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New Model of Potential Energy Functions for Atomic Solids and Application to Silicon Crystal*

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A new theoretical model of potential energy functions for atomic solids is developed. An angular factor is included in this model and its effect is discussed. Using this new model, a new preliminary potential for silicon crystal is derived. Calculated phonon dispersion curves, using this new potential, is given. A good agreement has been found.

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Developing simple model interatomic potential, which would permit direct calculation of the structural properties and energetics of complex systems, in particular semiconductors,[1-5] has been attracting considerable attention of more and more theoreticians. Pair potentials have long been used to describe rare-gas atoms, simple metals, and highly ionic systems. However, such interesting materials as semiconductors, ceramics and polymers, all exhibit covalent bonding characteristic, which creates serious problems for traditional empirical approaches. Recently, in a series of papers,[6-10] Murrell *et al.* developed a new method, the many-body expansion method to describe atomic solids. In this method, up to three-body interactions were involved. Results indicated that this kind of empirical potentials can reproduce the elasticity accurately. However, for describing phonon dispersions of crystals of family IV, larger deviations have been found.[8] It is considered that maybe more attention should be paid to describe covalent characteristic of atomic solids. This paper describes a new approach to the formulation of interatomic potentials for covalent systems as atomic solids. As an application of this general approach, a new empirical potential fitted to lattice energy, equilibrium geometry, elastic constants and Ramam frequency, for silicon is developed. In particular, despite its limitations, the present potential appears to be sufficiently "global" to be used in molecular-dynamics simulations.

Our general strategy to seek a potential which can reproduce phonon dispersions of atomic solids better, is a sum of two-body and three-body terms as same as the many body expansion method, but modified by a factor which represents angular effects.

$$V = \sum_i \sum_{j>i} V_{ij}^{(2)} + \sum_i \sum_{j>i} \sum_{k>j} \sigma V_{ijk}^{(3)} , \tag{1}$$

$$V_{ij}^{(2)} = -D(1 + \alpha \rho_{ij}^{n_1}) \exp(-\beta \rho_{ij}^{m_1}) , \tag{2}$$

$$\begin{aligned} V_{ijk}^{(3)} = \; & D\left[C_0 + C_1 Q_1 + C_2 Q_1^2 + C_3(Q_2^2 + Q_3^2) + C_4 Q_1^3 + C_5 Q_1 (Q_2^2 + Q_3^2) + C_6 Q_3 (Q_3^2 - Q_2^2)\right] \\ & \cdot \exp(-\kappa Q_1^{n_2}) \exp(-\tau \eta^{m_2}) , \end{aligned} \tag{3}$$

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where σ is a factor which can be used to adjust the proportion of three body terms.

$$Q_1 = \frac{1}{\sqrt{3}}(\rho_1+\rho_2+\rho_3)\,, \quad Q_2 = \frac{1}{\sqrt{2}}(\rho_2-\rho_3)\,, \quad Q_3 = \sqrt{\frac{2}{3}}\rho_1 - \frac{1}{\sqrt{6}}\rho_2 - \frac{1}{\sqrt{6}}\rho_3\,, \quad \eta = (\theta_{ijk}-\theta^\circ)\,,$$

$\rho = (r - r_e)/r_e$ is the reduced interatomic distance, θ° the reference bond angle and θ_{ijk} the maximum bond angle of triangle among ijk, jik and jki. Therefore, $V^{(3)}$ is totally symmetric under permutations of the atoms at the vertices of the triangle of side (ρ_1, ρ_2, ρ_3). A good theoretical model should give sufficient accurate descriptions in both of short and long ranges. Three-body interactions essentially are short-ranged and vanish rapidly as distances increase. In the long range, main interactions come from two-body terms. This is the reason why pair potentials, such as Lennard-Jones potentials, can be used satisfactorily in the simulation of liquids. Therefore, the forms of two- and three-body terms must be chosen very carefully such that they represent interactions in different ranges, respectively. In our model, a high power was chosen in the polynomial part of two-body terms such that in the long range, two-body interaction will be predominant. The existence of angular factor in three-body terms will ensure that the three-body interaction vanishes rapidly as the lattice is distorted and/or as the distances increase. The factor σ, will be used to adjust the proportion of two-body and three-body interactions. In fact, it is a weight factor. Therefore, our theoretical model will give globally descriptions in both of short and long ranges and have appropriate asymptotic forms for use in molecular dymanics and Monte Carlo calculations. For a diamond lattice, there are only three independent elastic constants: C_{11}, C_{12}, C_{44}. These are related to the harmonic matrix elements by[11] through the so-called long wavelength approximation. The definitions of harmonic force constant matrix elements can be found in Refs.11 and 12 and we not give them here.

Table 1. Potential energy function of silicon crystal.

n_1	4.0	C_0	−32.24977
m_1	1.0	C_1	9.79971
n_2	2.0	C_2	22.16416
m_2	1.0	C_3	7.58795
σ	1.0	C_4	−8.18431
α	570.95420	C_5	−3.90776
β	4.91230	C_6	8.58630
τ	9.66018		
κ	2.47761		

Table 2. Calculated elastic constants (10^{12} dyn·cm^{-2}), Raman frequency (10^{13} Hz).

	This work	(a)(Ref. 8)	(b) (Ref. 4)	Experiment
C_{11}	1.660	1.672	1.71	1.657
C_{12}	0.640	0.639	1.00	0.639
C_{44}	0.794	0.792	0.92	0.796
V_{Raman}	1.60	1.535	2.47	1.53

The new model has been used to derive the potential of silicon (diamond structure). The potential was fitted to the lattice energy, elastic constants and Raman frequency. The lattice

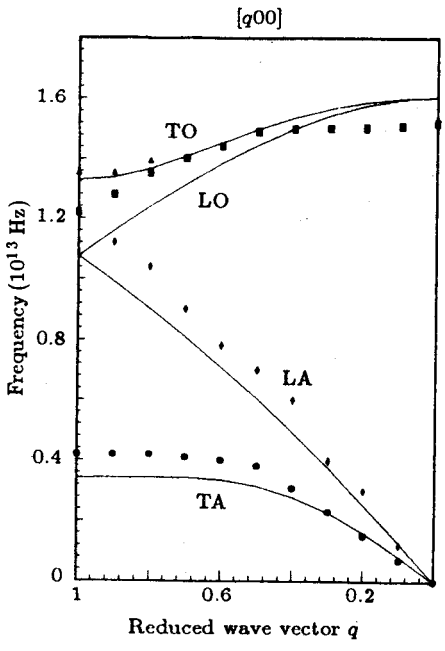

Fig. 1. Phonon dispersion curve, experimental data given by points.

energy was taken as 4.63 eV (Ref. 13) and the lattice spacing $l = 5.43$ Å (the internuclear distance $l\sqrt{3/4} = 2.35$ Å). The elastic constants and Raman frequency were taken from Cowley's paper:[13] C_{11}=1.657 × 10^{12}, C_{12}= 6.39 × 10^{11}, C_{44}=7.96 × 10^{11} dyn·cm^{-2}, ν_R= 1.53 × 10^{13} Hz. For selected values of n_1, m_1, n_2 and m_2, coefficients of two-body and three-body terms were optimized such that experimental data were reproduced. Table 1 gives the parameters of the potential and Table 2 the resulting elastic constants and Raman frequency and force constants. Compared with the results determined by Murrell[7] and Biswas,[4] it can been seen that the elastic constants obtained from our potential substantially are better than those from earlier potentials and as Murrell's potential, our potential gives a correct order of C_{12} and C_{44}. The potential was also used to calculate the phonon dispersion along [q00], and Fig. 1 shows the comparison of calculated results and experiment data. A good agreement has been obtained. It should be indicated that the derived potential is only preliminary one. When more experiment data, for example phonon dispersions, are added to the input file, a much better potential will be obtained and this work is now in progress.

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