Variation in electron work function with temperature and its effect on the Young’s modulus of metals

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INTRODUCTION

Material properties are fundamentally correlated to the electron behavior, which is largely reflected by the electron work function ($\varphi$). Recent studies have demonstrated that many properties of metallic materials are directly related to $\varphi$, which may provide a simple but fundamental parameter for material design. Since material properties are affected by temperature, in this article a simple model is proposed to correlate the work function with temperature, expressed as $\varphi(T) = \varphi_0 - \gamma(T)T^2$, where $\gamma$ varies with the crystal structure. This $\varphi$-$T$ relationship helps determine and understand the dependence of metal properties on temperature on a feasible electronic base. As a sample application, the established relationship is applied to determine the dependence of Young’s modulus of metals on temperature. The proposed relationship is consistent with experimental observations.

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Properties of metals are fundamentally determined by their electron behavior, which is largely reflected by the electron work function ($\varphi$). Recent studies have demonstrated that many properties of metallic materials are directly related to $\varphi$, which may provide a simple but fundamental parameter for material design. Since material properties are affected by temperature, in this article a simple model is proposed to correlate the work function with temperature, expressed as $\varphi(T) = \varphi_0 - \gamma(T)T^2$, where $\gamma$ varies with the crystal structure. This $\varphi$-$T$ relationship helps determine and understand the dependence of metal properties on temperature on a feasible electronic base. As a sample application, the established relationship is applied to determine the dependence of Young’s modulus of metals on temperature. The proposed relationship is consistent with experimental observations.

$E = E_0 - B\exp(-T_0/T)$

where $E_0$, $B$ and $T_0$ are empirical constants. However, such an empirical equation does not provide a clear mechanism for the described relationship. Besides, Anderson [16] has shown that this equation is only valid when the variation of the Poisson ratio with temperature is small.

A recent study by Hua and Li [9] has correlated the Young’s modulus of metals to their work function, with which the dependence of Young’s modulus on temperature could be predicted if the effect of temperature on work function can be established. As demonstrated, the Young’s modulus of metals, $E$, has a sextic relation with the work function expressed as

$E = \alpha e^2 \left( \frac{16^6 \times 18\pi^{10} h e^6}{e^2 \bar{n}^3} \right) 6 \varphi^6$ (2)

where $\alpha$ is Madelung’s constant, $a$ is the equilibrium lattice constant, $m$ is the electron mass, $e$ is the elementary charge, and $\varepsilon_0$ is the vacuum permittivity. A general expression that correlates the Young’s modulus with the work function is given as

$E = \beta \varphi^6$ (3)

where $\beta = 0.02233 \left[ \frac{\text{GPa}}{eV} \right]$ is the average value for various crystal structures [9]. This relationship is illustrated in
where $n$ is the free electron density [6]. The term $\frac{3}{2}k_B T$ is only the average energy of electrons according to the equipartition theorem, which states that the energy is shared between all accessible degrees of freedom, where each degree of freedom contributes $\frac{1}{2}k_B T$ to the average internal energy [19]. Each degree of freedom is a parameter that contributes to the state of a system and can be regarded as a classical harmonic oscillator with energy $k_B T$. However the equipartition theorem can only be used when the frequency of each oscillation is less than $\frac{k_B T}{\hbar}$ [19]. According to Bardeen and Pines [20], the plasma frequency for electrons (in SI units) in a solid is given by

$$\omega_p = \sqrt{\frac{ne^2}{m\epsilon_0}}$$  \hspace{1cm} (6)

which is much larger than $\frac{k_B T}{\hbar}$ at temperatures where materials are applied. Therefore the equipartition theorem is not applicable for the present case.

According to the free electron model, the total energy of free electrons inside a metal is given by:

$$U(T) = \int_0^\infty \varepsilon f(\varepsilon)D(\varepsilon)d\varepsilon$$  \hspace{1cm} (7)

where $f(\varepsilon)$ is the Fermi-Dirac distribution, given by

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \varepsilon_f}{k_B T}\right) + 1}$$  \hspace{1cm} (8)

$$D(\varepsilon) = \frac{\partial N}{\partial \varepsilon}$$  \hspace{1cm} (9)

is the density of states and $N$ is given as

$$N = V\left(\frac{2m\varepsilon_f^3}{3\pi^2\hbar^3}\right)^{3/2}$$  \hspace{1cm} (10)

Equation (9) thus becomes:

$$D(\varepsilon) = \frac{\partial N}{\partial \varepsilon} = \frac{3 N}{2 \varepsilon}$$  \hspace{1cm} (11)

The average energy for one electron at temperature $T$ is therefore equal to

$$\frac{U(T)}{N} = \frac{3}{2} \int_0^\infty f(\varepsilon)d\varepsilon = \frac{3}{2} \int_0^\infty \frac{d\varepsilon}{\exp\left(\frac{\varepsilon - \varepsilon_f}{k_B T}\right) + 1}$$  \hspace{1cm} (12)

Letting $x = \frac{\varepsilon - \varepsilon_f}{k_B T}$, the integral in (12) can be evaluated as

$$\frac{3}{2} k_B T \lim_{x \to \infty} \int_0^x \frac{dx}{e^x + 1} = \frac{3 \ln(2)}{2} k_B T$$  \hspace{1cm} (13)
The average values calculated using these two approaches (i.e. the equipartition theorem and the free electron model) are not appropriate choices for determining the change in work function with temperature, since electrons with the highest energy, rather than the average energy, contribute to the change in work function.

**DERIVATION OF \( \varphi(T) \) USING LENNARD JONES POTENTIAL**

The potential between two atoms, according to the Lennard-Jones potential is commonly expressed as [10]

\[
V(r) = \varepsilon_b \left[ \left( \frac{r_e}{r} \right)^{12} - 2 \left( \frac{r_e}{r} \right)^6 \right]
\]

where \( \varepsilon_b \) is the maximum value for the depth of the potential well, \( r \) is the distance between the two atoms and \( r_e \) is the equilibrium distance. It has been shown that the electron work function is related to the bond energy [10]. This relationship is given as

\[
\varphi(r_e) = C \varepsilon_b^{1/6}
\]

(15)

where \( \varphi(r_e) \) is the work function at equilibrium and \( C \) is a constant of proportionality. Since \( V(r_e) = -\varepsilon_b \),

\[
V(r_e) = -\frac{1}{C} \varepsilon_b^{5/6} \varphi(r_e)
\]

(16)

Because the atomic displacement or vibration, \( \Delta r = r - r_e \), is within a small range (\( r < 1.1 r_e \), otherwise the bond would become unstable [21]), equation (16) can be written as

\[
V(r) = -\frac{1}{C} \varepsilon_b^{5/6} \varphi(r)
\]

(17)

Combining equations (14) and (17), the expression for the work function is finalized as:

\[
\varphi(r) = -\varphi(r_e) \left[ \left( \frac{r_e}{r} \right)^{12} - 2 \left( \frac{r_e}{r} \right)^6 \right]
\]

(18)

Letting \( x = \frac{r - r_e}{r_e} \), \( \varphi(r) \) can be written as

\[
\varphi(r) = -\varphi_0 \left| \left( 1 + x \right)^{12} - 2 \left( 1 + x \right)^6 \right| \approx \varphi_0 - 36 x^2 \varphi_0
\]

(19)

Since the distance between the two atoms (the bond length) is affected by temperature, an expression for a temperature-dependent work function can be derived using this relationship. Since the change in potential energy is similar to that in work function (see Eqs. (14) and (18)), the temperature dependent \( x \) varies as [10]

\[
x = \frac{1}{r_e} \frac{36}{48} k_B T
\]

where we may have \( g = \frac{252}{\varepsilon_b} \) and \( f = \frac{36}{\varepsilon_b} \). Thus, \( x \) becomes

\[
x = \left( \frac{7}{48} \right) \frac{k_B T}{\varphi_0}
\]

(20)

Combining equations (19) and (20), we have

\[
\varphi(T) = \varphi_0 - 36 \left( \frac{7}{48} \right) \frac{k_B T}{\varphi_0} \varphi_0
\]

(21)

This expression can be generalized for solids by considering the potential due to the interaction of other adjoining atoms. The second term in equation (19) after the negative sign can be generally described as:

\[
36 \varphi_0 \sum_{i=1}^{N} w_i \left( \frac{< r_i - r_e >}{r_e} \right)^2 = \xi \varphi_0 \left( \frac{< r_i - r_e >}{r_e} \right)^2
\]

(22)

where \( < r_i - r_e > \) is average deviation or displacement of atom \( i \) away from the equilibrium position (chosen as origin). \( w_i \) is an energy contribution factor that counts the influence of the \( i \)th neighbor atom on the square of relative oscillation amplitude, \( x^2 \). This contribution is distance-dependent. e.g., the contributions from the nearest neighbour, 2nd and 3rd neighbour atoms are \( w_{r_{e_1}} = 1, w_{r_{e_2}} = 3.1 \times 10^{-2} \) and \( w_{r_{e_3}} = 2.7 \times 10^{-3} \), respectively (determined based on the Lennard-Jones potentials for \( r_e, 2r_e, 3r_e, \ldots \)). \( \varphi(T) \) then becomes

\[
\varphi(T) = \varphi_0 - \gamma \left( \frac{k_B T}{\varphi_0} \right)^2
\]

(23)

Combining equations (3) and (25), the Young’s modulus becomes

\[
E = \beta \left[ \varphi_0 - \gamma \left( \frac{k_B T}{\varphi_0} \right)^2 \right]^6
\]

(24)

Since the values for work function are available at the room temperature (i.e 295 K), the relationship for the Young’s modulus can be adjusted as

\[
E = \beta [\varphi_{295} - \gamma \left( \frac{k_B T}{\varphi_{295}} \right)^2]^6
\]

(25)

where \( \tau = T - 295 K \).

\( \gamma \) in eq. (22) can be written as \( \gamma = \xi (\frac{7}{48})^2 \) and \( \xi \) is:

\[
\xi = \sum_{i=1}^{N} \frac{< r_i - r_{e_1} >}{r_{e_1}}^2
\]

(26)
where $\chi_1 = \frac{<r_{e1} - r_{e4}>}{r_{e1}} = \alpha_L T$ and $\alpha_L$ is the linear thermal expansion coefficient of the metal. Considering the periodicity of the lattice, we have:

$$r_{ei} = r_{e1} + (i - 1)a$$  \hspace{1cm} (27)

where $a$ is the lattice parameter and $r_{ei}$ is the nearest neighbour distance, which equals $\frac{\sqrt{3}a}{2}$ for face-centred cubic (fcc) crystals and $\frac{\sqrt{2}a}{2}$ for body-centred cubic (bcc) crystals, respectively. Thus, $\xi$ for fcc structures becomes:

$$\xi_{FCC} = \frac{36}{\chi_1^2} \sum_{i=1}^{N} w_i \left( \chi_1 + \frac{\sqrt{2}(i - 1)}{1 + \sqrt{2}(i - 1)} \right)^2$$  \hspace{1cm} (28)

Similarly, for bcc structures, we have

$$\xi_{BCC} = \frac{36}{\chi_1^2} \sum_{i=1}^{N} w_i \left( \chi_1 + \frac{2}{\sqrt{3}}(i - 1) \right)^2$$  \hspace{1cm} (29)

Considering the interaction between two neighbouring atoms and calculating $\chi_1$ at the melting point (the distance between two neighbouring atoms in a metal is maximum at the melting point), the values for $\gamma$ for different metals are calculated and presented in Table 1. With the $\gamma$ values and those for $\beta$, the variation of the Young’s modulus with temperature is plotted and presented in Fig. 2. Experimental data are cited from ref. [22–36].

**SUMMARY AND DISCUSSION**

In summary, we propose a relationship between the work function of metals and temperature, $\varphi(T) = \varphi_0 - \gamma \left( \frac{k_B T}{\varphi_0} \right)^2$, where the coefficient $\gamma$ is dependent on the crystal structure. Based on this relationship, the temperature dependence of Young’s modulus is established. Using iron, silver, aluminum, nickel and copper as examples, variations in their Young’s moduli with temperature were predicted, which are supported by reported experimental observations. The $\varphi$-$T$ relationship is of significance not only to Young’s modulus but also helps predict the dependence of other intrinsic properties of metals on temperature on a feasible electronic base. The proposed relationship is general, since there is no specific assumption, which could limit the applicability of the relationship, required in the derivation.

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**TABLE I. Calculated values for $\gamma$ and estimated values of $\beta$, from figure 1.**

| Metal  | $\gamma$ | $\beta$ [\beta] |
|--------|----------|-----------------|
| Al     | 583      | 0.5             |
| Fe     | 438      | 1.1             |
| Ag     | 478      | 0.6             |
| Ni     | 318      | 0.5             |
| Cu     | 307      | 0.6             |

**FIG. 2. Variation in Young’s modulus of metals with temperature.** The solid line represents the prediction and the dashed lines are the experimental values.

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