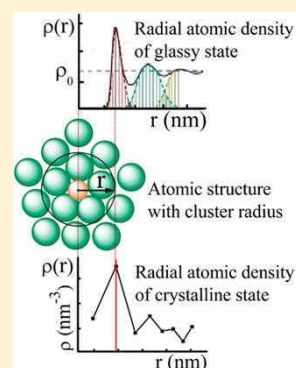


## Electrochemical Potential Derived from Atomic Cluster Structures

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## Supporting Information

**ABSTRACT:** Based on the atomic cluster structures and free electron approximation model, it is revealed that the electrochemical potential (ECP) for the system of interest is proportional to the reciprocal of atomic cluster radius squared, i.e.,  $\varphi = k \cdot (1/r^2)$ . Applied to elemental crystals, the correlation between atomic cluster radii and the ECP that we have predicted agrees well with the previously reported results. In addition, some other physicochemical properties associated with the ECP have also been found relevant to the atomic cluster radii of materials. Thus, the atomic cluster radii can be perceived as an effective characteristic parameter to measure the ECP and related properties of materials. Our results provide a better understanding of ECP directly from the atomic structures perspective.



Structure–property correlation has always been an ultimate goal for materials researchers, because the microscopic structure is a definitive factor dominating macroscopic properties of materials.<sup>1–3</sup> Electrochemical potential (ECP), as an intriguing global property to measure the escaping tendency of electrons from chemical species, plays a significant role in multidisciplinary areas such as physicochemistry, biomedicine, and materials science.<sup>4–6</sup> It has been demonstrated that both the variation and equilibrium toward stabilization of electron systems are completely determined by the ECP.<sup>7–10</sup> Several methods for evaluating the ECP have been proposed;<sup>11–14</sup> although these methods relate the ECP to various properties of atoms and molecules, in most cases there is a good agreement among these derived values. It is generally agreed that the ECP at a point is taken as the absolute position of the Fermi level that produces the electron density at that point.<sup>15</sup> According to the density functional theory, the ground-state properties of systems are unique functions of electron density;<sup>9,16</sup> thus, a numerical relation has been built between the ECP and electronegativity.<sup>17,18</sup> All these methods and quantities associated with ECP result from materials atomic structures because the ECP is not merely a number, but rather an inevitable consequence of atomic structures.<sup>19,20</sup> It is therefore necessary to correlate the ECP with the atomic structures of materials.

Because the ECP is relevant to the electron density for the system of interest, and certain electronic rule associated with the electron density upon atomic cluster structures has been deduced from the “cluster-plus-glue-atom” model,<sup>21–24</sup> we speculate that the correlations between the ECP and atomic cluster structures can be established accordingly. In this Letter, a method for correlating the ECP with the atomic cluster structures is presented. On the basis of the cluster-plus-glue-atom model,<sup>25–28</sup> which has been proven to be an efficient and practical tool for describing the atomic structure of materials by taking the atomic clusters as the basic structural building blocks,<sup>21,25</sup> we set the goal of demonstrating that the atomic cluster radius can be viewed as a characteristic parameter to measure the ECP. Under the direction of the free electron approximation model and atomic cluster structures,<sup>21,29–31</sup> we present an equation for the ECP directly with respect to the atomic cluster structures of materials.

The system equilibrium, actuated by the chemical potential equality, is a generic rule for majority substances.<sup>8,10</sup> With regard to given materials, the structural stabilization is ultimately adjusted by the ECP equilibrium of the corresponding electron system.<sup>9</sup> Under the conditions of the free electron

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approximation,<sup>29–31</sup> the ECP ( $\varphi$ ) or Fermi energy for the system of interest is expressed in the following form

$$\varphi = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad (1)$$

where the electron density,  $n$ , denotes the number of free electrons per unit volume. For a certain electron system,  $n$  can be approximately obtained via the correlation as

$$n = N/(4\pi r^3/3) \quad (2)$$

where  $N$  represents the number of free electrons in the electron system with  $r$  being its size. Concretely, eq 2 is constructed by combining the octet rule and the atomic cluster related electronic rule upon envisaging the corresponding electron system as an entire sphere with radius of  $r$ .<sup>24,26,32,33</sup> This  $r$  corresponds exactly to the radius of principal cluster in the cluster-plus-glue-atom model.<sup>23,25</sup> Accordingly, we can deduce the ECP in the following form

$$\varphi = \frac{\hbar^2 (9\pi N/4)^{2/3}}{2m} \cdot \frac{1}{r^2} \quad (3)$$

By substituting the electron mass  $m = 9.109 \times 10^{-31}$  kg and Planck constant  $\hbar = 1.055 \times 10^{-34}$  J·s into eq 3, the ECP can be expressed as

$$\varphi = 0.1405N^{2/3} \cdot \frac{1}{r^2} \quad (4)$$

If we let the proportionality coefficient in eq 4 be  $k$  (i.e.,  $k = 0.1405N^{2/3}$ ), the correlation between the ECP ( $\varphi$ ) and the atomic cluster radius ( $r$ ) can be finally written as

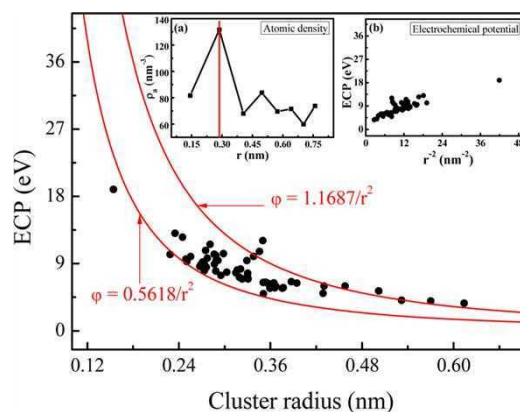
$$\varphi \text{ (eV)} = k \cdot \frac{1}{r^2} \quad (5)$$

where  $r$  is in nanometers and  $\varphi$  is in electronvolts. Equation 5 indicates that the ECP for the system of interest is a unique function of the atomic cluster radii. As for the proportionality coefficient  $k$  in eq 5, it can take different values within a specific range associated with  $N$ . It is believed to be definite values based on the generic electronic rule of the octet rule and its extension upon the atomic cluster structures of materials.<sup>24,26,32,33</sup> In this work, we deduced that  $k$  is in the range of 0.5618–1.1687, with the lower value of 0.5618 and the upper value of 1.1687 corresponding to  $N$  of 8 and 24, respectively, depending on the two cases of the octet rule and its extension of the specific electron cluster formula with regard to the atomic cluster structure-related electronic rule.<sup>25,32</sup>

Interestingly, a similar correlation suitable for bulk metallic glasses (BMGs) has been reported upon the cluster resonance model,<sup>22,24–26</sup> based on the Fermi sphere–Brillouin zone interactions.<sup>34–36</sup> It has been found that the  $k$  value of 0.5875 in that correlation for BMGs is within our discussed range. This particular case illustrates the applicability of the correlation deduced in our work. Thus, the ECP for the system of interest is proportional to the reciprocal of atomic cluster radius squared, while the atomic cluster radii of materials can be conveniently obtained from the cluster-plus-glue-atom model. Meanwhile, the principal atomic cluster structure is defined by a central force field model method.<sup>23</sup> In the cluster-plus-glue-atom model, the atomic interactions inside the cluster are stronger than other parts,<sup>21,25</sup> while the interatomic force constants (IFCs) can reflect the atomic interactions.<sup>23</sup> Accordingly, a central force field model has been developed

to define the cluster structure.<sup>27</sup> This method indicates that for a given material, those atoms with the largest IFCs serve as the central atoms of the cluster, those atoms with the smallest IFCs serve as the glue atoms of the model, while those atoms whose IFCs lie between the largest and smallest IFCs act as either the shell atoms of the cluster or the glue atoms of the model. Therefore, the central atom, shell atoms, and glue atoms in the cluster-plus-glue-atom model can be clearly distinguished. Then, through the combination of the atomic close-packing principle,<sup>21,38</sup> the principal atomic cluster structure can be determined conveniently. The general applicability and significance of this method have been verified systematically, especially for those complex alloys like quasicrystals and metallic glasses.<sup>23,25,28,27</sup>

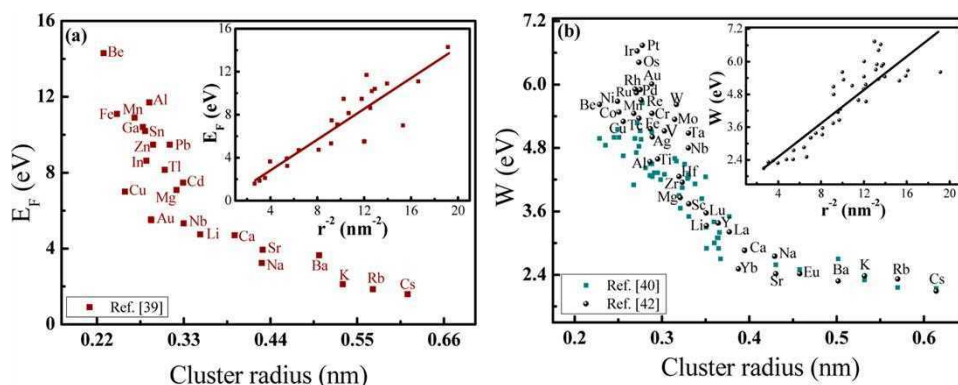
To confirm the validity of eq 5, we have investigated the correlation between the ECP and the atomic cluster radii for common elemental crystals, because their electrochemical quantities are readily available from the existing studies. The results are collected in Supporting Information. The basic structural data throughout this work is referred from Pearson's handbook,<sup>37</sup> and the atomic cluster structures of these elemental crystals are obtained solely by following the atomic close-packing property,<sup>23,38</sup> as reflected in inset map a of Figure 1, which shows that the atomic cluster radius corresponds to



**Figure 1.** Correlation between the ECP and cluster radius for the common elemental crystals. The values of ECP are referred from Nagle.<sup>12</sup> Inset map a presents that the cluster radius ( $r$ ) corresponds to the maximum atomic density ( $\rho_a$ ); inset b demonstrates that there is nearly a linear dependence between ECP and  $r^{-2}$ .

the maximum atomic density. Accordingly, the correlation between the ECP and atomic cluster radii for these elemental crystals is depicted in Figure 1. The results indicate that the ECP presents a descending trend with the atomic cluster radius increasing, just as the correlation revealed by eq 5. The two function curves with  $k$  of 0.5618 and 1.1687 in Figure 1 correspond to the two special cases of the octet rule and its extension of 24 electrons cluster formula, respectively.<sup>24,26,32,33</sup> The correlation between the existing ECP values<sup>12</sup> and atomic cluster radii for these elemental crystals agrees well with the correlation reflected by eq 5, which also demonstrates the reliability of the theoretical formulas deduced in this work.

To make further progress, several other physicochemical quantities, including Fermi energy, work function, and chemical hardness, have been investigated. Because these quantities are closely associated with the ECP and the ECP is a function of atomic cluster radius, it is expected that the Fermi energy, work function, and chemical hardness should also be functions of the



**Figure 2.** Correlations between the cluster radius and Fermi energy (a) and work function (b) for the common pure metals referred from the literature. The insert maps depict the variation of Fermi energy ( $E_F$ ) and work function ( $W$ ) with the reciprocal of cluster radius squared ( $r^{-2}$ ), respectively; the fitted lines correspond to  $E_F = 0.698r^{-2}$  and  $W = 0.316r^{-2} + 1.26$ .

atomic cluster radii. The Fermi energy ( $E_F$ ) is equivalent to the ECP of the system in the ground state at 0 K,<sup>15,20,39</sup> as formulated by the following equation

$$\varphi = E_F \quad (6)$$

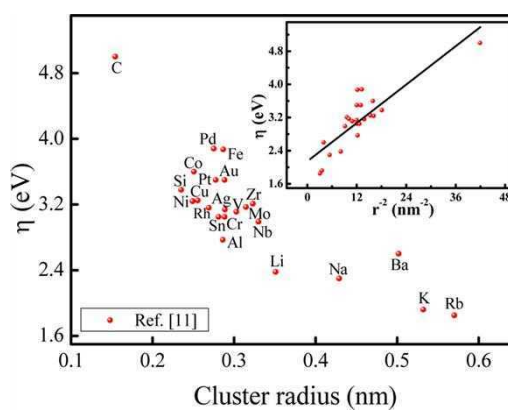
Accordingly, the correlation between  $E_F$  and  $r$  is presented in Figure 2a and insert map and shows that the Fermi energy is proportional to the reciprocal of the cluster radius squared. Based on the available  $E_F$  values of the pure metals, the correlation between  $E_F$  and  $r$  is fitted as  $E_F = 0.698r^{-2}$  with the correlation coefficient being 0.78. The work function ( $W$ ) is regarded as the energy required to remove an electron from the Fermi level of the metal to vacuum at 0 K<sup>40–43</sup> and is correlated with the ECP via the following formula

$$W = V_{\text{vac}} - \varphi \quad (7)$$

where  $V_{\text{vac}}$  denotes the vacuum electrostatic potential energy. The correlation between  $r$  and the available  $W$  values of pure metals is depicted in Figure 2b and insert map. It indicates that the variation trend of  $W$  with  $r$  is consistent with what we anticipated, and their correlation is formulated as  $W = 0.316r^{-2} + 1.26$  with correlation coefficient of 0.78. These results signify that both the  $E_F$  and  $W$  are functions of the atomic cluster radius, illustrating the close connections among the Fermi energy, work function, and the ECP. The chemical hardness ( $\eta$ ) is resistance of the ECP to change in the number of electrons ( $N$ )<sup>11,39</sup> and is coupled with the ECP via the following formula

$$\eta = \frac{1}{2} \left( \frac{\partial \varphi}{\partial N} \right)_v \quad (8)$$

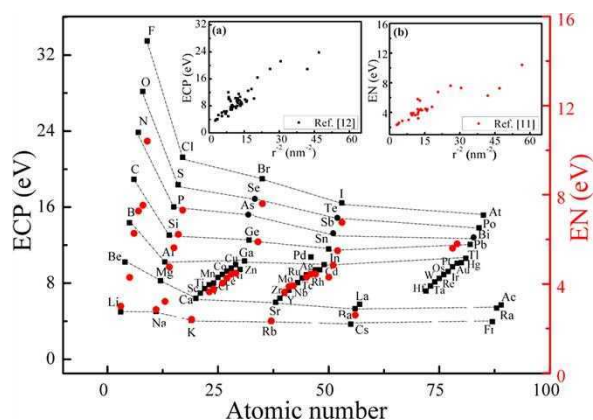
where  $v$  represents a fixed external potential. The correlation between the available  $\eta$  values and  $r$  of the corresponding elemental crystals is presented in Figure 3 and insert map, and the correlation between  $\eta$  and  $r$  is further fitted by  $\eta = 0.076r^{-2} + 2.19$  with correlation coefficient of 0.71. All of these physicochemical properties, directly or indirectly associated with the ECP, present similar variation trends with the atomic cluster radii, which further confirm the validity of eq 5. For transition-metal elements, there are relatively large deviations between our calculated ECP (and related quantities of  $E_F$ ,  $W$  as well as  $\eta$ ) and the available ECP (and related quantities of  $E_F$ ,  $W$  and  $\eta$ ) values. As shown in Figure 2 (b), the correlation coefficient for transition-metal elements is 0.66, while that for the other elements is 0.97. Even so, the overall tendency of our



**Figure 3.** Correlation between the chemical hardness and cluster radii for common elemental crystals. Insert map presents the variation trend of the chemical hardness ( $\eta$ ) with the reciprocal of cluster radius squared ( $r^{-2}$ ), and the fitted correlation is  $\eta = 0.076r^{-2} + 2.19$ .

present values for these transition-metal elements still keeps in consistent with that of the available ECP, Fermi energy, work function and chemical hardness values. The deviation for the transition-metal elements can be attributed to the fact that these strongly correlated systems do not strictly follow the free electron approximation, considering the complicated hybridized effects.<sup>29,30</sup> However, because the free electrons contribute to these transition-metal elements as well, the correlation between ECP and atomic cluster radius for transition metals is still consistent with that of the general trend.

Because the structural and electrochemical properties of materials primarily originate from relevant properties of the constituent elements and their interactions,<sup>21,38</sup> though they are not completely sufficient, we expect that an analogous relevance should also exist for the elemental atomic electrochemical properties. Accordingly, the relevant electrochemical quantities of the elements in the periodic table are referred and listed in Table SII. Figure 4 shows the correlation between the atomic number and the ECP for these elements, together with their values of electronegativity (EN).<sup>11,12</sup> The disparities of the values reported by different researchers are attributed to the different scales they adopted.<sup>13,17,18,20</sup> As expected, these elemental atomic electrochemical quantities depend almost linearly on the atomic cluster radii of the corresponding elemental crystals, as presented in the inset map of Figure 4. Meanwhile, the variation trends of the ECP and EN with the



**Figure 4.** Correlation between atomic number and ECP for the elements in the periodic table, together with their EN referred from the literature. The insert maps give the variation of the ECP (a) and EN (b) with the reciprocal of cluster radius squared ( $r^{-2}$ ).

atomic number strictly follow the general rule, i.e., the ECP of elements decreases with the atomic number from top to bottom in the same group, while it increases with the atomic number from left to right in the same period.<sup>20</sup> This can be readily understood from the electron density,<sup>12,16,21</sup> as will be illustrated subsequently. The existence of correlation between the atomic cluster radii and ECP, as well as EN for elements in the periodic table, again supports the correlation reflected by eq 5.

From the above discussion, we infer that the ECP and its related physicochemical properties present a similar variation correlation with the atomic cluster radii of materials. All of these phenomena are associated with the physical meaning of the correlation reflected by eq 5, as can be understood from the electron density perspective, because an inflow of electrons increases the ECP while an outflow decreases it.<sup>8,29</sup> Meanwhile, as the size of the atom or atomic cluster increases (decreases), the interaction between electrons becomes weaker (stronger) and its sensitivity to a change in a number of electrons decreases (increases).<sup>9,30</sup> Based on the octet rule and its extension of the atomic cluster structure related electronic rule,<sup>24,26,32,33</sup> the size of the atom or atomic cluster can be used to reflect the electron density. For either the transition-metal elements or the other elements, the electronic interaction and electron density increases (decreases) with the decrease (increase) of atom or atomic cluster radius. Therefore, the atomic cluster radii can be perceived as an effective characteristic structural parameter to measure the ECP and its related properties of materials. It is worth mentioning that although the present paper focuses on the fundamental elements and common elemental crystals, the correlation reflected by eq 5 has general significance, and the work along this direction is still underway.

In conclusion, an equation for estimating the ECP has been presented from the viewpoint of atomic cluster structures. It has been found that the ECP for the system of interest is proportional to the reciprocal of the cluster radius squared, i.e.,  $\varphi = k \cdot \frac{1}{r^2}$  with the coefficient  $k = 0.5618-1.1687$ . Our predicted correlation between  $\varphi$  and  $r$  agrees well with the correlation for BMGs and common elemental crystals. In addition, the correlations between the atomic cluster radii and some ECP-related quantities further confirm the reliability of our equation. Hence, the atomic cluster radius can serve as an

effective characteristic parameter for measuring the ECP and related properties of materials. All the results are directly relevant to the electron density of the system, because the electron-induced energy variation can be properly measured through the size of the atomic cluster containing certain electrons, which is reflected by the atomic cluster radii of materials. The present work offers an important insight for a better understanding of the ECP directly from the atomic cluster structures and thus provides theoretical guidance to further explore the interrelationship between materials' atomic cluster structures and their ECP-related properties.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b02759.

Basic structural data for the common elemental crystals and the corresponding atomic properties for the elements in the periodic table (PDF)

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### Notes

The authors declare no competing financial interest.

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