute (an open-shell impurity) in a solvent of electrons by reviewing the solution energy (or embedding energy) of a He atom vs. a H atom in a free electron gas as a function of electron density calculated from first-principles (see Methods), as shown in Fig. 1. The results of Fig. 1 are well known from previous studies [21], but here we re-consider them in a new context of electrophobicity. Helium, an electrophobic solute, dislikes electrons having a positive solution energy that increases with the increasing electron density. In contrast, H, is an electrophilic solute, likes electrons having a negative solution energy whose magnitude increases initially and then decreases with increasing electron density. The turn-around behavior for H solution energy that eventually becomes positive is because at too high an electron density, the positive electron-electron Coulomb repulsion dominates over the negative H-electron attraction. From this point onward we will therefore limit our calculations for relatively low electron density.

Next, we derive a simple analytical form to describe solute behavior in light of electrophobic interactions. We start by considering an impurity atom having a closed shell that acts as an electrophobic solute in a free-electron gas, we may approximate their repulsive interaction with the surrounding electron media using a hard-sphere potential, $V(r) = \begin{cases} \beta, & r = r_0 \\ 0, & r > r_0 \end{cases}$, as illustrated in Fig. 2a. If there are N atoms dispersed separately in the free electron gas, their total solution energy follows the classical solution $N(4\pi r_0^2)\beta$. Now if these N atoms segregate into a closely-packed crystalline structure, as shown by previous experiments [22] (see also Fig. 2b), assuming approximately a radius R ($R^3 \approx N r_0^3$) (Fig. 2a)