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A GRADIENT APPROXIMATION  
FOR CALCULATING DEBYE TEMPERATURES  
FROM PAIRWISE INTERATOMIC POTENTIALS

by

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Approximation par gradients pour calculer les températures Debye  
à partir de potentiels interatomiques dans le sens des paires

par

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Résumé

On donne une simple approximation par gradients pour calculer la température Debye efficace d'un cristal cubique à partir de potentiels interatomiques centraux dans le sens des paires. Pour les exemples du potentiel Morse appliqué à des métaux cubiques les résultats sont généralement en bon accord avec l'expérience.

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**A GRADIENT APPROXIMATION FOR CALCULATING DEBYE TEMPERATURES  
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**ABSTRACT**

A simple gradient approximation is given for calculating the effective Debye temperature of a cubic crystal from central pairwise interatomic potentials. For examples of the Morse potential applied to cubic metals the results are in generally good agreement with experiment.

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## 1. INTRODUCTION

The interatomic potential method is a powerful tool for modeling real solids<sup>(1)</sup>. It provides a means of relating microscopic properties to macroscopic properties, of extrapolating quantities of interest to little known regions and of correlating and comparing the behaviour of various solids. The concept begins with the assumption of a specific mathematical form for the potential function with variable parameters to be determined. This form may be central or non-central, pairwise or with other more elaborate summation schemes and its application may be limited or aim at generality. The next step in the process is to deduce numerical values of the potential parameters for the solid under consideration by relating functions of the potential, usually lattice sums, to experimentally measured quantities. One then has an effective interatomic potential for the solid. This method has proved to be very successful in dealing with cases where the motions of the solid atoms, or more specifically their ionic cores, are of interest, and indeed a vast literature exists on the subject.

In this work we will consider an additional equation to one of the most comprehensive, and widely-used, systems of interatomic potentials yet introduced. A direct but simple approximation for deducing the Debye temperature of a cubic crystal from lattice sums of a central pairwise

interatomic potential is given. As we shall see below this extra equation completes the system of equations needed to derive all the quantities necessary for the solid equation of state in a consistent manner from the interatomic potential. It also provides an additional means of testing interatomic potentials in general. Some of the results of this work have been quoted elsewhere<sup>(2)</sup> but the details of the calculations are given here for the first time.

## 2. METHOD

Girifalco and Weizer<sup>(3,4)</sup> (henceforth abbreviated GW) gave one of the most general and widely-applied systems of interatomic potentials. It is their system that we shall consider in the remainder of this work although the principles involved are applicable to other systems. GW used a Morse potential in the following form:

$$\phi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}] \quad (1)$$

This is a pairwise, central, attractive-repulsive potential which depends only on the value of the distance,  $r$ , between atoms. Its parameters are  $D$  the potential well depth,  $r_0$  the location of this well and  $\alpha$  a slope parameter. GW equated lattice sums of this potential and their derivatives to measured values of the bulk compressibility, lattice spacing and sublimation energy to obtain values of  $D$ ,  $r_0$  and

$a$  for several body-centred cubic (bcc) and face-centred cubic (fcc) metals. Given these parameters, expressions for the elastic constants and equation of state could be evaluated, again in terms of similar lattice sums. Generally good agreement with experiment was obtained. However the Debye temperature used in the equation of state was introduced extraneously - it was not calculated from the effective potentials. Here we shall remedy this defect.

Although we need not recapitulate all of the GW equations their notation will be used. In particular summations over the lattice will be expressed in the following manner:

$$\left[ \begin{array}{ccc} N_1 & N_2 & N_3 \\ & x & \\ & & yca \end{array} \right] = \sum_j l_j^{N_1} m_j^{N_2} n_j^{N_3} M_j^x e^{-ycaM_j} \quad (2)$$

The utility of this form is clear from equation (1). The distance of an atom from the origin, i.e. an arbitrary atom location on which the summation is based, has been denoted by:

$$r_j = (l_j^2 + m_j^2 + n_j^2)^{1/2} a = M_j a \quad (3)$$

Here "a" is half the unit cell distance and  $(l_j, m_j, n_j)$  a member of an integer set, the total set represents all atoms in the lattice. For bcc lattices  $l, m, n$ , must be all even or all odd

and for fcc  $1+m+n$  must be even. The parameter "y" in (2) assumes only the values 1 and 2. A further convenience is achieved by using:

$$\beta = e^{\alpha r_0} \quad (4)$$

Using this notation the sublimation energy  $U_0$ , equivalent to the cohesive energy of the lattice, may be expressed as:

$$U_0 = L\beta^2 \begin{bmatrix} 0 & 0 & 0 \\ & 0 & \\ 2\alpha a_0 & & 0 \end{bmatrix} - 2 L\beta \begin{bmatrix} 0 & 0 & 0 \\ & 0 & \\ \alpha a_0 & & 0 \end{bmatrix} \quad (5)$$

where  $L = D/2$  and  $a_0$  is the lattice half-spacing at equilibrium conditions. The equation of state is written:

$$P = - \frac{2\alpha L\beta}{3ca^2} \left\{ - \beta \begin{bmatrix} 0 & 0 & 0 \\ & 1 & \\ 2\alpha a & & \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ & 1 & \\ \alpha a & & \end{bmatrix} \right\} + \frac{3\gamma RT}{v} D\left(\frac{\theta}{T}\right) \quad (6)$$

where  $c = 4$  for bcc crystals and  $c = 2$  for fcc crystals. The other quantities have their usual meanings. The Gruneisenion  $\gamma$ , once  $\theta$  is established, may be taken to give the correct specific volume at NTP following the procedure of GW. The Debye temperature  $\theta$ , is required for use in the Debye specific heat function:

$$D\left(\frac{\theta}{T}\right) = 3\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx \quad (7)$$



At this point GW used established compilations of  $\theta$  but we shall now show that  $\theta$  can be derived by a simple approximation. Specifically we assume a lattice of identical harmonic oscillators, a reasonable assumption for metals at all but the lowest temperatures: let the restoring constant of the oscillator be  $q_i$ . Then:

$$\theta_i = (\hbar/k_B) (q_i/m)^{1/2} \quad (8)$$

where  $\hbar$  and  $k_B$  have their standard meanings and  $m$  is the atomic mass. The subscript "i" indicates a principle direction; here we have restricted ourselves to central potentials so that all directions are essentially similar however the method can easily be extended to the non-central case. Now  $q_i$  is simply the derivative of the force at equilibrium atomic separation:

$$\phi''(a_0) = -2\alpha a_0 D \left\{ \beta^2 \begin{bmatrix} 0 & 0 & 0 \\ -1 & & \\ 2\alpha a_0 & & \end{bmatrix} - \beta \begin{bmatrix} 0 & 0 & 0 \\ -1 & & \\ \alpha a_0 & & \end{bmatrix} \right. \\ \left. - \beta^2 \begin{bmatrix} 2 & 0 & 0 \\ -3 & & \\ 2\alpha a_0 & & \end{bmatrix} + \beta \begin{bmatrix} 2 & 0 & 0 \\ -3 & & \\ \alpha a_0 & & \end{bmatrix} \right. \\ \left. - 2\alpha a_0 \beta^2 \begin{bmatrix} 2 & 0 & 0 \\ -2 & & \\ 2\alpha a_0 & & \end{bmatrix} + \beta \alpha a_0 \begin{bmatrix} 2 & 0 & 0 \\ -2 & & \\ \alpha a_0 & & \end{bmatrix} \right\} \quad (9)$$

Hence  $\theta$  can be obtained using (8) and (9). The results obtained are shown in Table I (fcc metals) and Table II (bcc metals). The Morse constants for these calculations have been calculated from more recent experimental data than those of GW but there are few significant changes. An improved value of  $U_0$  was used for Al and parameters for Pd, Pt and Au were also calculated since the latter were not given by GW. Experimental data taken at both 0°K and 300°K were used to derive parameters for some of the metals; comparison showed that the differences were small. To check the calculated  $\theta$ 's, Tables I and II list experimental  $\theta$ 's as quoted by Kittel<sup>(5)</sup> and de Launay<sup>(6)</sup>, the former was considered to be the more acceptable compilation since it is more recent but the latter is more extensive. Hence where Kittel's table does not contain the desired  $\theta$  we have quoted the  $\theta$  given by de Launay<sup>(6)</sup>. These comparison show that with the exceptions of Au, Pb and K, the approximation is good to within  $\pm 15\%$  of the experimental number. There is no apparent reason why these particular metals should show worse agreement than the others except perhaps for K for which a central potential would be a rather poor approximation. One would also expect Na to be poor for the same reason and it may be that the agreement is fortuitous for this case.

We should note at this point that the Debye temperature per se, is not a particularly sensitive test of a potential function's ability to predict the vibrational characteristics

of a solid. In fact very much more elaborate but restricted potentials are commonly used to model thermal motions. However what we have demonstrated is a final equation to complete the method of achieving a wholly self-consistent equation of state expressed in terms of interatomic potentials. The system of GW has now been generalized so all of the macroscopic quantities of the solid can be predicted by expressions involving potentials. Furthermore any interatomic potential proposed for general modeling of a solid may be tested by this means.

### 3. CONCLUSIONS

The simple gradient method, as used for the examples of Morse potentials applied to cubic metals is a reasonable approximation for calculating Debye temperatures. In this way a completely self-consistent equation of state can be obtained in terms of interatomic potentials.

TABLE I  
FCC METALS

	$\underline{a_0 (\text{\AA})}$	$\underline{r_0 (\text{\AA})}$	$\underline{\alpha (\text{\AA}^{-1})}$	$\underline{D(\text{eV})}$	$\underline{\theta (\text{K})}$	$\underline{\theta_{\text{expt}}}$
Pb	4.914	3.674	1.257	.246	120	88*
Ag	4.069	3.087	1.418	.338	231	226*
Ni	3.516	2.797	1.389	.428	399	375*
Cu	3.604	2.851	1.379	.345	336	343
Al	4.032	3.319	1.167	.290	421	428
Au	4.064	3.005	1.618	.480	213	162
Pd	3.876	2.893	1.608	.479	298	275*
Pt	3.924	2.934	1.573	.707	267	230*

\*  $\theta_{\text{expt}}$  taken from Ref. (6), (others from Ref. (5))

1  
∞  
1

TABLE II  
BCC METALS

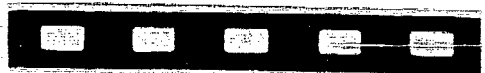
	$\underline{a_0 (\text{\AA})}$	$\underline{r_0 (\text{\AA})}$	$\underline{\alpha (\text{\AA}^{-1})}$	$\underline{D(\text{eV})}$	$\underline{\theta (\text{K})}$	$\underline{\theta_{\text{expt}}}$
Mo	3.149	2.990	1.492	.804	391	380*
W	3.160	3.023	1.439	.992	311	310*
Cr	2.885	2.810	1.471	.438	420	460*
Fe	2.867	2.871	1.355	.417	394	420*
Na	4.291	5.200	.613	.0663	167	156
K	2.598	3.191	.992	.0650	213	91

\*  $\theta_{\text{expt}}$  taken from Ref. (6), (others from Ref. (5))

1  
6  
1

4. REFERENCES

- (1) A few recent references on interatomic potentials are:  
I.M. Torrens, *Interatomic Potentials*, Academic Press, New York, 1972; V.N. Zharkov and V.A. Kalinin, *Equations of State for Solids at High Pressures and Temperatures*, Consultants Bureau, New York, 1971; P.C. Gehlen, J.R. Beeler and R.I. Jaffee, *Interatomic Potentials and Simulation of Lattice Defects*, Plenum Press, New York, 1972.
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