IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

A simple environment-dependent overlap potential and Cauchy violation in solid argon

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 236228

(http://iopscience.iop.org/0953-8984/19/23/236228)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 28/05/2010 at 19:11

Please note that terms and conditions apply.

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 236228 (10pp) doi:10.1088/0953-8984/19/23/236228

A simple environment-dependent overlap potential and Cauchy violation in solid argon

Masato Aoki and Tatsuya Kurokawa

Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

E-mail: masato@gifu-u.ac.jp

Received 9 January 2007, in final form 27 April 2007
Published 16 May 2007
Online at stacks.iop.org/JPhysCM/19/236228

Abstract

We develop an analytic and environment-dependent interatomic potential for the overlap repulsion in solid argon, based on an approximate treatment of the non-orthogonal tight-binding theory for closed-shell systems. The present model can reproduce the observed elastic properties of solid argon well, including the Cauchy violation at high pressures, yet it is very simple. A useful and novel analysis is given to show how the elastic properties are related to the environment dependence incorporated into a generic pairwise potential. The present study has a close link to the broad field of computational materials science, in which the inclusion of environment dependence in the short-ranged repulsive part of a potential model is sometimes crucial in predicting the elastic properties correctly.

1. Introduction

Recent progress in Brillouin spectroscopy at very high pressures [1, 2] has revealed that interatomic forces in face-centred cubic (fcc) solid argon must be far beyond any kind of two-body, central force model. Shimizu *et al* [1] precisely measured a large violation of the Cauchy relation up to 70 GPa and stressed the important role of many-body forces, in order to construct good potentials for high-density noble gases, which should be crucial in understanding their behaviour in planetary bodies by means of molecular simulations.

The Cauchy relation [3] for the elastic constants of cubic crystals at a hydrostatic pressure P is given by $C_{12} - C_{44} - 2P = 0$, which must be satisfied in centrosymmetric cubic crystals, including fcc solid argon, if the total energy is given by the sum of purely pairwise terms. The deviation from it is therefore a measure of the many-atom nature of interatomic interactions. The Aziz–Slaman model for high-pressure argon [4], which might be one of the most sophisticated yet simple ones thus far proposed, fails to reproduce any violation of the Cauchy relation, simply because the model is pairwise.

On the other hand, the *ab initio* density functional theory (DFT) approach using the pseudopotential planewave method [5], and that with projector-augmented wave

 © 2007 IOP Publishing Ltd Printed in the UK

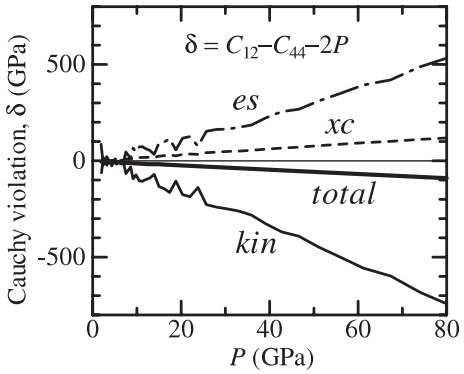

Figure 1. Total Cauchy violation, δ, decomposed into contributions from the kinetic (thin solid), electrostatic (dot–dashed), and exchange–correlation (dashed) energies.

implementation for core electrons [6], and the linear muffin-tin orbital (LMTO) method [7, 8] have successfully reproduced the observed elastic constants, as well as the density of the solid argon over the measured range of pressure. From these theoretical results, it should be a natural and logical consequence that one would expect to have a simple and reasonably accurate model for the many-atom interaction in condensed argon, by coarse-graining the *ab initio* electronic models to a rather empirical atomistic model.

The importance of many-body forces in solid argon at high pressures has been examined by several authors along the idea of many-atom expansion [9–11], in which one assumes that the total energy is 'additively' decomposable into N-atom ($N = 2, 3, 4 \ldots$) terms plus the additional energy of zero-point vibrations, and that the expansion is well convergent. The three-atom contribution from the exchange energy was emphasized [10] because it stabilizes argon in the fcc structure, rather than the hexagonal close-packed (hcp) structure, which is predicted by all the available pairwise models without zero-point energy [11]. However, it is pointed out that the convergence of this type of expansion becomes worse in a situation in which the many-atom effect is more important [11].

Meanwhile, the Kohn–Sham total energy within the DFT is comprised of the well-defined terms of kinetic, electrostatic and exchange–correlation energies. Pressure and elastic constants, which are proportional to the first and second derivatives of the total energy, are broken down into contributions from the three energy terms. Figure 1 shows the Cauchy violation defined by

$$\delta \equiv C_{12} - C_{44} - 2P, \tag{1}$$

and its breakdown into the contributions from kinetic (kin), electrostatic (es) and exchange–correlation (xc) energies predicted [8] by using an all-electron calculation within the DFT [12]. Each curve is plotted as a function of the total pressure. Clearly, the central role for the observed negative δ is played by the kinetic energy, which remains after the large cancellation by the opposite electrostatic and exchange–correlation contributions. It should be noted that non-zero contribution from the electrostatic energy immediately excludes a primitive picture of overlapping frozen atomic charge-density. Therefore, it is implied that deformation of density (wavefunctions) should be relevant. In general, there is no unique way of decomposing the DFT total energies to individual N-atom contributions because of overlapping many-atom interactions. We show that the many-atom interactions in elastic properties of solid argon can be modelled and explained without invoking the ansatz of additive many-atom expansion.

The purpose of this paper is to develop an analytic interatomic potential for solid argon that is based on the quantum mechanics of electrons, and that can reproduce the observed elastic properties, including the Cauchy violation at high pressures, well, yet is made as simple as possible. The problem we are to treat now has a close link to the broad field of computational materials science, since the inclusion of environment dependence in short-ranged repulsion is sometimes crucial [13–16] in obtaining reliable and transferable models for simulations in empirical and semi-empirical approaches.

In section 2, a tight-binding description for overlap repulsion in closed-shell atoms, which depends on atomic environment, will be presented as the theoretical base that underpins the more empirical and analytic model. General properties of the repulsive potential with environment-dependent parameters are analysed, and a simple functional form for the overlap repulsion is designed for argon and proposed in section 3. The result of the fitted analytic potential is presented in section 4, followed by conclusions in section 5.

2. Environment-dependent overlap repulsion: tight-binding description

A system of closed-shell atoms may be well described within the non-orthogonal tight-binding bond model (TBBM) [17, 18], in which the total binding energy is given by

$$E_{\mathrm{B}} = E_{\mathrm{cov}} + E_{\mathrm{ren}} + E_{\mathrm{rep}} + E_{\mathrm{vdW}}. \tag{2}$$

The first term is the covalent energy

$$E_{\mathrm{cov}} = 2\,\mathrm{Tr}[\mathsf{H}\mathsf{S}^{-1}] - 2\,\mathrm{Tr}[\mathsf{H}] = -2\,\mathrm{Tr}[\mathsf{H}\mathsf{O}\mathsf{S}^{-1}], \tag{3}$$

where H and $\mathsf{S} = 1 + \mathsf{O}$ are the Hamiltonian and overlap matrices defined by

$$(\mathsf{H})_{i\mu,j\nu} = \int \psi^*_{i\mu}(\mathbf{r})\hat{H}\psi_{j\nu}(\mathbf{r})\,\mathrm{d}^3r \tag{4}$$

and

$$(\mathsf{S})_{i\mu,j\nu} = \delta_{i,j}\delta_{\mu,\nu} + (\mathsf{O})_{i\mu,j\nu} = \int \psi^*_{i\mu}(\mathbf{r})\psi_{j\nu}(\mathbf{r})\,\mathrm{d}^3r, \tag{5}$$

in a basis set of atomic orbitals $\psi_{i\mu}$, where μ runs over orbitals on site i. The spin degeneracy enters as the prefactor 2 before the usual symbol Tr for the trace. The Hamiltonian operator $\hat{H}$ refers to the density of superposition of frozen atomic densities [18, 17]. Note that the inverse overlap matrix, S^{-1}, in equation (3) is equivalent to the density matrix in this case of a fully occupied system. The second term in equation (2), E_{ren}, is defined by

$$E_{\mathrm{ren}} = 2\,\mathrm{Tr}[\mathsf{H}] - 2\,\mathrm{Tr}[\mathsf{H}_{\mathrm{fa}}], \tag{6}$$

which accounts for the on-site energy shift due to the contraction or localization of free atomic orbitals on going into a condensed environment, and H_{fa} is a diagonal matrix of the free atomic energy levels. E_{rep} represents the contribution from the change in the electrostatic and exchange–correlation energies associated with *frozen* atomic charge densities as they are brought together from free space. Thus, this term is environmentally *independent* by construction, and it is usually approximated as a sum of repulsive pairwise potentials between atoms. E_{vdW}, added supplementarily to TBBM, denotes the van der Waals potential, which may be approximated using the empirical pairwise inverse power function of interatomic separation, that is $-c_6 R_{ij}^{-6}$.

In order to illustrate that equation (3) essentially represents the overlap repulsion, we now consider only the outermost p-shell states as the basis, and then the bond integral [19] part, B, may be separated from H as

$$\mathsf{H} = \epsilon_p \mathsf{S} + \mathsf{B}, \tag{7}$$

where ϵ_p is the common diagonal element of H. Further simplification can be made exploiting the Wolfsberg–Helmholtz [19] (or extended Hückel) approximation to write $\mathsf{B} = -b\mathsf{O}$ using a constant $b > 0$. We easily find

$$E_{\rm cov} = 2b\,{\rm Tr}[\mathsf{O}^2(1+\mathsf{O})^{-1}], \tag{8}$$

and see immediately that $E_{\rm cov} = 0$ if the basis is orthogonal (i.e. $\mathsf{O} =$ zero), and it turns into being repulsive when the O matrix is switched on. Note that equation (8) has no explicit dependence on ϵ_p. The name of this term, therefore, is only nominal for the noble gases as it gives overlap repulsion rather than the covalent bonding. The lowest-order term in equation (8) is given by $2b\,{\rm Tr}[\mathsf{O}^2]$, which may be broken down into contributions in a purely pairwise form

$$\Phi_{ij}(R_{ij}) = 4b\{|O_{{\rm pp}\sigma}(R_{ij})|^2 + 2|O_{{\rm pp}\pi}(R_{ij})|^2\}, \tag{9}$$

where $O_{{\rm pp}\sigma}(R_{ij})$ and $O_{{\rm pp}\pi}(R_{ij})$ are σ- and π-overlap integrals along interatomic separation $\mathbf{R}_{ij}$. The higher-order correction terms, which arise from multiplication of $(1+\mathsf{O})^{-1}$ in equation (8), or alternatively, multiplication of $(1+\mathsf{O})^{-1/2}$ from both sides of O^2 in a symmetric Löwdin form, would introduce many-atom effects as derived by Nguyen-Manh *et al* for environment-dependent bond integrals [20]. For simplicity of our model, we may neglect these higher-order corrections to write

$$E_{\rm cov} \cong {\rm Tr}[-2\mathsf{BO}] = \tfrac{1}{2}\sum_{i\neq j}\Phi_{ij}(R_{ij}) \equiv E_{\rm ovl}. \tag{10}$$

Assuming the Slater-type atomic p orbitals with exponential tail of $\exp(-\kappa_i r)$ for atom i, the bond and overlap integrals decay like $\exp[-\frac{1}{2}(\kappa_i+\kappa_j)R_{ij}]$, and the overlap potential equation (9) takes the form

$$\Phi_{ij}(R_{ij}) = (\text{polynomial of } R_{ij}) \times \exp[-(\kappa_i+\kappa_j)R_{ij}]. \tag{11}$$

A typical value of the decay constant (κ_i) evaluated within the DFT for the 3p orbitals of a free Ar atom is 2.0 Å^{-1}. We note that the contributions from the 3s shell could be included in the present formalism straightforwardly, which would add to equation (9) terms proportional to $|O_{{\rm ss}\sigma}|^2$ and $|O_{{\rm sp}\sigma}|^2$. However, the decay constant for the 3s orbital is 2.8 Å^{-1}, which is large enough to damp down $|O_{{\rm ss}\sigma}|^2$ and also $|O_{{\rm sp}\sigma}|^2$ to an order of magnitude smaller than $(|O_{{\rm pp}\sigma}|^2 + 2|O_{{\rm pp}\pi}|^2)$ within the range of atomic separations of our interest, that is, $R > 2.6$ Å, which corresponds to hydrostatic pressures up to 90 GPa. Therefore, the present p-shell approximation gives a good simplification to the construction of a minimal model, and the small contributions from the 3s shell may be effectively absorbed and taken care of in the fitting procedure.

An important environment effect can naturally be taken into account if we think of $\{\kappa_i\}$ as a set of variational parameters. It is a straightforward exercise to show for a hydrogen-like atom with an effective atomic number Z^* that (in atomic Rydberg units)

$$\int \psi_{i\mu}(\mathbf{r})(-\nabla^2 - 2Z^*/r)\psi_{i\mu}(\mathbf{r})\,{\rm d}^3r = (\kappa_i - Z^*/2)^2 - (Z^*/2)^2 \tag{12}$$

with $-(Z^*/2)^2$ being the lowest p energy level; we see that the parabolic penalty for an augmented κ arises from an increase in kinetic energy due to localization. This parabolic behaviour occurs as a result of the change in the effective radius of the atomic wavefunction, regardless of the particular form of the atomic pseudopotentials. Therefore, we may assume for the diagonal matrix elements of $\hat{H}$ that

$$(\mathsf{H})_{i\mu,i\mu} = (\kappa_i - \kappa_{i0})^2 + \epsilon_{i0} = \epsilon_{ip}(\kappa_i), \tag{13}$$

where κ_{i0} and ϵ_{i0} are constants, and thus, $E_{\rm ren}$ has the role of a penalty for the localization of atomic orbitals through equation (13), while the localization will reduce the magnitude of

overlap repulsion. Therefore the optimum values of $\{\kappa_i\}$ will be determined by minimizing $E_{\rm ovl} + E_{\rm ren}$ with respect to each κ_i. In the case of p shells, given a simplified form for overlap potential $\Phi_{ij} = 6q \exp[-(\kappa_i + \kappa_j)R_{ij}]$ with a constant q, this minimization leads to

$$\Delta\kappa_i = \kappa_i - \kappa_{i0} = \sum_{j(\neq i)} q R_{ij} \exp[-(\kappa_i + \kappa_j)R_{ij}]. \tag{14}$$

The set of solutions is indeed environment dependent, and we see that the constant κ_{i0} is the solution for the limiting case of infinitely separated atoms. Since the penalty due to increase in the kinetic energy is steep, $\Delta\kappa_i/\kappa_{i0}$ would be small enough to replace κ_i in the exponential in equation (14) with κ_{i0}. This solves the equation to give an explicit $\Delta\kappa_i$ that is exact to first order, that is, $\Delta\kappa_i = \gamma_i/6$ with

$$\gamma_i = \sum_{j(\neq i)} q R_{ij} \exp[-(\kappa_{i0} + \kappa_{j0})R_{ij}] = -\left(\frac{\partial E_{\rm ovl}}{\partial \kappa_i}\right)_0, \tag{15}$$

where the subscript 0 in the last expression denotes the evaluation at $\Delta\kappa_j = 0$ for any j. The energy increase $\Delta E_{\rm ren}$ due to this minimization is given exactly by the sum of $3(\Delta\kappa_i)^2$, which partially sets off and just halves the lowest-order decrease in overlap energy as

$$\Delta E_{\rm ren}(\{\Delta\kappa_i\}) + \Delta E_{\rm ovl}(\{\Delta\kappa_i\}) = \sum_i 3(\Delta\kappa_i)^2 - \sum_i \gamma_i \Delta\kappa_i = -\tfrac{1}{2}\sum_i \gamma_i \Delta\kappa_i. \tag{16}$$

The resultant lowering, $\frac{1}{2}\Delta E_{\rm ovl}$, may more simply be given to first order by employing $\frac{1}{2}\Delta\kappa_i$ instead of $\Delta\kappa_i$ in the overlap energy, namely

$$\Delta E_{\rm ren}(\{\Delta\kappa_i\}) + \Delta E_{\rm ovl}(\{\Delta\kappa_i\}) = \Delta E_{\rm ovl}(\{\tfrac{1}{2}\Delta\kappa_i\}). \tag{17}$$

This treatment *eliminates* $\Delta E_{\rm ren}$ and simplifies the functional form of the potential, which is to be proposed in the next section.

The environmental effect that we are looking at is a tendency that more contracted atomic orbitals are preferred in a denser environment. The physics behind it has been beautifully justified in the pioneering work by Skinner and Pettifor [21], who have implemented the chemical pseudopotential theory using the orbital exponent as a variational parameter within the Harris–Foulkes scheme [22, 23], and found that the orbital exponents (the κ in our notation) of hydrogen atoms in the molecule, and in simple cubic and fcc lattices are strongly environment dependent, as stated above.

3. Analytic model for solid argon

Let us first analyse some general properties of a repulsive potential that is a function of environment-dependent parameters as well as the distance.

Provided that the functional form of the repulsive interatomic potential is given by

$$\Phi_{ij}(R_{ij}; \lambda_i + \lambda_j) \tag{18}$$

with the environment-dependent parameters (λ) that are written as a sum of pairwise functions, namely

$$\lambda_i = \sum_{k(\neq i)} \rho(R_{ik}), \tag{19}$$

the Cauchy violation can be calculated analytically for a cubic lattice. The result is written as [8]

$$\delta = \frac{2}{9\Omega}\left[\alpha_0^2 \sum_{j(\neq 0)} \frac{\partial^2 \Phi_{0j}}{\partial \lambda_0^2} + \alpha_0 \sum_{j(\neq 0)} R_j \frac{\partial^2 \Phi_{0j}}{\partial R_j \partial \lambda_0}\right] \tag{20}$$

with

$$\alpha_0 = \sum_{k(\neq 0)} R_k \rho'(R_k), \tag{21}$$

where Ω is the atomic volume and $R_j = R_{0j} = \sqrt{x_j^2 + y_j^2 + z_j^2}$ is the distance to atom j from the central atom $i = 0$ at the origin. The prime on ρ denotes the distance derivative. Note that all lattice sites are equivalent under a homogeneous strain. α_0 represents the strength of the environmental effect on atom 0. Since $\rho(R)$ at this point is completely arbitrary, we may assume that it is a positive and monotonically decreasing function of distance in the range of interest; hence $\alpha_0 < 0$. It may also be a physically reasonable assumption that the repulsive potential $\Phi_{0j}(> 0)$ is also a monotonically decreasing function of distance in the range of interest. We see from equation (20) for the case of very weak α_0 that negative Cauchy violation occurs if $\partial^2\Phi_{0j}/\partial R_j \partial\lambda_0 > 0$. This condition is likely to be fulfilled, since an environmental effect tends to weaken the overlap repulsion to give $\partial\Phi_{0j}/\partial\lambda_0 < 0$, as we have seen in the previous section. The expression for the pressure from Φ is given by

$$P = -\frac{1}{6\Omega}\left[\sum_{j(\neq 0)} R_j \frac{\partial\Phi_{0j}}{\partial R_j} + 2\alpha_0 \sum_{j(\neq 0)} \frac{\partial\Phi_{0j}}{\partial\lambda_0}\right]. \tag{22}$$

The first term in the square brackets represents the pairwise component. We see that the environmental effect, the second term, causes a reduction in pressure, as expected.

A simple functional form of overlap repulsion that takes into account the physics of the environment effect as we have discussed is now proposed, that is,

$$\Phi_{ij}(R_{ij}; \lambda_i + \lambda_j) = \exp(-\lambda_i)\exp(-\lambda_j) V_R(R_{ij}), \tag{23}$$

where V_R is an environmentally independent pairwise function. The environmental effect on site i enters in a very simple separable form through the factor $\exp(-\lambda_i)$, which corresponds to the contraction factor $\exp(-\Delta\kappa_i R_{ij})$. However, the direct dependence on the particular length R_{ij} has been dropped for simplicity. This manner of parameterization for the environmental effect can also be seen in the 'breathing-shell model' (see [24, 25] and references therein) and 'compressible ion model' [26] for oxides, such as MgO. Both models are provided with the parameters that correspond to the variation in effective size of the ionic cores, and a reduction in core size causes an exponential reduction as λ_i in the present model does. It should be noted that a kind of penalty function has been eliminated from the present model, as was justified in the previous section. The contraction factor of type $\exp(-\Delta\kappa_i R_{ij})$ was modelled by Nguyen-Manh *et al* in the form of a screened Yukawa-type potential [16, 15] and it was used to explain Cauchy pressures in transition metal intermetallics within tight-binding and Harris–Foulkes approaches.

It follows from the functional form proposed above that full expressions for the pressure P, Cauchy violation δ, adiabatic bulk modulus B, and the cubic elastic constants C_{11}, C_{12}, C_{44} are given by

$$P = \tfrac{1}{3}(-v + 2u\alpha_0), \tag{24}$$

$$\delta = \tfrac{4}{9}(-\alpha_0 v + u\alpha_0^2), \tag{25}$$

$$B = \tfrac{2}{3}P + \tfrac{1}{3}K + \delta, \tag{26}$$

$$C_{11} = -P + P^s + K^s + \delta, \tag{27}$$

$$C_{12} = \tfrac{1}{2}(3P + K - P^s - K^s) + \delta, \tag{28}$$

$$C_{44} = \tfrac{1}{2}(-P + K - P^s - K^s) \tag{29}$$

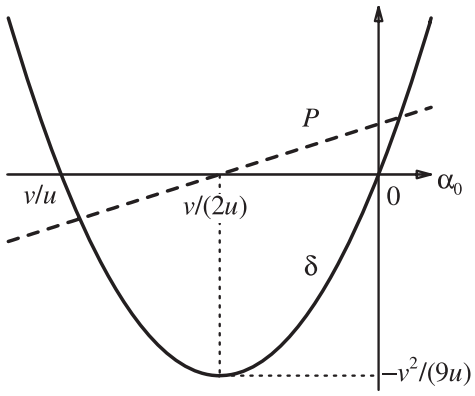

Figure 2. The Cauchy violation, δ, and pressure, P, as a function of strength of environment dependence, α_0, for the repulsive potential.

with

$$P^s = \tfrac{1}{3}(-v^s + 2u\alpha_0^s), \tag{30}$$

$$K = \tfrac{1}{3}(w - 2u\beta_0), \qquad K^s = \tfrac{1}{3}(w^s - 2u\beta_0^s), \tag{31}$$

where u equals the energy density and v, w also are similar quantities determined by first- and second-order derivatives of the potential, and u^s, v^s, w^s are weighted sums. These are defined by

$$u = \frac{1}{2\Omega}\sum_{j(\neq 0)} \Phi_{0j}, \qquad u^s = \frac{1}{2\Omega}\sum_{j(\neq 0)} \Phi_{0j}s_j, \tag{32}$$

$$v = \frac{1}{2\Omega}\sum_{j(\neq 0)} R_j\Phi'_{0j}, \qquad v^s = \frac{1}{2\Omega}\sum_{j(\neq 0)} R_j\Phi'_{0j}s_j, \tag{33}$$

$$w = \frac{1}{2\Omega}\sum_{j(\neq 0)} R_j^2\Phi''_{0j}, \qquad w^s = \frac{1}{2\Omega}\sum_{j(\neq 0)} R_j^2\Phi''_{0j}s_j, \tag{34}$$

with $s_j = (x_j^4 + y_j^4 + z_j^4)/R_j^4$. Together with α_0, three other quantities representing the strength of environment dependence are defined:

$$\alpha_0^s = \sum_{k(\neq 0)} R_k\rho'(R_k)s_k, \tag{35}$$

$$\beta_0 = \sum_{k(\neq 0)} R_k^2\rho''(R_k), \qquad \beta_0^s = \sum_{k(\neq 0)} R_k^2\rho''(R_k)s_k. \tag{36}$$

Equations (24) and (25), seen as linear and quadratic functions of α_0 respectively, explain how the negative Cauchy violation occurs when an environment dependence is introduced, as presented instructively in figure 2. It is to be noted that $\alpha_0 = v/(2u)$ is an unphysical point where our 'repulsive' potential is found to be no longer repulsive, giving $P = 0$. Therefore, the magnitude of the dimensionless parameter α_0 should usually be much smaller than $|v/(2u)|$. An instructive example may be the case of inverse-power-law potential, $\Phi \propto R^{-n}$, in which the critical value can easily be found to be $v/(2u) = -n/2$. These analyses should be useful in understanding how the environmental dependence in the repulsive potential worked for the problem of small or negative Cauchy pressure ($C_{12} - C_{44}$ for cubic systems, $C_{13} - C_{44}$ and $C_{12} - C_{66}$ for tetragonal or hexagonal systems) in transition metals

Table 1. The parameters for V_R and ρ (see equations (37) and (38)) fitted to solid argon.

A (J)	a_1 (Å^{-1})	a_2 (Å^{-2})	μ_1 (Å^{-1})	μ_2 (Å^{-2})	g	ν (Å^{-1})
2.10×10^{-15}	−0.5819	0.093 09	3.000	−0.039 96	80.0	3.60

and intermetallic compounds [16, 15]. In these covalently bonded systems at equilibrium, a negative pressure $P_{\rm bond}$ from the attractive covalent bond energy counterbalances the positive one from the repulsion. In figure 2, this situation corresponds to the 'high-pressure' case in which $P = |P_{\rm bond}|$ and a negative contribution of δ with $v/(2u) < \alpha_0 < 0$.

Finally, parameterizations for the functions $V_R(R)$ in equation (23) and $\rho(R)$ in equation (19) must be determined. They are basically similar and are described by a superposition of the square of two-centre overlap integrals. Using equations (11) and (14) as a guide, we employ the following functions, namely

$$V_R(R) = A(1 + a_1 R + a_2 R^2) \exp(-\mu_1 R - \mu_2 R^2) \tag{37}$$

and

$$\rho(R) = g \exp(-\nu R), \tag{38}$$

where the parameters A, μ_1, g, ν are essential, and a_1, a_2, μ_2 are for flexibility of the fitting.

We do not explicitly include the pairwise $E_{\rm rep}$ in the present model, because it is actually unknown, but may not be dominant, and therefore we may think of it as being absorbed effectively in the pairwise component of overlap repulsion unless it proves significant.

4. Results

Using the model of overlap repulsion plus the pairwise van der Waals potential ($-c_6 R_{ij}^{-6}$) with the Lennard-Jones parameters for argon [27], i.e. $c_6 = 4\varepsilon\sigma^6$ with $\varepsilon = 1.67 \times 10^{-21}$ J and $\sigma = 3.40$ Å, the parameters are fitted to the results [8] by *ab initio* full-potential LMTO calculations with the generalized gradient approximation of PW91 (GGA-PW91) [28] for the exchange–correlation, since GGA-PW91 results are remarkably in good agreement with the experimental results for solid argon. However, GGA-PW91 is known always to predict positive pressures, and a small positive pressure even at the experimental lattice constant $a = 5.13$ Å for equilibrium at zero pressure. The adjusted parameters are listed in table 1.

Figure 3 shows the elastic properties of fcc solid argon predicted by the present model compared with the experimental results. The agreement is impressive. However, a negative curvature in predicted δ at very high pressures can be seen as a small deviation, which is reflected in B, C_{11}, C_{12} (and not in C_{44}) as can be understood from the δ-term (and its absence) in equations (26)–(29). This will be corrected if we design a more flexible function for ρ. But if we do so, we also need to evaluate neglected terms, for example, the higher-order many-atom effects due to $(1 + \mathsf{O})^{-1}$ factor, which will be handled in a separate study.

The stability problem of fcc against hcp is still very subtle even with the present environment-dependent model without zero-point energy. The result is very sensitive to the cutoff. For example, using only the present repulsive model (without $E_{\rm vdW}$), the fcc–hcp difference in enthalpy is evaluated to be −0.01 meV at 20 GPa and 0.11 meV at 60 GPa if we include 86 neighbours within six shells in the fcc structure and equivalently within nine shells in the hcp structure. The difference in the zero-point energy [9] would be dominant. Therefore the environmental or many-atom effect in the overlap repulsion may not be a remedy for the problem of fcc stability.

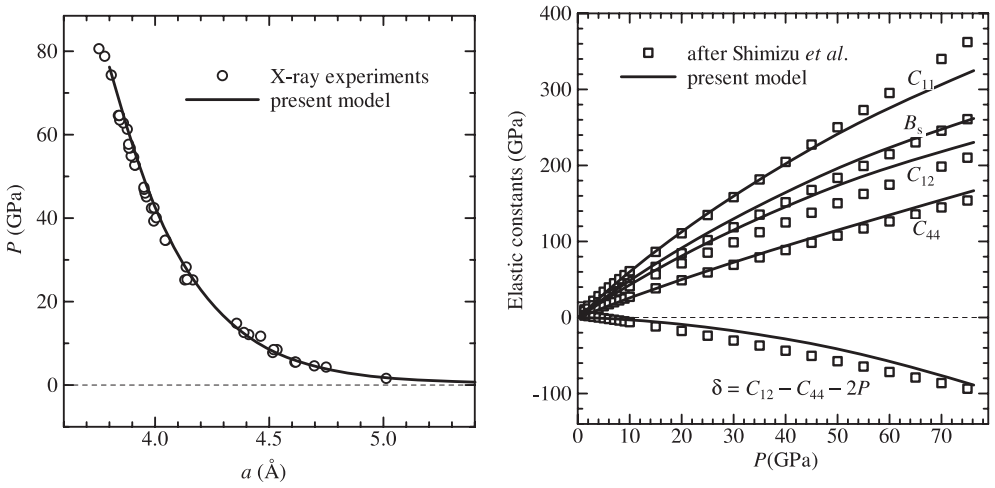

Figure 3. Left: pressure versus lattice constant. Circles denote x-ray observation (see references in [1]). Right: elastic constants versus pressure: the present model (solid lines) compared with experimental results by Shimizu *et al* [1].

5. Conclusion

We have developed an analytic and environment-dependent interatomic potential for the overlap repulsion in solid argon. The functional form, of environment dependence in particular, is simple and physically transparent, being based on the non-orthogonal tight-binding theory for closed-shell systems. The present model was shown to reproduce the observed elastic properties of solid argon well, including the Cauchy violation at high pressures.

A useful and novel analysis has clearly demonstrated how the elastic properties are related to the environment dependence incorporated into a generic pairwise potential. It is speculated that the present functional provides not only an excellent description for the elastic properties of a solid noble gas, but also a useful description for the problem of small or negative Cauchy pressures in covalently bonded systems.

Acknowledgments

The authors would like to thank Dr Duc Nguyen-Manh for useful conversations about their works on Cauchy pressure, Professor Y Shimizu and S Sasaki for helpful information on their experiments, and Dr T Iitaka for stimulating information at the onset of the present study. MA thanks the Kogyo-Club of the Faculty of Engineering, Gifu University for financial support.

References

[1] Shimizu H, Tashiro H, Kume T and Sasaki S 2001 *Phys. Rev. Lett.* **86** 4568
[2] Grimsditch M, Loubeyre P and Polian A 1986 *Phys. Rev.* B **33** 7192
[3] Born M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (New York: Oxford University Press)
[4] Aziz R A and Slaman M J 1990 *J. Chem. Phys.* **92** 1030
[5] Iitaka T and Ebisuzaki T 2002 *Phys. Rev.* B **65** 012103
[6] Tse J S, Klug D D, Shpakov V and Rodgers J R 2002 *Solid State Commun.* **122** 575
[7] Tsuchiya T and Kawamura K 2002 *J. Chem. Phys.* **117** 5859 and references therein
[8] Aoki M 2003 *Rev. High Pressure Sci. Technol.* **13** 218 (in Japanese)

[9] Rosciszewski K, Paulus B, Flude P and Stoll H 2000 *Phys. Rev.* B **62** 5482
[10] Lotrich V F and Szalewicz K 1997 *Phys. Rev. Lett.* **79** 1301
[11] Schwerdtfeger P, Gaston N, Krawczyk R P, Tonner R and Moyano G E 2006 *Phys. Rev.* B **73** 064112
[12] Savrasov S Yu and Savrasov D Yu 1992 *Phys. Rev.* B **46** 12181
[13] Tang M S, Wang C Z, Chan C T and Ho K M 1996 *Phys. Rev.* B **53** 979
[14] Haas H, Wang C Z, Fahnle M, Elsasser C and Ho K M 1998 *Phys. Rev.* B **57** 1461
[15] Mrovec M, Nguyen-Manh D, Pettifor D G and Vitek V 2004 *Phys. Rev.* B **69** 94115
[16] Nguyen-Manh D, Pettifor D G, Znum S and Vitek V 1998 *Tight-Binding Approach to Computational Materials Science* (*Mater. Res. Soc. Symp. Proc.* vol 491) ed P E A Turchi, A Gonis and L Colombo (Pittsburgh, PA: Materials Research Society) pp 353–8
[17] Finnis M W 2003 *Interatomic Forces in Condensed Matter* (New York: Oxford University Press)
[18] Sutton A P, Finnis M W, Pettifor D G and Ohta Y 1988 *J. Phys. C: Solid State Phys.* **21** 35
[19] Pettifor D G 1995 *Bonding and Structure in Molecules and Solids* (New York: Oxford University Press)
[20] Nguyen-Manh D, Pettifor and Vitek V 2000 *Phys. Rev. Lett.* **85** 4136
[21] Skinner A J and Pettifor D G 1991 *J. Phys.: Condens. Matter* **3** 2029
[22] Harris J 1985 *Phys. Rev.* B **31** 1770
[23] Foulkes W M C and Haydock R 1989 *Phys. Rev.* B **39** 12520
[24] Sangster M J L 1973 *J. Phys. Chem. Solids* **34** 355
[25] Matsui M 1998 *J. Chem. Phys.* **108** 3304
[26] Marks N A, Finnis M W, Harding J H and Pyper N C 2001 *J. Chem. Phys.* **114** 4406
[27] Kittel C 2005 *Introduction to Solid State Physics* 8th edn (New York: Wiley)
[28] Perdew J P 1991 *Electronic Structure of Solids' 91* ed P Ziesche and H Eschrig (Berlin: Akademie Verlag)