On the Roles of Interatomic Interactions and Coordination Numbers on Einstein Temperatures of 3D Transition Metals

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ABSTRACT: We have investigated the roles of the coordination numbers and interatomic interactions on the Einstein temperatures \( \Theta_e \) for a number of bcc 3D transition metals. We have employed a few of the popular transition metal pseudopotentials in the calculations aiming at a comparative survey of the roles of these pseudopotentials on the Einstein temperature, the role of the neighboring atoms on the latter emerges as a by-product of the calculations.

Over the last two decades there have been numerous calculations aiming to investigate the cohesive and thermodynamic (Pettifer, 1983; Hafner, 1987; Young, 1992) properties of metals and alloys in terms of the pairwise interatomic interactions involved in the global energetics. Among many other applications, the calculations of the thermomechanical properties, e.g., Einstein temperatures \( \Theta_e \) in terms of pair potentials, have drawn much interest (Rahman and Salek, 1992) in recent years. Because of certain obvious reasons, the major bulk of the available calculations were aimed at the simpler systems. With the advent of the realistic forms of pair interactions (Wills and Harrison, 1983; Finnis and Sinclair, 1984; Bretonnet and Silbert, 1992), however, there have been a number of calculations on the transition metals (Karaoghlu and Rahman, 1994). Even though the basis of these transition metal interatomic potentials is the so-called force-theorem (Mackintosh and Andersen, 1980) controlling the cancellation between relaxations in the one particle potential and self-energy corrections, the decompositions of the potentials can be achieved in various ways. Whatever the mode of decomposition might be, the effective pair potential can be profitably written as a sum of the interactions arising from the screened Coulomb repulsion, the bond bonding contribution and a repulsive contribution inherent to the shift of the centre of the d-band. Concurrently a trend based on the multi-ion interactions ([Finnis and Sinclair, 1984] and the d-phase shift (Bretonnet and Silbert, 1992) has been broadly successful in calculating the various structural and thermodynamic properties of transition metals.

It is relevant to mention here that since most of the structural and thermodynamic properties are global in nature, the average profile, and not any specific detail of the pair potential, is of vital importance for these cases. On the other hand, since the differential derivatives of the pair potentials at the lattice vector positions are involved in calculating the Einstein temperature, any fine details of the pair potentials at every relevant point is equally important. In particular the profile of the pair potential at the first lattice vector is of specific importance in this special situation; this is because the major contribution of \( \Theta_e \) comes from the nearest neighbours for almost all of the systems. The present attempt enabled us to look at these aspects.

Formulations and Calculations

The main ingredients in the present calculation are the pair potentials \( \phi(r) \) due to Wills and Harrison (WH), 1983, Finnis and Sinclair (FS), 1984 and Bretonnet and Silbert (BS), 1992. Once the pair potential is known, it can be
related to the Einstein temperature at a temperature $T$ as follows (Hasegawa and Young, 1980):

$$\frac{3M}{k_B} [k_B T_\text{E}(T)]^2 = \sum_{R \neq 0} [\nabla^2 \Phi(r)]_R$$

(1)

where $M$ is the ionic mass, $k_B$ the Boltzmann constant and $R$ is a lattice vector of the underlying lattice. For spherically symmetric approximation we write

$$0_e^2(\tilde{T}) = \frac{1.823 \times 10^7}{W} \sum_{R \neq 0} \left( \frac{d^2 \Phi}{dr^2} + \frac{2}{r} \frac{d \Phi}{dr} \right)_R$$

(2)

where $W$ is the atomic weight of the element. The differential terms in eq. (2), i.e.,

$$g = \left( \frac{d^2 \Phi}{dr^2} \right)_R, \quad T = \left( \frac{2}{r} \frac{d \Phi}{dr} \right)_R$$

(3)

are respectively known as the radial and tangential force constants. The experimental Einstein temperature $\theta_{\text{exp}}$ is deduced from the experimental entropy $S_{\text{exp}}$ (Hulten et al., 1973) through the approximate relation

$$S_{\text{exp}}(T) = 3k_B \left[ \frac{\theta_{\text{E}}}{T} \right] - \ln \left( 1 - e^{-\theta_{\text{E}}/T} \right)$$

(4)

The input parameters in calculating the various forms of $\Phi(r)$ at room temperature have been obtained from Wills and Harrison, 1983, Finnis and Sinclair, 1984 and Bretonnet and Silbert, 1992, respectively. The calculated $\Phi(r)$ for Cr are shown in Figure 1. The profiles of these pair potentials in the regions of interest are remarkably distinct. The deep minimum in the WH-$\Phi(r)$, attributed almost entirely to the d-d matrix element, supercedes those appearing in the other two. The shallow minimum in the BS-$\Phi(r)$ is on the other hand a reflection of the predominant sp contribution over the d-contribution arising from the inverse scattering mode. The FS-$\Phi(r)$ representing a simple form of the multi-ion interactions is apparently seen as an 'average' of the two other pair potentials. A similar trend is noticed in the pair potentials of the other 3d transition metals concerned.

Results and Discussion

The values of the Einstein temperature $\theta_{\text{E}}$ for V, Cr, Mn and Fe as calculated from the various pair potentials considering the various neighbouring contributions are presented in Table 1. Looking at these results it is noticed that for most of the systems about 80% contributions to the Einstein temperatures, irrespective of the model pair potentials, come from the nearest neighbours alone. This is a manifestation of the essence of the Einstein model that an atom vibrates independently in an averaged field (mean field) in the presence of all other atoms and consequently

![Figure 1](image-url)

Figure 1. The pair potentials $\Phi(r)$ for Cr as calculated by using the Wills-Harrison (WH), Finnis-Sinclair (FS) and Bretonnet-Silbert (BS) model potentials. The local field factor used in the calculations is due to Ichimura and Utsunomiya, 1980. The input quantities used in the calculations correspond to room temperature.
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the dragging effects, e.g., anharmonicities caused by any long range ordering, are secondary. Results for V, the top element of the group, are very consistent with the experimental value. For Cr, while the FS pair potential reproduces a fairly consistent value for $\theta_E$, the WH and BS potentials visibly underestimate it. The most noticeable situation is observed in the case of Mn. While the WH and BS potentials generate very consistent values of $\theta_E$, the FS potential totally fails to produce any real value for $\theta_E$, the latter situation arises presumably because of the unphysical nature of the curvature of $\phi(r)$ at the relevant lattice vector positions. This gives rise to an upright tangential force constant associated with the FS pair potential in conjunction with the present prefixed bcc crystal structure. Mn, under normal thermodynamic conditions, belongs to a complex bcc (A12) prototype structure and so any consideration of such a structure may overcome the unphysical nature of the respective force constant; this remains to be looked at. For Fe, the FS pair potential seems to be relatively superior to the other two potentials even though the overall situation is within an acceptable range.

Conclusions

In the present investigation we have reported on the fine details of the profile of $\phi(r)$ at the lattice vector positions of several 3d transition metals through calculating their Einstein temperatures $\theta_E$. The overall assessment shows that all the 3d transition-metal pair potentials reproduce these quasi-local dynamic quantities within a certain degree of consistency (except for Mn with the FS pair potential). This qualitative consistency may also lead to the conclusion that any local thermomechanical quantities, e.g., elastic constants, may also be reproduced consistently by employing these pair potentials; this is because the elastic constants are also derived from the derivatives of $\theta_E$ at only the first lattice vector position. In conclusion, we should make a critical remark that the present theoretical scheme used in the calculations is based on the harmonic approximation and semiempirical potentials, whereas the experimental results contain the effects of many-body forces, arising from the nonlinear response and the anharmonicity inherent in any solid. Work considering these points is in progress.

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* Mn corresponds to a complex bcc structure (Hasegawa and Young, 1980).
+ Deduced from eq.4 taking $S_{opp}$ from Hultgren et al, 1973.
# $\theta_{Exp} = (2/3)\theta_{Exp}$ (Rahman and Salek, 1992). $\theta_{Exp}$ is the experimental Debye temperature (Kittel, 1996).
References


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