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ARTICLES

Interatomic potentials via the effective-action formalism

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We present a method for generating interatomic potentials from first-principles calculations. Using the effective-action formalism we describe a classical system of interacting atoms in terms of the expectation value of the pair density operator. Such a description naturally leads to the concept of the effective two-body interatomic potential. This is similar in spirit to the Kohn-Sham potential that arises in density-functional theory; however, in this case, the system is reduced from a fully interacting many-body system to an auxiliary system that interacts via a renormalized two-body potential. This potential contains the effects of three- and higher-body correlations and can be calculated via a systematic self-consistent procedure. This method can be trivially extended to the generation of higher-order interatomic potentials. [S0163-1829(98)09539-3]

I. INTRODUCTION

Computational first-principles techniques in condensed-matter physics are rapidly improving in both speed and accuracy. However, the quantum-mechanical treatment of the electronic degrees of freedom in such simulations still limits the size of the system to about 10^2 atoms. Interatomic potentials have emerged as an alternate and faster method to study large systems on the order of 10^6-10^8 atoms. They have become of fundamental importance in many areas of condensed-matter physics and materials science ranging from the study of defect formation energies to atomic structure of solid surfaces to computer simulations related to phase transitions, fracture, plastic deformation, melting and sintering. It is with this in mind that there has been a tremendous drive to produce reliable interatomic potentials that will be successful at predicting dynamical properties of many-body systems as first-principles calculations have been in predicting ground-state properties in the past several decades.

There have been several different approaches to interatomic potentials in the past several decades. One such approach derives interatomic potentials from first principles by some sort of an approximation scheme. These methods[1–6] give a good qualitative and sometimes quantitative understanding of the bonding in condensed-matter systems. Even though they have failed in producing good potentials, these approaches have generated important connections between effective interatomic potentials and electronic structure. Of these, the tight-binding models have been the most useful and have generated a wealth of insight into the nature of interatomic potential expansion of the cohesive energy.[5,6]

Although some of these techniques have been extended to deal with the more difficult class of materials such as transition metals and semiconductors, they have not enjoyed the attention that fitted potentials have in recent years. Fitted potentials require physical intuition to guide in choosing appropriate parametrized functional forms that can be fitted to a database of experimental or *ab initio* calculations. These effective interatomic potentials represent interactions among constituents of a system for which the electronic degrees of freedom have been somehow ''integrated out.'' This allows for a simpler description of the system but still expresses, in a clearer fashion, the basic physics involved. Assuming the validity of the Born-Oppenheimer approximation, one is led to the general expectation that an energy function exists that describes the total configurational energy of the system. Using Carlsson's[7] terminology and classification, this energy may be represented by pair potentials, cluster potentials, or cluster functionals and is the basic starting point of fitted methods. Most of the attention in the area of interatomic potentials is focused on generating good transferable potentials for covalent material. The problem lies in the complex quantum-mechanical effects that must be described by these effective interactions.

Examples of the more well-known potentials include the pioneering potential of Stillinger and Weber[8] which is a third-order cluster potential and was constructed to describe properties of silicon. Biswas and Hamann[9] introduced a third order cluster potential expansion with the three-body potential having a separable form. However, it may not always be advantageous to expand the cohesive energy in such a way. There is direct theoretical evidence[5] to suggest that in some systems such cluster potential expansions may either diverge or converge poorly. Another innovative but fundamentally different scheme is that of Tersoff[10–12] whose later versions improved on the number of fitting parameters. The Tersoff potentials are an example of a third-order cluster functional that includes a term that depends on the local bonding environment. The Tersoff potentials contain a great deal of physical insight and seem to have validity away from the equilibrium structure. The quality of these potentials have been studied[13] and, although they have their strengths and weaknesses, the fact remains that these potentials have poor transferability properties. Perhaps the reason is a need for a better description of the local environment. A perfect example of that is the thermodynamic interatomic force field potential of Chelikowsky *et al.*,[14] in which the environment is described by a so-called ''dangling-bond vector.'' Bazant *et al.*[15] have introduced environmentally dependent terms in their cluster potential-like expansion. Their potentials are in qualitative agreement with the various complex quantum-mechanical effects that dominate covalent material. Mei, Cooper, and Lim[16] used a formal expansion motivated by generalized pseudopotential theory but introduced a simple local variable function that transforms the volume-dependent energy term into many-body interactions. Although these and many other potentials were formulated with a great deal of physical insight, none have yet to demonstrate good transferability qualities. The reason may be that it is just too ambitious a task to try and fit all the qualitatively different properties in bonding of various structures into a simple potential form.

With this in mind, it may be advantageous to produce environmentally dependent effective interatomic potentials that contain the relevant physics through configurational information of a reference environment. Such effective potentials developed for a bulk reference environment may not be useful in surface calculations; however, potentials for such environments may be developed as well. Such an approach was attempted by Dagens[17] using the proposition of Carlsson *et al.*[5] for using an effective cluster expansion valid only for a restricted set of physical configurations. Their reference environment was the hard-sphere gas for which they used the Percus-Yevick approximation for the pair distribution function. Their findings were in general quite satisfactory. The point here is that if the effective potentials are calculated in a reference environment that contains the higher-order correlations, then a good description of systems that are not too different from the reference environment should result.

A statistical mechanical approach was taken early on through functional methods to generate such effective interactions. Most of the early work using functional methods was based on density-functional theory (DFT).[18,19] The idea was to renormalize the interparticle potential that arises from strong multiparticle correlations in the system. This was in sharp contrast to the conventional Ursell-Mayer expansion theory[20] where the interparticle correlations are given in terms of the bare interaction. The DFT approach brings a simplified picture to the many-body problem and puts into perspective the nature of the approximations that are implemented. The concept was extended to include a two-body external source term, to zeroth order in the external field, to deal with a weak three-body term.[21] Although the basic concepts are the same, the method to be introduced approaches the problem of interacting systems in a different manner than other functional approaches. It yields explicit expressions for the higher-order correlations and allows for the systematic improvement of the effective potential.

In what follows, we describe an approach to the generation of effective interatomic potentials from first-principles calculations via the effective-action formalism.[22–24] We formulate the theory so that the system is described by an ion pair-density. Such a pair density description will then naturally lead to a concept of effective two-body interatomic potentials. This is in sharp contrast with the *ad hoc* manner in which effective interatomic potentials are usually defined. This approach is quite analogous with density-functional theory[24,25] where the description of the system is based on the density. In the latter case, the fully interacting system is transformed into a noninteracting system in the presence of an auxiliary local source, the Kohn-Sham potential. This Kohn-Sham potential is determined by a self-consistent procedure that contains the effects of electron correlations and reproduces the exact density of the fully interacting system. Here, a pair-density-based description naturally leads to an auxiliary system of ions interacting only via a two-body potential. This potential contains the effects of three and higher-body correlations and reproduces the exact pair density of the fully interacting system. There is a systematic self-consistent procedure, similar to density-functional theory,[24,26] which can be used to generate this two-body interatomic potential.

In Sec. II, the effective-action formalism will be introduced and an expression for the effective two-body interatomic potential in terms of statistical fluctuations will be presented. In Sec. III, we show how the formalism yields a simple self-consistent procedure for generating the two-body potentials. The many-body quantum-mechanical properties of the system may be incorporated into the interatomic potential by utilizing the information gathered on the phase space trajectories, via an *ab initio* molecular-dynamics or Monte Carlo calculation.

II. THEORY

Let us define the grand potential $W[\Phi]$,

$$e^{-\beta W[\Phi]}=\mathrm{Tr}\left\{\exp\left[-\beta\left(\hat{H}+\int d\mathbf{r}d\mathbf{r}'\,\Phi(\mathbf{r},\mathbf{r}')\hat{n}_2(\mathbf{r},\mathbf{r}')\right)\right]\right\}, \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the system and $\beta\sim 1/T$. Analogous to the chemical potential, the auxiliary source Φ coupled to the ion pair-density operator $\hat{n}_2$,

$$\hat{n}_2(\mathbf{r},\mathbf{r}')=\sum_{\alpha\neq\alpha'}\delta(\mathbf{r}-\mathbf{x}_\alpha)\delta(\mathbf{r}'-\mathbf{x}_{\alpha'}), \tag{2}$$

generates the statistical average of the ion pair-density operator at a specific temperature

$$\frac{\delta W[\Phi]}{\delta\Phi(\mathbf{x},\mathbf{x}')}=\frac{\mathrm{Tr}\left\{\hat{n}_2(\mathbf{x},\mathbf{x}')\exp\left[-\beta\left(\hat{H}+\int d\mathbf{r}d\mathbf{r}'\,\Phi(\mathbf{r},\mathbf{r}')\hat{n}_2(\mathbf{r},\mathbf{r}')\right)\right]\right\}}{\mathrm{Tr}\left\{\exp\left[-\beta\left(\hat{H}+\int d\mathbf{r}d\mathbf{r}'\,\Phi(\mathbf{r},\mathbf{r}')\hat{n}_2(\mathbf{r},\mathbf{r}')\right)\right]\right\}}=\overline{n}_2(\mathbf{x},\mathbf{x}'). \tag{3}$$

The system can be described in terms of $\overline{n}_2$ as opposed to the external source Φ. This can be performed with a functional Legendre transformation,

$$\Gamma[\overline{n}_2]=W[\Phi]-\int d\mathbf{r}d\mathbf{r}'\,\Phi(\mathbf{r},\mathbf{r}')\overline{n}_2(\mathbf{r},\mathbf{r}'). \tag{4}$$

Here Φ is assumed to be a functional of $\overline{n}_2$ through Eq. (3). Differentiating $\Gamma[\overline{n}_2]$ with respect to $\overline{n}_2$ yields

$$\frac{\delta\Gamma[\overline{n}_2]}{\delta\overline{n}_2(\mathbf{x},\mathbf{x}')}=-\Phi(\mathbf{x},\mathbf{x}'). \tag{5}$$

Our original system is restored by setting the auxiliary source Φ to zero, giving the variational property,

$$\left.\frac{\delta\Gamma[\overline{n}_2]}{\delta\overline{n}_2(\mathbf{x},\mathbf{x}')}\right|_{\overline{n}_2=\overline{n}_2^*}=0 \tag{6}$$

where $\overline{n}_2^*$ represents the exact ion pair density of the fully interacting system. Since, the functional $\Gamma[\overline{n}_2]$ is strictly convex this extremum is also a minimum.[24,26]

In order to proceed farther, we use the inversion method[22,27] to evaluate $\Gamma[\overline{n}_2]$ in Eq. (4). This may be achieved by separating $\hat{H}$ into

$$\hat{H}=\hat{K}+\lambda\hat{U}, \tag{7}$$

where $\hat{K}$ is the kinetic-energy piece, $\hat{U}$ is the internal energy of the system, and λ is a coupling constant that will allow us to expand in powers of U. By expanding the right side of Eq. (4) in a power series in λ,

$$\Phi[\overline{n}_2,\lambda]=\sum_{l=0}\lambda^l\Phi_l[\overline{n}_2], \tag{8}$$

$$W[\Phi,\lambda]=\sum_{l=0}\lambda^l W_l[\Phi], \tag{9}$$

we can get an expression for each order in $\Gamma[\overline{n}_2]$, as

$$\begin{aligned}\Gamma_l[\overline{n}_2]={}&W_l[\Phi_0]+\sum_{k=1}^{l-1}\int d\mathbf{r}d\mathbf{r}'\,\frac{\delta W_{l-k}[\Phi_0]}{\delta\Phi_0(\mathbf{r},\mathbf{r}')}\Phi_k(\mathbf{r},\mathbf{r}')\\&-\delta_{l,0}\int d\mathbf{r}d\mathbf{r}'\,\Phi_0(\mathbf{r},\mathbf{r}')\overline{n}_2(\mathbf{r},\mathbf{r}')\\&+\sum_{m=2}^{l}\frac{1}{m!}\sum_{\substack{k_i\geq 1\\k_1+\cdots+k_m\leq l}}\\&\times\int\prod_{i=1}^{m}d\mathbf{r}_i\,\frac{\delta^m W_{l-(k_1+k_2+\cdots+k_m)}[\Phi_0]}{\delta\Phi_0(\mathbf{r}_1,\mathbf{r}_1')\cdots\delta\Phi_0(\mathbf{r}_m,\mathbf{r}_m')}\\&\times\Phi_{k_1}(\mathbf{r}_1,\mathbf{r}_1')\cdots\Phi_{k_m}(\mathbf{r}_m,\mathbf{r}_m').\end{aligned} \tag{10}$$

The functionals Φ_l can be obtained from Eq. (5) by

$$\frac{\delta\Gamma_l[\overline{n}_2]}{\delta\overline{n}_2(\mathbf{x},\mathbf{x}')}=-\Phi_l(\mathbf{x},\mathbf{x}'). \tag{11}$$

It should be noted here that, because of Eq. (14), Γ_l depends on all $\Phi_{l'}(\mathbf{x},\mathbf{x}')$ with $l'\leq l-1$.

Consider the zeroth-order term,

$$\Gamma_0[\overline{n}_2]=W_0[\Phi_0]-\int d\mathbf{r}d\mathbf{r}'\,\Phi_0(\mathbf{r},\mathbf{r}')\overline{n}_2(\mathbf{r},\mathbf{r}'), \tag{12}$$

which corresponds to the auxiliary system that contains only pair interactions mediated by the potential $\Phi_0(\mathbf{x},\mathbf{x}')$:

$$\begin{aligned}W_0[\Phi_0]=-\frac{1}{\beta}\ln\mathrm{Tr}\Bigg\{\exp\Bigg[-\beta\Bigg(\hat{K}+\int d\mathbf{r}d\mathbf{r}'\,\Phi_0(\mathbf{r},\mathbf{r}')\\\times\hat{n}_2(\mathbf{r},\mathbf{r}')\Bigg)\Bigg]\Bigg\}.\end{aligned} \tag{13}$$

The purpose of the potential $\Phi(\mathbf{x},\mathbf{x}')$ was to generate the expectation value of the ion pair density operator $\overline{n}_2$ in the fully interacting system, therefore, the two-body potential $\Phi_0(\mathbf{x},\mathbf{x}')$ generates the same exact expectation value $\overline{n}_2$ in the auxiliary system described by Eq. (13),

$$\frac{\delta W_0[\Phi_0]}{\delta\Phi_0(\mathbf{x},\mathbf{x}')}=\overline{n}_2(\mathbf{x},\mathbf{x}'). \tag{14}$$

From this point of view, we identify Φ_0 as an effective two-body interatomic potential.

To arrive at an expression for Φ_0, which will yield the correct density of the fully interacting system, we use the variational principle

$$\frac{\delta\Gamma[\overline{n}_2]}{\delta\overline{n}_2(\mathbf{x},x')}=0\Rightarrow\sum_{l=0}\lambda^l\frac{\delta\Gamma_l[\overline{n}_2]}{\delta\overline{n}_2(\mathbf{x},x')}=0. \tag{15}$$

Using Eq. (11) for $l=0$ we have that

$$\Phi_0(\mathbf{x},\mathbf{x}') = -\sum_{l=1} \lambda^l \frac{\delta\Gamma_l[\overline{n_2}]}{\delta\overline{n_2}(\mathbf{x},\mathbf{x}')}, \tag{16}$$

where $\Gamma_l[\overline{n_2}]$ is given by Eq. (10). This expression allows us to systematically calculate Φ_0 to any order. For example, to first order, Φ_0 is given by

$$\Phi_0(\mathbf{x},\mathbf{x}') = \beta \int d\mathbf{r}d\mathbf{r}' \{\overline{Un_2(\mathbf{r},\mathbf{r}')} - \overline{U}\overline{n_2}(\mathbf{r},\mathbf{r}')\} \frac{\delta\Phi_0(\mathbf{r},\mathbf{r}')}{\delta\overline{n_2}(\mathbf{x},\mathbf{x}')}, \tag{17}$$

where $\lambda=1$ restores the original system. The bars stand for statistical averages with respect to Φ_0 in the auxiliary system, that is, for any operator $\hat{O}$,

$$\overline{O} = \frac{\mathrm{Tr}\left\{\hat{O}\exp\left[-\beta\left(\hat{K} + \int d\mathbf{r}d\mathbf{r}'\,\Phi_0(\mathbf{r},\mathbf{r}')\hat{n}_2(\mathbf{r},\mathbf{r}')\right)\right]\right\}}{\mathrm{Tr}\left\{\exp\left[-\beta\left(\hat{K} + \int d\mathbf{r}d\mathbf{r}'\,\Phi_0(\mathbf{r},\mathbf{r}')\hat{n}_2(\mathbf{r},\mathbf{r}')\right)\right]\right\}} \tag{18}$$

and

$$\frac{\delta\Phi_0(\mathbf{r},\mathbf{r}')}{\delta n_2(\mathbf{x},\mathbf{x}')} = [-\beta(\overline{n_2(\mathbf{r},\mathbf{r}')n_2(\mathbf{x},\mathbf{x}')} - \overline{n_2}(\mathbf{r},\mathbf{r}')\overline{n_2}(\mathbf{x},\mathbf{x}'))]^{-1} \tag{19}$$

is the inverse of the fluctuations in $\hat{n}_2$.

One should note from Eq. (17) that if the full interaction is of the pair type, $\hat{U} = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\,U(\mathbf{r},\mathbf{r}')\hat{n}_2(\mathbf{r},\mathbf{r}')$, then $\Phi_o(\mathbf{r},\mathbf{r}') = \frac{1}{2}U(\mathbf{r},\mathbf{r}')$ for the variation of Eq. (15) to be satisfied. It should also be obvious from Eq. (17) that if $\hat{U}$ is of the pair type, then Φ_0 will not depend on thermodynamic quantities such as temperature and density. In this case, even if there are long-range correlations, they are cancelled out by the inverse of the fluctuations in $\overline{n_2}$. However, when the interactions are no longer of the pair type then Φ_0 will depend on the temperature and the density of the system in a nontrivial way through the ensemble averages.

Equation (17) is interestingly similar in form to the effective interatomic potential derived by Carlsson[28] via the maximum entropy method. However, in the maximum entropy method there is no variational scheme to solve for the effective interatomic potential. As will be shown in the next section, this formalism yields a procedure by which to solve for the effective interatomic potential. The procedure does not require the calculation of $\delta\Phi_0/\delta\overline{n_2}$, which is very important from a practical point of view since such a calculation would involve the inversion of large matrices.

It is important to point out that this method generalizes in an easy way to third- and higher-order effective interatomic potentials. For example, to generate three-body effective interatomic potentials, a three-body external source replaces the nonlocal source in Eq. (1) and the ion three-body density operator replaces the ion pair density operator. In this case, the system is described by the three-body density and the rest of the machinery follows as described above.

III. APPLICATION

The appearance of $\delta\Phi_0/\delta\overline{n_2}$ in Eq. (17) seems discouraging, however, it turns out that the solution is rather simple. Equation (17) was arrived at by imposing the variational condition (6). If one follows the arguments leading to Eq. (14), then it is obvious that solving

$$\frac{\delta\tilde{\Gamma}[\Phi_0]}{\delta\Phi_0} = 0, \tag{20}$$

where

$$\tilde{\Gamma}[\Phi_0] = \Gamma[\overline{n_2}[\Phi_0]], \tag{21}$$

is equivalent to solving Eq. (6). In other words, the potential Φ_0, which satisfies Eq. (20), generates the exact pair density $\overline{n_2^*}$, which satisfies Eq. (6). This is due to the one-to-one correspondence between Φ_0 and $\overline{n_2}$. We thus have an alternate variational principle that does not require the calculation of $\delta\Phi_0/\delta\overline{n_2}$ and is therefore easier to solve.

There is now a means of getting at an interatomic potential through a steepest descent self-consistent iterative procedure. In its simplest form, the self-consistent scheme will proceed as follows: (1) Start with a guess at Φ_0. (2) Calculate the necessary fluctuations from Eq. (22) at some temperature using first-principles molecular dynamics, Monte Carlo, or any other appropriate scheme. (3) Calculate the gradient of $\tilde{\Gamma}[\Phi_0]$,

$$\frac{\delta\tilde{\Gamma}[\Phi_0]}{\delta\Phi_0(\mathbf{x},\mathbf{x}')} = -\beta\{\overline{Un_2(\mathbf{x},\mathbf{x}')} - \overline{U}\overline{n_2}(\mathbf{x},\mathbf{x}')\} + \beta\int d\mathbf{r}d\mathbf{r}'\,\Phi_0(\mathbf{r},\mathbf{r}')\{\overline{n_2(\mathbf{r},\mathbf{r}')n_2(\mathbf{x},\mathbf{x}')} - \overline{n_2}(\mathbf{r},\mathbf{r}')\overline{n_2}(\mathbf{x},\mathbf{x}')\}. \tag{22}$$

(4) Update Φ_0 by

$$\Phi_0^{i+1}(\mathbf{x},\mathbf{x}') = \Phi_0^i(\mathbf{x},\mathbf{x}') - \alpha^i \frac{\delta\tilde{\Gamma}[\Phi_0]}{\delta\Phi_0(\mathbf{x},\mathbf{x}')}, \tag{23}$$

where α^i defines the step length in the ith iteration. (5) If not converged, go to step 2.

Another point that makes this method even more attractive computationally is the fact that the dynamics is controlled by Φ_0. That is, we begin with a guess for the interatomic potential Φ_0 and generate configurations with this potential in a Monte Carlo or molecular-dynamics algorithm. For each configuration generated, we can obtain the internal energy from, for example, a first-principles calculation. This is the only quantity that we require externally. Then, each internal energy associated with a specific configuration will be weighted by our guessed potential, as given in Eq. (18), in order to calculate quantities like $\overline{U}$ in Eq. (22). It is the information from the first-principles energetics that tells us how to adjust the potential in order to satisfy Eq. (20). Once $\tilde{\Gamma}$ has been minimized, we have an interatomic potential that could be used in large scale atomistic simulations to calculate various thermodynamic quantities including quantities such as vacancy formation energy and the velocity-velocity correlation function. Of course, the systems in which these quantities are calculated must have physical properties that are closely related to the ones in which they were generated.

We have implemented the above scheme on a Lennard-Jones 6-12 system to see whether it can be recovered from our iterative scheme. Since the calculations in real space would require minimizing on a large number of parameters, we have expanded the effective potential in a set of linearly independent functions so that we can reduce the number of parameters in which to minimize on. Convergence to the correct values is achieved and we continue to examine the stability of the scheme. This simple potential is not a test of the method but rather a test of the stability of the numerical scheme. We are also working on other self-consistent methods that are noted to have better convergence qualities.

IV. DISCUSSION

The motivation behind the work described here is to provide an unambiguous way of defining and computing interatomic potentials. The approach described in this paper provides the necessary tools to study effective interatomic potentials and their dependence on the reference environment in which they were generated. This will allow us to better understand how to package such potentials for use in studying large systems.

One of our immediate goals is to test this method with a potential that has more than a pair term in it. Such a test will allow us to quantify the reproducibility of this method and study the transferability of the effective interatomic potentials. We expect our recovery procedure to fare well because our interatomic potentials contain higher-order correlations built into them. Furthermore, because we have introduced a nonlocal source in the grand potential our effective interatomic potentials contain angular information. This is a very important point and should not be confused with other schemes where the starting point is a pair potential that is a function only of the interatomic distance and may be true for systems at temperatures well above the melting point. Such systems will have translational and rotational symmetry due to the lack of short-range ordering. However, for systems near their melting points, short-range order does persist giving rise to angular dependence.

We have presented this theory for systems that we assume are adequately described by a two-body potential. If this is not the case, then as we have mentioned above, the formalism can be extended to a three-body potential. In this way the system will be more accurately described and the convergence properties of the perturbative expansion will be improved. This is in analogy with density-functional theory where for certain systems a description in terms of the current density or spin density is required because the electron density alone is not sufficient.

We would like to further emphasize that although the idea of generating interatomic potentials from statistical mechanical techniques is not new, the method introduced above leads to new results which have practical advantages over other techniques. By using a single general theory, we get out a systematic definition of what effective interatomic potentials are and how to go about generating them. It is based on statistical mechanical principles and requires the calculation of statistical mechanical averages.

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