

## Reply to “Comment on ‘Energy and pressure versus volume: Equations of state motivated by the stabilized jellium model’ ”

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In a recent paper [Phys. Rev. B **63**, 224115 (2001)], we proposed two equations of state based upon microscopic insight into the cohesion of a solid: the stabilized jellium equation of state (SJEOS) and its augmented version (ASJEOS). In this Reply, we address the issues raised by Holzapfel in his Comment on that paper. We show that, according to the number of independent fitting parameters used, our ASJEOS is comparable with Holzapfel’s third-order adapted polynomial (AP3) and that the ASJEOS performs slightly better than AP3 for the materials (Al, Li, and Mo) and pressure range ( $P \lesssim 15$  Mbar) discussed in our paper. We compare the advantages and the disadvantages of ASJEOS and AP3, and discuss the behavior of the equations of state as they approach the strong-compression and strong-expansion limits.

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We recently proposed the simple stabilized jellium equation of state (SJEOS) and its advanced version, the augmented SJEOS (ASJEOS),<sup>1</sup> in which the bonding energy  $\varepsilon$  and pressure  $P = -(d\varepsilon/dx)/(3v_0x^2)$  are found from

$$\varepsilon^{SJEOS}(x) = \frac{a}{x^3} + \frac{b}{x^2} + \frac{c}{x} + d, \quad (1)$$

$$\varepsilon^{ASJEOS}(x) = \begin{cases} \frac{a}{x^3}g(x) + \frac{b}{x^2} + \frac{c}{x} + d & (x \leq 1), \\ \left[ \frac{A}{x^3} + \frac{B}{x^2} + \frac{C}{x} + D \right. \\ \left. + (A+B+C+D)F \right. \\ \left. \times (x-1) \right] e^{-F(x-1)} & (x > 1), \end{cases} \quad (2)$$

where  $g(x)$  is chosen to satisfy  $g(x) \rightarrow 1$  as the compression ratio  $x = (v/v_0)^{1/3} \rightarrow 1$ ,  $g(x) \rightarrow fx$  as  $x \rightarrow 0$ , and  $g'(1) = g''(1) = g'''(1) = 0$ . Here  $v$  is the atomic volume, and  $v_0$  is its equilibrium value. When we introduced these equations, we were regrettably unaware of the prior  $L$ th-order adapted polynomial (APL), another advanced equation of state by Holzapfel.<sup>2,3</sup> We shall compare them here and answer the questions and argument raised in the Comment.<sup>4</sup> In this Reply, we will use the original notation of our paper for the equilibrium parameters of a solid, i.e.,  $B_0$  for the bulk modulus and  $B_1$  for its first derivative with respect to pressure, instead of  $K_0$  and  $K'_0$  of the Comment.

The simplest equation of state is our SJEOS. Based upon

the structureless pseudopotential or stabilized jellium model<sup>5</sup> of a metal, it is nearly ideal for the description of the regime  $x \approx 1$ . By putting in the correct physics around equilibrium, we have used the SJEOS to correct the errors that arise in the density functional calculation of the equation of state due to an error in the predicted equilibrium volume. After our article was published, we learned that Eq. (1), without the  $d$  term and without the pseudopotential justification, was proposed by Bardeen<sup>6</sup> in 1938.

Point 4 of the Comment finds Fig. 1 of Ref. 1 “misleading,” but that figure only demonstrates that the SJEOS works well for its underlying microscopic model, while standard equations of state, intended to describe real solids over a wide range of  $x$ , do not. For a demonstration that the SJEOS also works for the ordinary jellium model and for a pedagogic discussion of cohesion, see Ref. 7. Point 3 of the Comment also states incorrectly that the SJEOS has one more input parameter than Holzapfel’s earlier H12. In fact, the SJEOS pressure requires only  $v_0$ ,  $B_0$ , and  $B_1$ , while the H12 pressure requires those three inputs plus the atomic number  $Z$ . The SJEOS energy does require a further input, the cohesive energy  $\varepsilon_0$ , which enters via the parameter  $d$ , while the H12 energy does not even exist in closed analytic form.

The ASJEOS starts from the SJEOS, then modifies it to account for core overlap under strong compression and for atom formation under strong expansion. In particular, the  $x^{-3}$  pseudopotential repulsion of Eq. (1) is screened down to  $x^{-2}$  by the factor  $g(x)$  as  $x \rightarrow 0$ . For a compressed real metal without ion cores, the ASJEOS should reduce to the SJEOS, and it does so for monatomic close-packed metallic hydrogen where  $B_1 = 3$  makes  $a = 0$ ; see Fig. 1 and Table I of Ref.

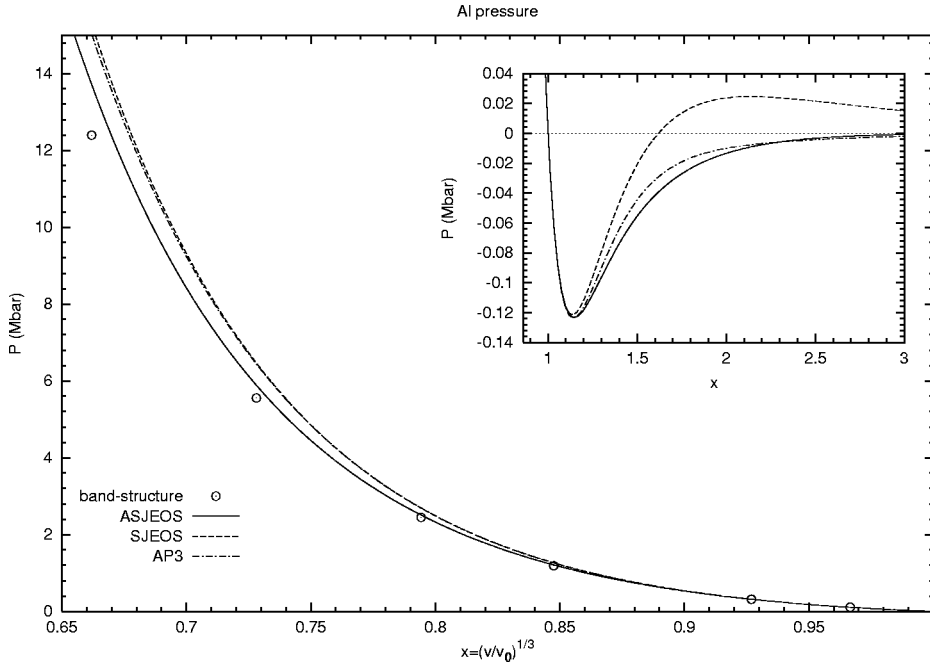


FIG. 1. Pressure  $P$  vs compression ratio  $x$  for Al.

5 and the caption of Table II of Ref. 1. On the other hand, the APL and earlier Holzapfel equations of state are based upon the physics of the Thomas–Fermi model or strong-compression limit. Thus the APL starts from the Fermi-gas pressure (or kinetic energy) of all (core+valence) electrons in the limit  $x \rightarrow 0$ , then screens it out as  $x$  increases. Since cohesion does not occur in the Thomas-Fermi theory, it is introduced into the Holzapfel equations of state in a plausible but purely phenomenological way. Interestingly, the equation of state for stabilized jellium with equilibrium radius  $r_0 = 1.6$  bohr, representing monatomic metallic hydrogen, is essentially

$$P(x) = \frac{3B_0}{x^5}(1-x), \quad (3)$$

where  $B_0 = P_0^{FG}/3$  and  $B_1 = 3$ , which can be represented exactly by the SJEOS, ASJEOS, and APL forms. Equation (3) follows from the stabilized jellium energy of Eq. (22) of Ref. 1 by setting the pseudopotential repulsive energy  $\bar{w}_R$  to zero and neglecting the correlation energy  $\epsilon_c$  in comparison with the exchange energy  $\epsilon_x$ .

The APL energy function is not (contrary to the Comment) “much simpler” than the ASJEOS, and to us it looks more complicated and less transparent. Transformation of the APL from its pressure to its energy form involves the expo-

TABLE I. The equation of state coefficients for the AP3 and ASJEOS in the Fermi-gas limit (in Mbar), using inputs based upon band-structure calculations in the local density approximation.

Metal	$P_0^{FG}$	$P_0^{ASJEOS}$
Al	16.6	20.9
Li	1.08	1.21
Mo	128.8	49.2

ponential integral, whereas the ASJEOS involves only simpler functions in both pressure and energy forms. Moreover, the APL has two nonlinear fitting parameters  $v_0$  and  $c_0$ , compared to only one,  $v_0$ , for the ASJEOS. This fact permits fitting the ASJEOS parameters to the  $\epsilon(x)$  or  $P(x)$  reference data via a system of four linear equations [Eqs. (26)–(29) of Ref. 1]. The APL, on the other hand, requires a nonlinear fitting to find  $c_0$  or equivalently  $B_0$ .

In Holzapfel’s classification, the order of an equation of state is the number of its independent fitting parameters, excluding  $v_0$  and excluding any free-atom input. The typical independent fitting parameter of a first-order equation of

TABLE II. Equilibrium parameters for Al, Li, and Mo, obtained by fitting the SJEOS, ASJEOS, and AP3 to band-structure energies in a narrow range of  $x$  around equilibrium ( $v_0$  in bohr<sup>3</sup>,  $\epsilon_0$  in hartree,  $B_0$  in Mbar).

	SJEOS	ASJEOS	AP3
Al			
$v_0$	107.944	107.911	107.946
$\epsilon_0$	0.154	0.154	0.154
$B_0$	0.821	0.824	0.820
$B_1$	4.743	4.964	4.739
Li			
$v_0$	127.924	127.915	127.915
$\epsilon_0$	0.075	0.075	0.075
$B_0$	0.151	0.150	0.151
$B_1$	3.337	3.442	3.341
Mo			
$v_0$	101.843	101.824	101.855
$\epsilon_0$	0.460	0.460	0.460
$B_0$	2.924	2.941	2.947
$B_1$	4.010	4.203	4.015

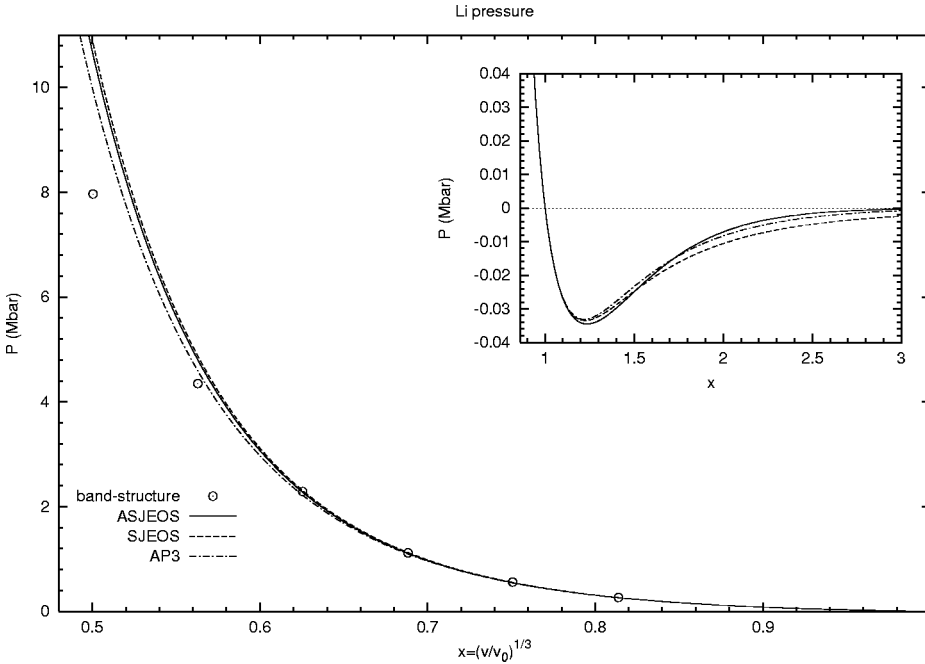


FIG. 2. Pressure  $P$  vs compression ratio  $x$  for Li.

state is the bulk modulus  $B_0$ , while those of a second-order equation of state are  $B_0$  and  $B_1$ . The ASJEOS is a third-order equation of state, with fitting parameters  $B_0$ ,  $B_1$  and cohesive energy  $\epsilon_0$ , plus the highest occupied orbital energy within the local density approximation as the free-atom input which fixes  $F$ . Point 3 of the Comment mistakenly identifies the fixed constants  $h=42$  and  $f=6.8$  of Eqs. (36)–(38) in Ref. 1 as additional fitting parameters. Thus the ASJEOS is most fairly compared to the AP3, which has the same number of fitting parameters plus the atomic number  $Z$  as the free-atom input, but not to the AP4, which has one more independent fitting parameter. Just as the AP3 can be systematically improved by adding parameters (AP3  $\rightarrow$  APL,  $L > 3$ ), our ASJEOS could be improved by making some of its constants ( $f$  and  $h$ ) material dependent or by treating the free-atom parameter  $F$  as a nonlinear independent fitting parameter.

As point 5 of the Comment says,  $\epsilon^{AP3}(x)$  is properly analytic over the whole range of  $x$ , while our  $\epsilon^{ASJEOS}(x)$  has a discontinuous fourth derivative with respect to  $x$  at the equilibrium value  $x=1$ . As a benefit of this discontinuity,  $P^{ASJEOS}(x)$  for  $x < 1$  depends upon two fewer parameters than for  $x > 1$ : one fitting parameter ( $\epsilon_0$ ) and one nonlinear free-atom parameter ( $F$ ) are absent for  $x < 1$ . In other words, under compression, to which the experimental data are limited, the ASJEOS pressure is really a second-order equation of state with no free-atom input. In this category, the ASJEOS is remarkably accurate and useful.

Both the AP3 and ASJEOS are physically motivated interpolations between known  $x \rightarrow 0$  and  $x \rightarrow \infty$  behaviors, with material-dependent parameters fitted around  $x=1$ . In the  $x \rightarrow 0$  or strong-compression limit,

$$P^{AP3}(x) \rightarrow \frac{P_0^{FG}}{x^5}, \quad (4)$$

$$P^{ASJEOS}(x) \rightarrow \frac{P_0^{ASJEOS}}{x^5}, \quad (5)$$

where

$$P_0^{FG} = \frac{(3\pi^2)^{2/3}}{5} \frac{\hbar^2}{m_e} \left( \frac{Z}{v_0} \right)^{5/3}, \quad (6)$$

$$P_0^{ASJEOS} = 3B_0(3.8B_1 - 10.4). \quad (7)$$

Only the AP3 gives the correct coefficient  $P_0$  for this limit, although the ASJEOS is not too bad (Table I). Under experimental conditions, this limit is very remote (less so for the lighter elements like Li than for the heavier ones).

In the  $x \rightarrow \infty$  or strong-expansion limit,

$$P^{AP3}(x) \rightarrow -\frac{3B_0c_3}{x} e^{-c_0(x-1)}. \quad (8)$$

Thus, when  $c_3$  is negative,  $P^{AP3}(x)$  improperly approaches 0 from above, as in the cases of Li and Mo (shown below). In the same limit,

$$P^{ASJEOS}(x) \rightarrow -\frac{\epsilon_0 F^2}{3v_0 x} e^{-F(x-1)}, \quad (9)$$

which properly approaches zero from below, since  $\epsilon_0 > 0$ .

Now we shall compare the SJEOS, ASJEOS, and AP3 for the metals Al, Li, and Mo, for a range of finite compressions ( $P \leq 15$  Mbar) and expansions ( $x \leq 3$ ). As in Ref. 1, we start from the results of band-structure (linear combination of Gaussian-type orbitals) calculations of the energy in the local density approximation, to which we fit each of the equations of state in a narrow range<sup>1</sup> of  $x$  around  $x=1$  to extract the equilibrium parameters  $\epsilon_0$ ,  $v_0$ ,  $B_0$ , and  $B_1$ , shown in Table II, and thus the parameters of the considered equations of state. We then plot the pressure or energy (Figs. 1, 2, and 3)

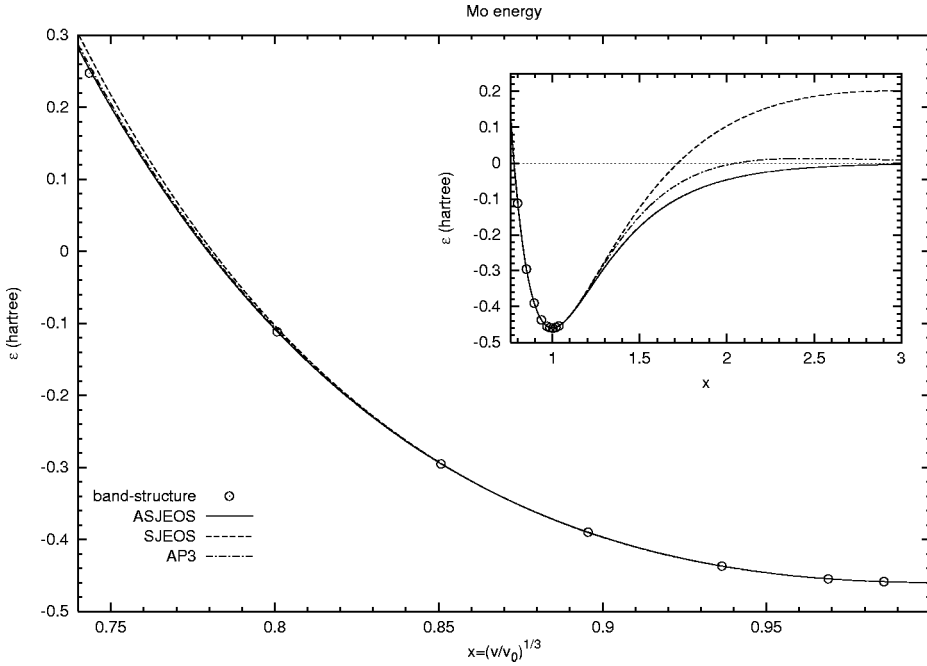


FIG. 3. Energy  $\varepsilon$  vs compression ratio  $x$  for Mo. Note that the AP3 energy has an unphysical but weak maximum around  $x=2.5$ .

from each equation of state, using its own set of equilibrium parameters, for comparison with the band-structure data over a much broader range of  $x$ . (Note that in Ref. 1 we used the ASJEOS equilibrium parameters to plot *both* the ASJEOS and SJEOS; here we find that the SJEOS works a little better with its own equilibrium parameters.)

Table II shows that the equilibrium parameters are essentially the same when constructed from the SJEOS, ASJEOS, or AP3, although  $B_1$  from the ASJEOS is as much as 5% larger than  $B_1$  from the other two equations of state. Figures 1, 2, and 3 show that the pressure increases too fast under compression in the SJEOS, as it probably would in a pseudo-potential calculation. For the Al, the ASJEOS and AP3 yield a lesser overestimation of the pressure under compression, with the ASJEOS giving the more realistic result. For Li, which shows a  $2s \rightarrow 2p$  electronic phase transition<sup>1</sup> at  $x = 0.6$ , we should focus on the region  $x \geq 0.6$ , where the ASJEOS and AP3 are both very accurate, with the ASJEOS slightly better. For Mo, both the ASJEOS and AP3 provide nearly perfect descriptions, with the ASJEOS again slightly better. Although the results for other materials or pressure ranges may differ, for these cases we find that the ASJEOS is either slightly better than or at least no worse than the AP3.

Points 6–10 of the Comment are mostly concerned with Thomas–Fermi theory and the high-compression limit. Figure 1 of the Comment shows that the AP2 can fit the Thomas-Fermi pressure over a wide range of densities, while some other equations of state cannot. Thus this figure does for the APL what Fig. 1 of Ref. 1 does for the ASJEOS: it shows that the chosen equation of state can properly describe its underlying microscopic model. The Thomas-Fermi model is valid for strong compression, where the stabilized jellium model is not; conversely, the stabilized jellium model is valid around equilibrium, where the Thomas-Fermi model is not. Note that the maximum of the horizontal axis of Fig. 1 of the Comment is  $r_{TF} = 1$  nm, which corresponds to an extreme

expansion for Al ( $x=2.7$ ), Li ( $x=4.0$ ), and Mo ( $x=1.9$ ). The region of this figure where the Thomas-Fermi model has some relationship to reality is roughly  $r_{TF} \lesssim 0.1$  nm, where the exact curve can be fitted by all the considered equations of state (and also by the ASJEOS).

The SPL (Lth-order screened polynomial) and MJL (modified jellium) models introduced in points 8 and 9 of the Comment are not the ASJEOS, but are APL-like constructions applied not to the pressure (as in the APL), but to the energy form. Like the ASJEOS and unlike the APL, these models have a power series expansion of the energy around  $x=0$ :

$$\varepsilon(x) = \sum_{n=-2}^{\infty} a_n x^n. \quad (10)$$

The corresponding pressure is then

$$P(x) = -\frac{1}{3v_0} \sum_{n=-2}^{\infty} n a_n x^{n-3}. \quad (11)$$

Note that the  $x^{-3}$  or  $n=0$  term in the pressure of Eq. (11) necessarily vanishes, while it does not in the APL. It appears that the Thomas-Fermi pressure has a nonzero  $x^{-3}$  contribution and thus that the Thomas-Fermi energy has no expansion of the form (10).

To see this, let us write the high-compression series for the pressure as

$$\frac{P}{P^{FG}} = 1 - k_1 \left( \frac{r_{TF}}{a_0} \right) + k_2 \left( \frac{r_{TF}}{a_0} \right)^2 + \dots, \quad (12)$$

where  $P^{FG} = P_0^{FG}/x^5$ ,  $r_{TF} = Z^{1/3} r_0 x$ , and  $a_0 = \hbar^2/m e^2$ . Table II of Ref. 8 suggests that

$$k_1^{TF} = 0.4073, \quad k_2^{TF} = 0.05. \quad (13)$$

TABLE III. Comparison of the exact high-pressure screening constant  $k_1^{TFD}$  of Eq. (12) with its AP3 approximation. The AP3 parameters  $c_0$ ,  $c_2$ , and  $c_3$ , found from the best fit of the AP3 to band-structure energies, are also shown.

Metal	$c_0$	$c_2$	$c_3$	$k_1^{TFD}$	$k_1^{AP3}$
Al	1.906	0.703	0.643	0.445	0.222
Li	0.870	-0.358	-0.159	0.507	0.511
Mo	2.678	-1.154	-0.973	0.424	0.570

Since  $k_2^{TF}$  does not seem to vanish, the Thomas-Fermi energy appears to have no expansion of the form (10). The exact<sup>9</sup> high-compression limit is given by Thomas-Fermi-Dirac theory, in which the screening constant is<sup>10</sup>

$$k_1^{TFD} = \left( 0.4073 + \frac{0.2073}{Z^{2/3}} \right). \quad (14)$$

Equation (14) is most easily derived by assuming a uniform electron density in which a lattice of nuclei is immersed and representing the energy per unit cell as a sum of kinetic, Madelung, and exchange terms, somewhat as in Ref. 5. The

$Z^0$  or Thomas-Fermi term in Eq. (14) is specific for a close-packed lattice. Although the  $Z^{-2/3}$  term in Eq. (14) from the exchange energy breaks the Thomas-Fermi scaling, its effect is relatively modest (Table III). Within the AP3 we find

$$k_1^{AP3} = \frac{1 + c_0 - c_2 - c_3}{Z^{1/3} \frac{r_0}{a_0}}. \quad (15)$$

Table III compares  $k_1^{AP3}$  to the exact  $k_1^{TFD}$  for Al, Li, and Mo. The level of agreement is not bad, but the discrepancy for Al could be related to the too-high AP3 pressure found for Al in Fig. 1. If it is, then better results might be found from the AP4 fitted to  $B_0$ ,  $B_1$ ,  $\epsilon_0$ , and  $k_1^{TFD}$ .

In summary, both the ASJEOS and AP3 seem to be useful equations of state. At least for Al, Li, and Mo at  $P \leq 15$  Mbar, they represent significant advances over earlier equations of state (see Ref. 1). While the AP3 has some advantages over the ASJEOS, the converse is also certainly true, contrary to the Comment.<sup>4</sup>

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