

Effects of Grain Size on the Diffusion Activation Energy and Melting Point

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A thermodynamic method based on bonding energy and surface thermodynamics was developed to accurately investigate the diffusion activation energy and melting point of metallic nanomaterials. The results indicated that the diffusion activation energy, melting point of metallic nanomaterials follow an approximate inverse proportional relationship with the nanosize. Furthermore, the self-diffusion activation energy and melting point of Au, Cu, and the inter-diffusion activation energy of Fe nanomaterials were validated, the experimental results agree well with our theoretical model. This method provided a new approach to evaluate the diffusion activation energy and melting point of nanomaterials.

1. Introduction

It is well known that diffusion is the only way for migration in solid material. Research on the diffusion processes at the nanoscale allows us to better understand and grasp the essential characteristics of nanomaterials and improve traditional preparation processes (Yu and Zhan, 2014; Boulaoued et al., 2016; Shao et al., 2015). To study diffusion at the nanoscale level, there are two approaches currently used: experiment and classical theoretical modeling. The first approach makes use of the experimental method. Kolobov et al. (2001), for example, studied the diffusion activation energy in an ultrafine-grained Ni alloy, and they showed that the diffusion activation energy of nanomaterials is equivalent to the free surface. Amouyal et al. (Amouyal et al., 2007; Salman et al., 2015; Mahmoudi and Mejri, 2015; Wang et al., 2015) discovered that the diffusion rate of nanomaterials in an ultrafine-grained Cu-Zr alloy is about three orders of magnitude higher than the same ingredients in coarse grain materials. In addition, other results also showed that the traditional lattice and grain boundary diffusion theory cannot fully explain the diffusion process at the nanoscale (Wang et al., 2010; Liu et al., 2006; Valiev et al., 2000). However, other experimental results showed that the grain boundary diffusion rates of nanomaterials are equal to those of coarse-grained materials (Kolobov et al., 2002; Herth et al., 2001; Fujita et al., 2002). The second approach makes use of classical theoretical model. For instance, Jiang et al. (2004) and Kesarev et al. (2011) researched the diffusion activation energy of nanocrystalline materials, and proposed their thermodynamic/grain boundary model. Cao et al. (Cao and Lei, 2007; Cao and Lei, 2008; Yu et al., 2015a) researched the diffusion of nanomaterials with respect to the Gibbs free energy driving force, and they proposed a nonlinear diffusion model. Liu et al. (Liu et al., 2006; Brown and Ashby, 1980) and Matsushita et al. (Matsushita et al., 2007; Jiang et al., 2003; Qi et al., 2007) predicted the diffusion activation energy of nanomaterials based on the vacancy formation energy and vacancy migration energy.

These experimental results and theoretical models have been able to elucidate some information regarding the diffusion activation energy of nanomaterials, but as we all known that the macroscopic thermodynamic properties of crystalline materials are intrinsically determined by bonding energy (Huang et al., 2017; Yu et al., 2015b). Therefore, the change of bonding energy is the key to explain the variation of the thermodynamic properties of nanomaterials. Consequently, in this paper, we present a model based on bonding energy. By investigating the energy variation of a nanoparticle, intrinsic interrelation between the diffusion activation energy and melting point is established, revealing the effects of size of nanocrystalline materials.

2. Thermodynamic model

According to thermodynamic theory and bonding energy theory, at constant temperature and pressure under reversible conditions, the surface tension σ is defined as the work done to a unit area of surface between two phases:

$$\Delta W = \sigma \cdot \Delta S \quad (1)$$

where ΔW is the increase of surface energy, ΔS is the unit area of surface.

Based on our surface energy model (Yu et al., 2015b), the surface tension and surface energy are affected by grain size, and the surface tension of nanomaterials σ_{nano} is given by

$$\sigma_{nano} = Z_s \cdot N \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta}\right) \cdot E_{bulk} \quad (2)$$

Where Z_s is the change of the coordination number of the lattice, N is the atom number in a unit area, r is the atomic radius, R is the grain radius, η is the atomic packing factor for different crystal structures (table 1 illustrates the values of the atomic packing factor η for different crystal structures), E_{bulk} is the atom bond energy of the bulk material.

Table 1: The values of the atomic packing factor (ξ) for different crystal structures

No.	Crystal structure	η (%)
1	Body-centered cubic (bcc)	0.68
2	Face-centered cubic (fcc)	0.74
3	Close-packed hexagonal (hcp)	0.74

In order to describe the energy state of nanomaterial grains, we can assume a thermodynamic process: in a perfect crystal, all the atoms (with radius r) are located at equilibrium lattice positions. If a spherical particle (with radius R) is taken out from this perfect crystal and the change of the surface area is $\Delta S=4\pi R^2$ (we can ignore the contraction of the lattice, that is because, the study show that the surface lattice contraction is very small (Jiang et al., 2004)). During the above thermodynamic process, the energy of this particle would increase with the amount W_R (this energy is equal to the bond crushing energy and fracture energy of the perfect crystal)

$$W_R = \sigma_{nano} \cdot 4\pi R^2 \quad (3)$$

It is worth noting that, this thermodynamic process adapt to a very small grain. Based on the atomic structure, the volume of the particle can be calculated by:

$$\frac{4}{3}\pi \cdot R^3 \cdot \eta = \frac{4}{3}\pi \cdot r^3 \cdot N_n \quad (4)$$

Where, N_n is the atom number of this particle. That is

$$N_n = (R^3 \cdot \eta) / r^3 \quad (5)$$

Therefore, from Eq(3) and Eq(5), the increase surface energy W_R can be explained by

$$W_R = \sigma_{nano} \cdot 4\pi \cdot \frac{N}{\eta} \cdot \frac{r^3}{R} \quad (6)$$

Some algebraic rearrangement leads to

$$W_R = N_n \cdot N \cdot Z_s \cdot 4\pi \cdot r^2 \cdot \left(\frac{r}{R} \cdot \frac{1}{\eta}\right) \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta}\right) \cdot E_{bulk} \quad (7)$$

Referring to the cohesive energy of the perfect crystal and vacancy formation energy model (Yu et al., 2014), the cohesive energy of particle W_0 (for the perfect crystal) can be defined as

$$W_0 = N_n \cdot (N \cdot Z_s \cdot E_{bulk}) \cdot 4\pi \cdot r^2 \quad (8)$$

Where, it is interesting to note that the surface tension of an atom is $N \cdot Z_s \cdot E_{bulk}$, because the values of the atomic packing factor $\eta=1$ (only one atom, different form Eq(2)).

Form Eq(7) and Eq(8), we can get the cohesive energy of the nanoparticle W_r

$$W_r = W_0 - W_R \quad (9)$$

Some algebraic rearrangement leads to

$$W_r = N_n \cdot N \cdot Z_s \cdot 4\pi \cdot r^2 \cdot \left[1 - \left(\frac{r}{R} \cdot \frac{1}{\eta} \right) \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta} \right) \right] \cdot E_{bulk} \quad (10)$$

So, we can ignore cohesive energy of particle W_0 (the perfect crystal) and write as

$$\frac{W_r}{W_0} = \frac{W_0 - W_R}{W_0} = 1 - \left(\frac{r}{R} \cdot \frac{1}{\eta} \right) \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta} \right) \quad (11)$$

That is

$$W_r = 1 - \left(\frac{r}{R} \cdot \frac{1}{\eta} \right) \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta} \right) \cdot W_0 \quad (12)$$

Based on conservation of energy, the change of energy of the spherical particle is equal to the increase of the Gibbs free energy and the decrease of the cohesive energy when the spherical particle is removed from the perfect crystal. Therefore Eq(12) can be written as

$$\frac{W_r}{W_0} = \frac{G_r}{G_0} = \frac{U_r}{U_0} = 1 - \left(\frac{r}{R} \cdot \frac{1}{\eta} \right) \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta} \right) \quad (13)$$

Where, G_r is the Gibbs free energy of the nanoparticle, G_0 is the Gibbs free energy of perfect crystal. U_r is the cohesive energy of the nanoparticle, U_0 is the cohesive energy of perfect crystal.

In addition, the nanoparticles entropy influenced by the grain size is very small, the diffusion activation energy of nanoparticle $Q_r \approx G_r$, so we can have

$$\frac{Q_r}{Q_0} = 1 - \left(\frac{r}{R} \cdot \frac{1}{\eta} \right) \cdot \left(1 - \frac{r}{R} \cdot \frac{1}{\eta} \right) \quad (14)$$

As can be seen from this equation, Furthermore, it is worth noting that, Eq(14) only apply nanoparticles with crystal structure.

3. Results and discussion

3.1 Self-diffusion activation energy of nanoparticles

Figure 1 is the diffusion activation energy and diffusion coefficient of Au nanoparticles. Figure 1a is the diffusion activation energy of Au nanoparticles calculated by our model (solid line) and Eq(13) (Yu and Zhan, 2014) (hollow circle symbol). Figure 1b is the size effects of the diffusion coefficient of Au nanoparticles calculated by our model (solid line). In figure 1, the diffusion activation energy and diffusion coefficient rapidly change with its grain size. Recent studies have shown that the nanoscaled/bulk diffusion activation energy ratio of 2 nm Au nanoparticles is approximately 3/4 at room temperature. In figure 1a, within the limits of experimental error, our theoretical model can predict the size effect of the diffusion activation energy, and it

agrees well with the experimental results. The diffusion activation energy and melting point have an approximate inverse relationship with its radius. As the size of the nanocrystals decreases, the diffusion activation energy decreases. In addition, the melting point of Au nanoparticles was used to calculate the diffusion activation energy (according to materials thermodynamics, the cohesive energy is proportional to the melting point). The experimental results came from our vacancy model (Yu et al., 2014)). As can be seen, the diffusion activation energy of Au nanoparticles calculated by Eq(14) and the melting point by Eq(13) are very close. That is to say, the melting point can be calculated directly by the diffusion activation energy. This idea provided a new approach to evaluate the diffusion activation energy and melting point of nanomaterials. In Figure 1b, the diffusion coefficient of the Au bulk material is $D_0=1\times 10^{-36} \text{ m}^2\cdot\text{s}^{-1}$ (Martienssen and Warlimont, 2005; Dick et al., 2009; Shibata et al., 2002). However, the diffusion coefficient of 2 nm Au nanoparticles is approximately $D_r=1\times 10^{-28} \text{ m}^2\cdot\text{s}^{-1}$ (Mayer and Feldman, 1992; Tyrrell and Harris, 2013) at room temperature. That is to say, $D_r/D_0=1\times 10^8$ ($\ln(D_r/D_0)=17.95$), at room temperature, the diffusion of nanomaterials is much faster than bulk diffusion in normal cases.

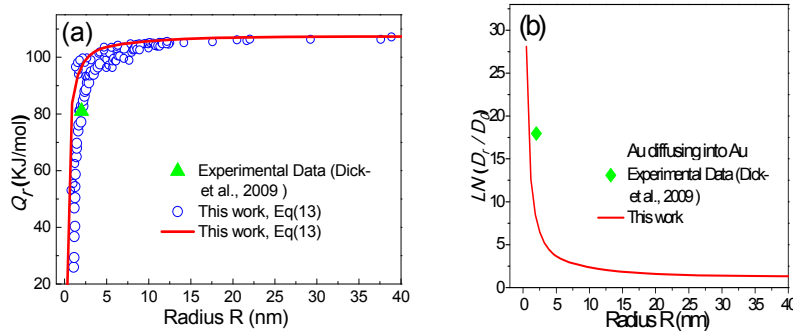


Figure 1: The nanoscaled diffusion activation energy of Au nanomaterials calculated by our model (figure 1a, solid line), and the size effects of the diffusion coefficient of Au nanomaterials (figure 1b, solid line). $r_{Au}=0.1442 \text{ nm}$ (Brown and Ashby, 1980), $\eta=0.74$, $Q_0=1.76 \text{ e}_v=170 \text{ kJ}\cdot\text{mol}^{-1}$ (Martienssen and Warlimont, 2005; Dick et al., 2009), the experimental data derived from reference (Shibata et al., 2002), $D_0=1\times 10^{-36} \text{ m}^2\cdot\text{s}^{-1}$, $Q_0=4\times 10^{-6} \text{ kJ}\cdot\text{mol}^{-1}$ (Mayer and Feldman, 1992; Tyrrell and Harris, 2013).

3.2 Self-diffusion activation energy and melting point of nanoparticles

Figure 2 shows the self-diffusion activation energy and melting point of Cu nanomaterials. Figure 2a is the diffusion activation energy of Cu nanoparticles, figure 2b is the melting point of Cu nanoparticles, they are all calculated by our model (solid line), and Jiang et al. (Zhu et al., 2015; Luo et al., 2011) and Guisbiers et al. (Guisbiers and Kazan; 2008) (dashed lines), plotted versus the nanoparticles diameter and compared to experimental data (Dick et al., 2009).

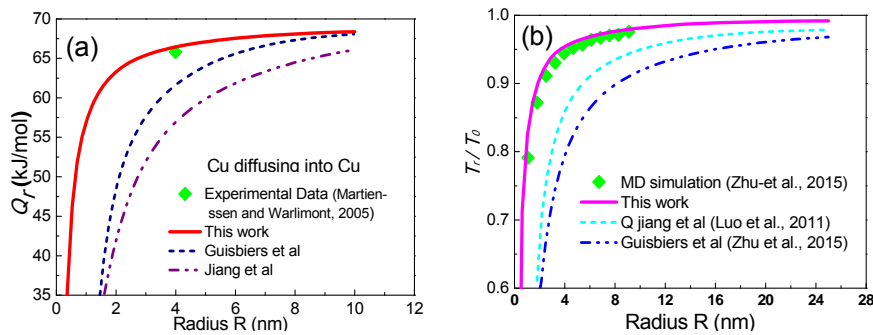


Figure 2: The nanoscaled diffusion activation energy of Cu nanomaterials calculated by our model (solid line), and Jiang et al. and Guisbiers et al. (dashed lines), plotted versus the nanomaterials diameter and compared to experimental data (Dick et al., 2009). $r_{Cu}= 0.1278 \text{ nm}$ (Martienssen and Warlimont, 2005), $\eta=0.74$, $Q_0= 69.7 \text{ kJ}\cdot\text{mol}^{-1}$ (Dick et al., 2009; Zhu et al., 2015)

In the image, our model (solid line) is compared to the experimental results, correspondingly the data provided by Jiang et al. (Zhu et al., 2015; Luo et al., 2011) and Guisbiers et al. (Guisbiers and Kazan, 2008) (dashed lines). The experimental values are higher than those of Jiang et al. and Guisbiers et al., while the values calculated by our model are in good agreement with the experimental results. Furthermore, our model

referring to size effect of surface tension, is different form (according to the current academic, k is a constant), is more accurate and reasonable.

3.3 Inter-diffusion activation energy of nanoparticles

Figure 3 is the inter-diffusion activation energy of Cr which diffusing into Fe nanomaterials calculated by our model, plotted versus the nanoparticles diameter and compared to experimental data (Guisbiers and Kazan; 2008). R is the radius of Fe nanomaterials, and the diffusion activation energy is the inter-diffusion activation energy $Q_0=218 \text{ KJ}\cdot\text{mol}^{-1}$ (Johnstone, 2010). In this Figure, our thermodynamic model can also apply to the inter-diffusion of vacancy diffusion mode, and agree well with the experimental results.

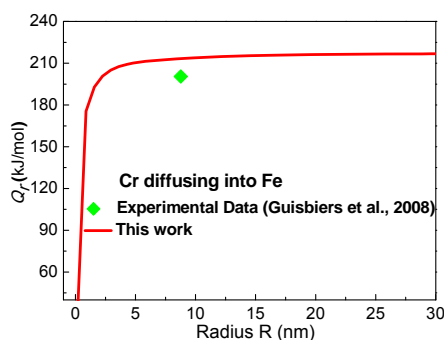


Figure 3: The nanoscaled interdiffusion activation energy of Cr which diffusing into spherical Fe nanomaterials calculated by our model (solid line). $r_{\text{Fe}}=0.1241 \text{ nm}$ (Martienssen and Warlimont, 2005), $\eta=0.74$, $Q_0= 218 \text{ kJ}\cdot\text{mol}^{-1}$ (Johnstone, 2010).

4. Conclusion

According to bonding energy and surface thermodynamics, we proposed a new theoretical model based on changes of the radius of spherical particles. This model can easily calculate the diffusion activation energy and melting point at nanoscale. According to this model, at constant temperature and pressure and under reversible conditions, the diffusion activation energy and melting point have an approximate inverse relationship with its radius. As the size of the nanomaterials decreases, the Gibbs free energy and diffusion activation energy decreases.

Acknowledgments

This work was supported by the Chinese National Science Foundation (grant Nos. 51601081 and 51665022).

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