On the binding energy of atoms in crystals and the speed of sound

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Abstract

The speed of sound depends on the structure and on the material properties of the crystal, such as the density and the Young's modulus. On the other hand, from atomistic arguments it is possible to link the Young's modulus to other material properties. These observations drive to a relation between the binding energy of the atoms in a crystal (which is one of the parameters appearing in the Mie-Lennard-Jones potential), the speed of sound in the longitudinal direction and the mass of one atom in the lattice. Applications of this relation to noble gases and few metals are presented and the results compared to others taken from literature.

Keywords: Binding Energy; Cohesive Energy; Mie Potential; Lennard-Jones Potential; Sound velocity

1. Introduction

The speed of sound in solids depends on the structure and on the material properties of the crystal. When the medium is a bar, the speed of sound c_s, in the longitudinal direction, can be expressed in terms of the ratio between the Young's modulus Y and the density ρ [1]:

$$c_s^2 = Y/\rho. \tag{1}$$

On the other hand, the Young's modulus, defined as the ratio between the strain and the stress, can be derived from atomistic arguments [2,3] based on the Mie-Lennard-Jones potential [4].

Combining the two expressions we obtain a relation between the binding energy and the speed of sound in the crystal, in the longitudinal direction. Its derivation is presented in Sec. 2.

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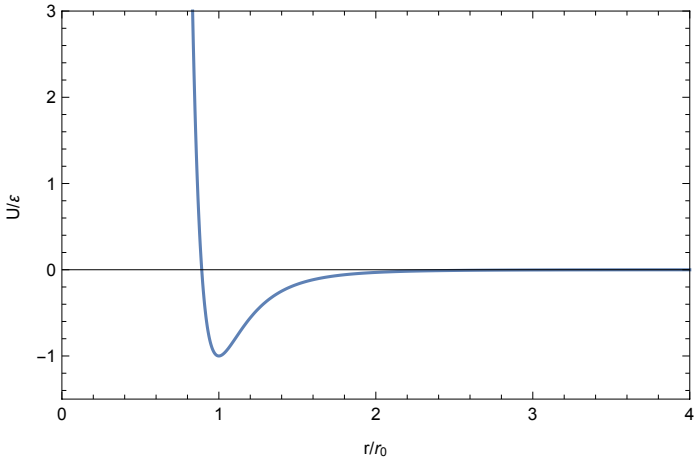

Figure 1: The Mie-Lennard-Jones potential.

2. Theory

2.1 Young's modulus from Mie and Lennard-Jones potential

The Mie potential is a simple particle-pair potential composed of two terms representing the repulsive and attractive forces between the particles. Following the approach proposed in refs. [2,3], it is used here to represent the forces acting between the atoms in the crystal. Its formulation is the following one [5,6]:

$$U(r) = \frac{\varepsilon}{m-n}\left(n\left(\frac{r_0}{r}\right)^m - m\left(\frac{r_0}{r}\right)^n\right), \tag{2}$$

where ε is the binding energy of the interacting particles (the energy required to separate them) and r_0 is the equilibrium distance between two particles. The exponents depend on the material.

A most used form, with $n = 6$ and $m = 12$, is the 12-6 Lennard-Jones potential [e.g. 7]:

$$U(r) = \varepsilon\left(\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^6\right). \tag{3}$$

With reference to Fig. 1, which plots function $U(r)$, parameters ε and r_0 are the depth of the potential $U(r)$ and its position, respectively.

The Young's modulus can be obtained from the definition of the Mie potential. Taking the derivative of the potential provides the force between the particles:

$$F(r) = -\frac{mn}{(m-n)}\frac{\varepsilon}{r}\left(\left(\frac{r_0}{r}\right)^m - \left(\frac{r_0}{r}\right)^n\right), \tag{4}$$

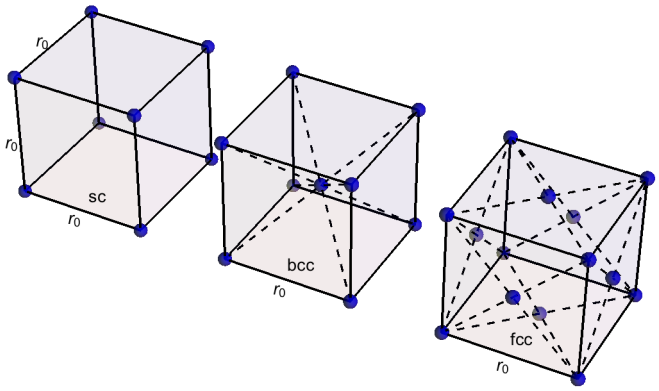

Figure 2: Cubic lattices: simple, body centered and face centered.

It can be seen that $F(r_0) = 0$, which proves that for $r = r_0$ the potential $U(r)$ has a minimum. In the framework of our approach, r_0, which is the equilibrium distance, is also the size of the crystal cell as illustrated by the simple cube (sc) lattice in Fig. 2, representative of the internal structure of the bar.

Let us apply a force F to the bar extremities. The atoms will be displaced from r_0 to r. Young's modulus Y is defined as the ratio between stress (force per unit surface, $F(r)/r_0^2$) and strain (relative deformation, $(r - r_0)/r_0$) in the limit as the strain goes to 0. Therefore, in mathematical terms, Young's modulus can be written as:

$$Y = \lim_{r \to r_0} \frac{F(r)/r_0^2}{(r - r_0)/r_0}. \tag{5}$$

Taking into account that $F(r_0) = 0$, Eq. (5) can be written as:

$$Y = \frac{1}{r_0} \lim_{r \to r_0} \frac{(F(r) - F(r_0))}{(r - r_0)}, \tag{6}$$

which, in virtue of the derivative definition, is equivalent to:

$$Y = \frac{1}{r_0} \left. \frac{\mathrm{d}F(r)}{\mathrm{d}r} \right|_{r=r_0}. \tag{7}$$

Computing the derivative of $F(r)$ from Eq. (4) we obtain:

$$Y = mn \frac{\varepsilon}{r_0^3}. \tag{8}$$

2.2 Relation between binding energy and speed of sound

From Eq. (1) and Eq. (8) we obtain:

$$c_s^2 = mn\frac{\varepsilon}{\rho r_0^3}. \tag{9}$$

The term at denominator, ρr_0^3, i.e. the density multiplied by the atom-cell volume, is the mass M of a single atom-cell in a cubic lattice, where a simple cubic structure has been assumed, which enables writing:

$$\rho = M\,/r_0^3\ . \tag{10}$$

Substituting Eq. (10) into Eq. (9) provides the relation between binding energy and speed of sound in the longitudinal direction:

$$\varepsilon = \frac{Mc_s^2}{mn}. \tag{11}$$

Even if it has been assumed a simple cubic structure, this relation is valid for body centered (bcc) and face centered (fcc) cubic structures (see Fig. 2) as well (cf. Appendix A).

3. Values of binding energy for several elements

Eq. (11), has been used to compute the binding energy ε for several elements having cubic structure, where the mass of the atom M is defined as the ratio between the atomic weight A and the Avogadro number N_{Av}:

$$M = A\,/N_{\mathrm{Av}}\ . \tag{12}$$

The elements studied are: 4 noble gases, Ne, Ar, Kr and Xe, which at solid state have fcc crystal structure [8], 7 metals with fcc and 3 metals with bcc structure. Both the 12-6 Lennard-Jones and Mie potentials have been used. The data used in the formula, taken from references [9-13], is presented in Table 1.

3.1 Values of binding energy using the 12-6 Lennard-Jones potential

For this formulation Eq. (11) has been used with the values $n = 6$ and $m = 12$. The results for 4 noble gases are presented in Table 2 and compared to the ones obtained by Horton [6] solving a two-equation system set by fit of two crystal properties: the sublimation energy and the 0°K lattice size. The results for 8 metals are presented in Table 3 and compared to the ones obtained by Heinz et al. [7] and Kanhaiya et al. [14], who used a molecular dynamics

Table 1: Data used in the evaluation of the binding energy for the elements studied.

	Atomic Weight	Crystal Structure	Speed of Sound (m/s)	Reference
Ne	20.149	fcc	1290.	[9]
Ar	39.948	fcc	1630.	[10]
Kr	83.8	fcc	1335.	[11]
Xe	131.3	fcc	1150.	[12]
A1	26.9815	fcc	6420.	[13]
Au	196.967	fcc	3240.	[13]
Pb	207.2	fcc	2160.	[13]
Ni	58.6934	fcc	6040.	[13]
Pt	195.078	fcc	3260.	[13]
Ag	107.868	fcc	3650.	[13]
Cu	63.546	fcc	4760.	[13]
Fe	55.845	bcc	5950.	[13]
Mo	95.94	bcc	6250.	[13]
W	183.84	bcc	5220.	[13]

approach. The results for molybdenum and tungsten are also provided but no comparison is available.

Table 2: Binding energy (eV) for noble gases using the 12-6 Lennard-Jones potential.

	This work	Horton
Ne	0.00483	0.0045
Ar	0.01528	0.01473
Kr	0.0215	0.02028
Xe	0.025	0.02859

3.2 Values of binding energy using the Mie potential

For this formulation Eq. (11) has been used with the values of n and m taken from Magomedov's work [5]. The results for 4 noble gases and 10 metals are presented in Tables 4 and 5, respectively, and compared to the ones obtained by Magomedov [5], who used an approach based on the preservation of measured quantities such as sublimation energy and thermal expansion coefficient. The approximation of interaction of only nearest-neighbor atoms has been adopted.

4. Conclusion

A relation between the binding energy in crystals and the speed of sound has been derived on the basis of the Mie and Lennard-Jones potentials. The 12-6 Lennard-Jones potential shows a quite good agreement with other results from literature, whereas the Mie potential shows higher differences, which can

Table 3: Binding energy (eV) for 10 metals using the 12-6 Lennard-Jones potential.

	This work	Heinz et al.	Kanhaiya et al.
A1	0.1601	0.1743	–
Au	0.2977	0.2294	–
Pb	0.1392	0.127	–
Ni	0.3083	0.245	–
Pt	0.2985	0.3382	–
Ag	0.2069	0.1977	–
Cu	0.2073	0.2046	–
Fe	0.2846	–	0.2601
Mo	0.5395	–	–
W	0.7211	–	–

Table 4: Binding energy (eV) for noble gases using the Mie potential.

	This work	Magomedov	n	m
Ne	0.0028	0.0045	5.83	21.39
Ar	0.01	0.015	6.62	16.69
Kr	0.0148	0.0205	6.56	15.92
Xe	0.0173	0.0285	6.73	15.42

Table 5: Binding energy (eV) for 10 metals using the Mie potential.

	This work	Magomedov	n	m
A1	0.4239	0.5714	2.49	10.92
Au	0.7027	0.6387	1.96	15.56
Pb	0.31	0.3399	2.27	14.24
Ni	0.8149	0.7506	3.56	7.65
Pt	0.6372	0.9795	2.53	13.33
Ag	0.4673	0.4944	3.08	10.35
Cu	0.5884	0.5895	3.03	8.37
Fe	0.8975	1.0838	3.54	6.45
Mo	2.3635	1.7042	2.14	7.68
W	1.7695	2.2068	3.42	8.58

reach 40%. It is emphasized that this relation, expressed by Eq. (11), has only a theoretical purpose. It adopts some approximations such as to limit atoms interactions to nearest neighbors, therefore it is not supposed to be used for detailed calculations of interatomic interactions in crystals, where appropriate and accurate force fields have been derived. Moreover, these force fields are applicable to all kinds of crystals and to other forms of solid matter, whereas our approach is limited to crystals of pure elements.

The values of the binding energy computed for various elements depend on the form of the potential. Values associated to the 12-6 Lennard-Jones potential cannot be compared with the ones associated to the Mie potential. This is due to the fact that the values of the binding energy ε, the exponents n and m, the r_0 distance, have to be seen as part of an inseparable whole.

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Appendix A. Case of face and body centered cubic structures

Eq. (11), expressing the relation between the binding energy and the square of speed of sound, has been obtained in case of simple cubic structure. We show here that the cases of face centered (fcc) and body centered (bcc) cubic structures respond to the same relation.

In case of fcc or bcc structures (Fig. 2), the lattice can be seen as N_{Lat} embedded lattices with cells of size r_0, where one of the lattices is related to the vertices and:

- three others to the center of the faces, in case of fcc,
- the other one to the center of the body, in case of bcc.

Summarizing, N_{Lat} is 4 for fcc and 2 for bcc. Therefore the surface r_0^2 is affected by N_{Lat} pairs of interacting particles and the force appearing in Eq. (4) has to be multiplied by N_{Lat}, which conducts to a Young modulus N_{Lat} times higher than in the case of simple cubic structure:

$$Y = N_{\mathrm{Lat}} mn \frac{\varepsilon}{r_0^3}. \tag{A.1}$$

This means that the square of the speed of sound, which is proportional to Y according to Eq. (1), is N_{Lat} times higher too and Eq. (9) becomes:

$$c_s^2 = N_{\mathrm{Lat}} \frac{mn\varepsilon}{\rho r_0^3}. \tag{A.2}$$

On the other hand, in a fcc or bcc lattice cell there is more than one atom. This number is N_{Lat}, which drives to replace Eq. (10) by the following one:

$$\rho = N_{\mathrm{Lat}} M \,/ r_0^3 \ . \tag{A.3}$$

Substituting Eq. (A.3) into Eq. (A.2) and solving with respect to ε we obtain the relation between binding energy and speed of sound:

$$\varepsilon = \frac{M c_{\mathrm{s}}^2}{mn}, \tag{A.4}$$

which is the same as Eq. (11).

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