

Diatomic Molecules and Metallic Adhesion, Cohesion, and Chemisorption: A Single Binding-Energy Relation

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It has been discovered that a single relation between binding energy and interatomic spacing can describe the energetics of diatomic molecules, bulk metals, bimetallic interfaces, and gas atom-metal surface interactions.

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Universal features associated with bonding in diatomic molecules have long been recognized.¹ Potential-energy relations—for example, Morse or Rydberg functions—involving a few parameters in simple analytic forms have been found to represent well the energetics of a wide variety of diatomic molecules.

Such two-atom potential functions are not appropriate for metals, however. For metals it is well known that there are strong volume-dependent forces which can never be expressed as pairwise interactions.² Despite this, we will show that a *single* binding-energy relation can be found which accurately describes diatomic molecules as well as adhesion, cohesion, and chemisorption on metals. This universality reveals a commonality between the molecular and metallic bond.

For metals, the total energy as a function of interatomic distance is very difficult to obtain theoretically and cannot be determined by use of modern experimental techniques. However, we have previously discovered^{3,4} separate universal relations $E^*(a^*)$ for adhesion, chemisorption, and cohesion of the form

$$E(a) = \Delta E E^*(a^*), \quad (1)$$

where

$$a^* = (a - a_m)/l. \quad (2)$$

$E(a)$ is the total energy as a function of the interatomic separation distance a , ΔE is the equilibrium binding energy, a_m the equilibrium separa-

tion, and l the scaling length. In our previous work, the length l was assumed to be proportional to the screening length of the host electron gas at an appropriate equilibrium electron density. Tests of Eqs. (1) and (2) using *ab initio* results for $E(a)$ revealed accurate universal relations $E^*(a^*)$ for adhesion of simple metals and chemisorption on simple metals. The accuracy was less apparent for cohesion of metals. Different universal relations $E^*(a^*)$ were found for chemisorption, adhesion, and cohesion. It will be shown that these differences are not necessary.

It would be highly desirable to relate metallic universality to that of diatomic molecules. Screening lengths have little meaning for molecules, however. In this paper we will take the scaling length to be a free parameter. This is done so that we can compare the binding-energy versus distance relation for all the different physical systems, including diatomic molecules, on a common footing. If one knows the universal relation, $E^*(a^*)$, ΔE and l can be found from any two independent observable measurements of the binding-energy relation. For example, if we assume that the equilibrium binding energy, ΔE , can be measured, then l can be found by taking the second derivative of Eq. (1):

$$l = \left\{ \frac{\Delta E}{d^2 E(a)/da^2|_{a_m}} \frac{d^2 E^*(a^*)}{da^{*2}} \Big|_{a^*=0} \right\}^{1/2}. \quad (3)$$

The value of $d^2 E^*/da^{*2}|_0$ is arbitrary, and it is

convenient to set it equal to 1. Thus,

$$l = \left\{ \frac{\Delta E}{d^2 E(a)/da^2|_{a_m}} \right\}^{1/2} \quad (4)$$

In this way, the scaling length can be determined from ΔE and the second derivative of the energy with respect to displacement at equilibrium. The latter quantity can be determined by the vibrational frequency of a chemisorbed atom or an isolated diatomic molecule, an interfacial elastic constant, or a bulk modulus, depending on which state of matter is of interest.

Equation (4) can be tested with the available *ab initio* $E(a)$ results. The excellent accuracy found earlier^{3,4} in $E^*(a^*)$ for adhesion and chemisorption was maintained by use of Eq. (4). The accuracy for cohesion was significantly improved. Most importantly, we found that the resultant universal relations $E^*(a^*)$ for adhesion, cohesion, chemisorption, and isolated diatomic molecule energetics were all the same to a high degree of accuracy. Representative results are shown in Fig. 1 for each of the four types of interactions. One can see that all of the universal relations fall on top of each other. That is, while the numbers ΔE and l vary from material to material, $E^*(a^*)$ does not.

Thus, there is a single binding-energy relation for all these seemingly diverse systems. The metallic bond at an interface or in the bulk maintains a common dependence on interatomic spacing. This commonality extends to gas atoms interacting with metals and to the diatomic molecular bond. This reveals a fundamental relationship between the molecular and metallic bond. There is an underlying simplicity in nature that has not been recognized heretofore.

Note that H_2^+ can be solved exactly and this, together with the variety of approximations used for the three other systems in the figure, argues that this universality is not due to a theoretical approximation. Finally, note that the differences found in our earlier work in the universal relations for adhesion, cohesion, and chemisorption are not needed. They presumably have their origin in the assumption that l is proportional to an equilibrium screening length which is somewhat arbitrarily defined for each system.

A knowledge of the existence of universality implies relationships between seemingly disparate physical phenomena. In a forthcoming publication we will show that considerations of universal relations allow metallic surface energies to be determined in terms of the cohesive ener-

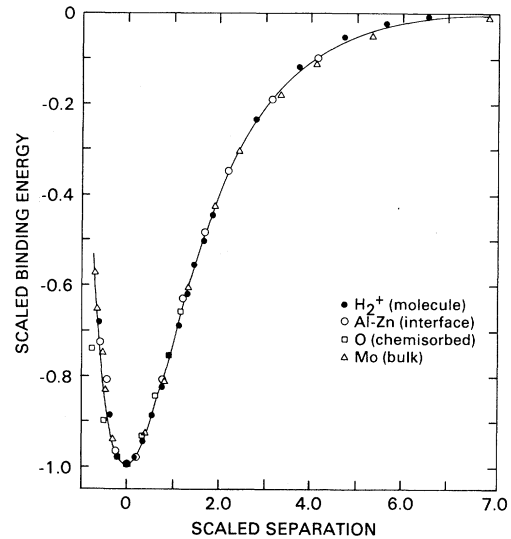


FIG. 1. Binding energy as a function of interatomic separation for four systems as noted, scaled as described in the text. The H_2^+ results were taken from Ref. 5, the Al-Zn interface energies from Ref. 3, the oxygen chemisorption binding energy from Ref. 6, and, finally, the Mo binding energy from Ref. 7.

gies. Also, a simple relationship between adsorbate-substrate vibrational stretch frequencies and desorption energies follows from the universal relationship.

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