Response to "Comment on 'Relationship between two-body interatomic potentials in a lattice model and elastic constants'"

R. A. Johnson
Materials Science Department, University of Virginia, Charlottesville, Virginia 22901
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Both 1 and $-2/3$ have been used in lattice models for the parameter n referred to by Shukla. n equals $-2/3$ for the kinetic energy of a free-electron gas, but the example presented in the earlier paper was not intended to apply to a free-electron gas and thus needs no correction. Additional comments on the role of this parameter in the volume-dependent energy of metals are presented.

In two earlier papers,[1,2] a set of equations was derived relating two-body interatomic forces, volume-dependent forces, and the elastic constants of a crystal. The volume-dependent energy per unit undeformed volume in a monatomic crystal was taken as

$$E_v = \sum_q P_q \left(\frac{V}{V_0}\right)^{n_q}, \tag{1}$$

with V and V_0 the deformed and undeformed volumes, respectively, and P_q and n_q parameters. No assumptions were made as to the origin of these volume-dependent terms, and it is possible to expand any actual volume dependence in such a series about the equilibrium volume.

For central potentials in a cubic lattice with just one volume-dependent contribution,

$$C_{12} - C_{44} = Pn(n+1). \tag{2}$$

It was mentioned that the relation

$$C_{12} - C_{44} = 2P \tag{3}$$

is obtained with $n=1$. In this case,

$$\Delta W = P\Delta V, \tag{4}$$

with W the total volume-dependent energy, and the parameter P is equivalent to a pressure. This choice of n is implicit in many defect calculations based on empirical potentials through the boundary conditions employed. In these models, the volume dependence provides a force for lattice contraction while the two-body forces yield a force for lattice expansion.

The volume dependence of the kinetic energy of a free-electron gas goes as $V^{-2/3}$ and, as mentioned by Thomas,[3] implies $n=-\frac{2}{3}$ in an expression such as Eq. (1). In this case, the volume dependence provides a force for lattice expansion.

Correlation and exchange approximations give additional volume-dependent terms.[4,5] Although they are not necessarily polynomial in form, they can be expanded about the equilibrium volume to yield a form such as Eq. (1). The example with $n=1$ was not intended to apply to a free-electron gas and thus there is no need to correct it to $n=-\frac{2}{3}$ as in the comment by Shukla.[6]

The problem of the volume-dependent contribution to the elastic constants has caused appreciable confusion for many years and is still current. Since an equilibrium condition provides a coupling between the volume dependence and the two-body force dependence, correct equations can be written which appear to be contradictory. For example, with the notation used by Shukla,[6] the bulk modulus is

$$B = \tfrac{1}{3}\left[(C_{11})^{sr} + 2(C_{12})^{sr}\right] + K_e - \tfrac{1}{3}P_e. \tag{5}$$

However, P_e is related to the two-body forces and Thomas[3] writes

$$B = B^{sr} + K_e. \tag{6}$$

Both Eqs. (5) and (6) are equivalent with appropriate two-body (or short-range) expressions.

Much of the confusion arises because of slightly different definitions of "elastic constants." As discussed earlier[1,2] and in greater detail by Martin,[7] there are Brugger elastic constants based on the Lagrangian strain parameter, linear elastic constants based on linear strain, effective elastic constants based on the velocity of sound, and the thermodynamic definition of compressibility. The commonly used K_e referred to by Thomas[3] and Shukla[6] is derived from the 4th definition. However, it is then often related to elastic constants from other definitions. Equation (2) is valid for either the linear,[1] Brugger,[2] or compressibility definitions.

This same problem surfaces in a recent comment by Upadhyaya[8] in which he writes

$$C_{12} - C_{44} = K_e - 2P_e \tag{7}$$

for cubic symmetry. He then assumes

$$P_e = \tfrac{3}{5} K_e \tag{8}$$

and finds

$$C_{12} - C_{44} = -\tfrac{1}{5} K_e \tag{9}$$

in disagreement with other authors but in agreement with Martin.[7] Thomas[3] showed that

$$K_e = n(n-1)P\,, \tag{10}$$

$$P_e = -nP\,, \tag{11}$$

which, for a free-electron gas with Eq. (2) and $n = -\frac{2}{3}$, gives Eqs. (7) and (8). Thus, Upadhyaya's result is based on a free-electron-gas model and requires no further assumptions.

If $K_e' = K_e - \frac{1}{3} P_e$ is taken as the electron-gas contribution to the bulk modulus from Eq. (5), Eq. (7) becomes

$$C_{12} - C_{44} = K_e' - \tfrac{5}{3} P_e\,.$$

The result $C_{12} - C_{44} = 0$ arises from incorrectly taking

$$P_e = \tfrac{3}{5} K_e'$$

rather than Eq. (8). $C_{12} - C_{44} = 0$, in fact, implies $n = -1$.

A model with $C_{12} - C_{44} = K_e$ is not necessarily incorrect. However, it implies that both the volume-dependent and two-body force contributions to the energy are independently in equilibrium and, except for the trivial case of $n = 0$, that more than one volume-dependent term is required in Eq. (1). A model based on these assumptions with K_e as a parameter for fitting phonon dispersion curves, to which Upadhyaya objects, is then perfectly valid.

[1]R. A. Johnson, Phys. Rev. B 6, 2094 (1972).
[2]R. A. Johnson, Phys. Rev. B 9, 1304 (1974).
[3]J. F. Thomas, Jr., Scr. Metall. 5, 787 (1971).
[4]M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1958).
[5]W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), p. 320.
[6]M. M. Shukla, Phys. Rev. B 23, 3091 (1981).
[7]J. W. Martin, J. Phys. C 8, 2837 (1975).
[8]J. C. Upadhyaya, Phys. Rev. B 18, 2961 (1978).