

Classical molecular dynamics simulations of crystal lattices with truncated Taylor series-based interatomic potentials



Shrikant Kshirsagar^a, Kranthi K. Mandadapu^{b,c,*}, Panayiotis Papadopoulos^a

^a Department of Mechanical Engineering, University of California, Berkeley, United States

^b Department of Chemical and Biomolecular Engineering, University of California, Berkeley, United States

^c Chemical Sciences Division, Lawrence Berkeley National Laboratory, United States

ARTICLE INFO

Article history:

Received 3 December 2015

Received in revised form 4 March 2016

Accepted 20 March 2016

Available online 29 April 2016

Keywords:

Molecular dynamics

Taylor series

Anharmonicity

Lennard–Jones

Specific heat

Thermal conductivity

ABSTRACT

This article discusses a general method for constructing interatomic potentials based on truncated Taylor series expansion. Specifically, it addresses the scope of application of the method, and demonstrates its practical importance in capturing anharmonicity for a Lennard–Jones solid. In particular, the third-order terms in the truncated potential are shown to accurately approximate the thermal conductivity of the standard interaction Lennard–Jones potential. The paper also describes an efficient algorithm for locating the equilibrium lattice site of an atom in a three-dimensional crystal lattice displaced from its equilibrium position.

Published by Elsevier B.V.

1. Introduction

Molecular Dynamics (MD) is an invaluable computational tool for the bridging of real- and phonon-space analysis techniques. A key advantage of MD over conventional lattice dynamics methods is that it allows for the natural inclusion of anharmonic effects, which are crucial in estimating most thermophysical properties [1].

The application of MD to the quantitative analysis of material response and properties is predicated upon the availability of accurate and efficient potentials. In principle, such potentials are intended to represent interatomic interactions between charged atomic particles. While *ab initio* MD is possible, its scope is extremely limited due to its prohibitive computational cost. Moreover, potential energy surfaces, which are solutions of the electronic Schrödinger equation within the Born–Oppenheimer approximation, are not readily available for most interesting systems. For this reason, one typically relies on a coarse empirical approximation to the true quantum-mechanical potential. Ideally, empirical potentials should have a simple functional form to speed up the evaluation of the forces acting on an atom and also be transferable to

many systems under different loading conditions. Thus, designing a general empirical interatomic potential that approximates the actual (unknown) solution of the Schrödinger equation is a challenging task. In practice, the choice of functional form and parameters is often based on fitting to available experimental data (e.g., equilibrium geometry of stable phases, cohesive energy, elastic moduli, vibrational frequencies, temperatures of the phase transitions, etc.). Unsurprisingly, a potential that is tailored to one set of experimental data for a given material does not necessarily predict with accuracy the response of the same material beyond the narrow scope of this data. For example, if a potential has been designed to reproduce mechanical properties, such as the experimental values of the lattice constant and elastic constants for a crystal phase, one should not expect it to accurately predict thermal transport properties [2].

Recent analytical work has introduced a general method of constructing interatomic potentials based on a truncated Taylor series expansion of the (unknown) potential function of the crystal to a given order [3,4]. The coefficients in the Taylor series may be obtained from a given interatomic potential or through *ab initio* methods, e.g., Density Functional Theory (DFT) calculations. The latter enables the use of interatomic potentials of *ab initio* accuracy for MD simulations, thereby removing one of the major limitations of classical MD, that is, the dependence on purely empirical potentials.

* Corresponding author at: Department of Chemical and Biomolecular Engineering, University of California, Berkeley, United States.

While past work [3,4] focused on the application of the method of truncated Taylor series potential, it did not include any information on the conditions under which this method is applicable. Further, it is not clear how many terms in the Taylor series expansion are required to accurately estimate thermophysical properties of crystal lattices, such as heat capacity and thermal conductivity, the latter of which depends strongly on the degree of anharmonicity of the potential energy. This is particularly important because inclusion of higher-order terms becomes computationally expensive in terms of storage of force constants. In addition, calculating these higher-order force constants for real materials using an *ab initio* method such as DFT is extremely challenging. As a result, most DFT-based methods are currently limited to computation of terms up to the third-order in the Taylor series expansion.

This article expands on the previous work by addressing the range of applicability of the truncated Taylor series expansion method. It also demonstrates the effectiveness of this method in yielding accurate estimates of equilibrium properties such as heat capacity as well as transport properties such as thermal conductivity. The latter affirms the sufficiency of the third-order terms in representing the anharmonicity of crystal lattices, thereby clarifying the importance of the third-order terms in relation to higher-order terms in the potential energy expression of solid crystals. For simplicity, the method is illustrated for an ideal Lennard–Jones (LJ) crystal, as the closed functional form of an LJ solid allows for an accurate determination of the error incurred in the estimation of thermophysical properties by approximating the potential energy with a truncated Taylor series. It must be noted that the predictive capacity of this method is not limited to materials whose potential is explicitly known. Indeed, the real utility of this method is in enabling the use of interatomic potentials of *ab initio* accuracy to make more accurate predictions of thermophysical properties for a range of temperatures.

The article is organized as follows: Section 2 includes an introduction of the fundamental concepts of the truncated Taylor series technique and addresses the conditions under which it may be applied. It also includes a section on the appropriate statistical mechanical expressions for stress and heat flux to be used with the truncated Taylor series potential. Details on the implementation of the method for the case of a Lennard–Jones (LJ) crystal are presented in Section 3. This is followed in Section 4 by a discussion of implementation and a comparison of specific heat and thermal conductivity values using this method and a classical LJ potential. Concluding remarks are offered in Section 6.

2. Theory

2.1. Background on interatomic potentials

In any crystal at finite temperature, the atoms undergo small-amplitude vibrations about their equilibrium lattice positions. This allows the potential energy U to be expanded in a Taylor series about its equilibrium value U_0 in terms of the displacements of the atoms from their equilibrium positions, in the form

$$U = U_0 + \sum_{i;\alpha} \Pi_i^\alpha u_i^\alpha + \frac{1}{2!} \sum_{i,j;\alpha,\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{i,j,k;\alpha,\beta,\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots \quad (1)$$

Here, u denotes the atomic displacement, i, j, k label the different atoms and α, β, γ denote the Cartesian directions. In addition, the force constants (FCs) Π_i^α , $\Phi_{ij}^{\alpha\beta}$, $\Psi_{ijk}^{\alpha\beta\gamma}$ denote respectively the first, second and third partial derivatives of U with respect to the displacements evaluated in the equilibrium configuration. Without loss of generality, the constant term U_0 may be set to 0 by adjusting the

reference level of the potential energy. Furthermore, $\Pi_i^\alpha = 0$ since the equilibrium configuration corresponds to a minimum of the potential energy, Therefore, Eq. (1) may be reduced to

$$U = \frac{1}{2!} \sum_{i,j;\alpha,\beta} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_j^\beta + \frac{1}{3!} \sum_{i,j,k;\alpha,\beta,\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma + \dots \quad (2)$$

The components F_i^α of the total force acting on atom i may be obtained from Eq. (2) as

$$F_i^\alpha = -\frac{\partial U}{\partial u_i^\alpha} = -\sum_{j;\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta - \frac{1}{2!} \sum_{j,k;\beta,\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^\beta u_k^\gamma - \dots \quad (3)$$

For simple systems (e.g., an LJ crystal) the FCs may be calculated analytically. However, for many realistic systems, where highly accurate interatomic potentials are not known, *ab initio* methods based on DFT may be employed to compute the FCs in Eq. (3). In this manner, one may, in principle, construct interatomic potentials of *ab initio* accuracy up to any given order.

2.2. Range of validity

Classical MD simulations are meaningful when the temperature is high enough to render the classical Maxwell–Boltzmann distribution of atomic velocities a good approximation to the corresponding quantum statistical distribution. This is the case when the temperature is at least in the range of the Debye temperature of the material [5, Chapter 23].

For the purpose of accurately estimating many thermophysical properties of materials, including transport properties such as thermal conductivity, it is sufficient to include the effect of anharmonicity of the potential and truncate the Taylor series in Eq. (2) at the third order [4], as discussed in the Introduction. This truncation is predicated on the assumption that the displacement \mathbf{u} of the atoms about their equilibrium positions is “small” in the sense that

$$\max_{ij} (\|\mathbf{u}_i\|, \|\mathbf{u}_j\|) \ll \|\mathbf{R}_j - \mathbf{R}_i\| \equiv \|\mathbf{R}_{ij}\|, \quad (4)$$

for all pairs of atoms (i, j) with equilibrium positions \mathbf{R}_i and \mathbf{R}_j . This truncation also serves the purpose of limiting the computational expense of the resulting MD simulations. For solids, condition (4) is typically satisfied unless the temperature is close to the melting point.

The precise meaning of the inequality condition (4) may be articulated as follows: the temperature of the solid must remain low enough so that no atom displaces so far away from its equilibrium position that the resultant force on it is directed away from that position. Fig. 1 illustrates, for the simple case of a

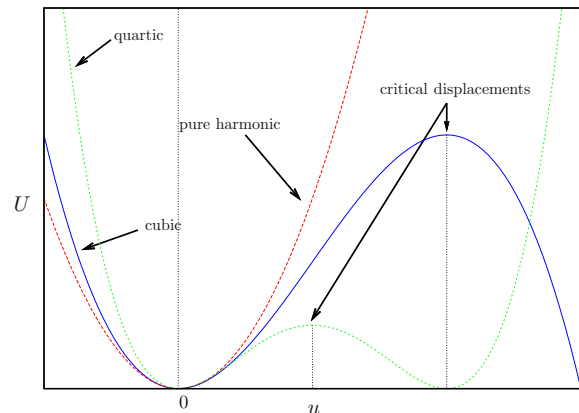


Fig. 1. Schematic depiction of a pure harmonic and anharmonic potentials derived from Taylor series expansion of a general crystal potential energy.

Download English Version:

<https://daneshyari.com/en/article/1559866>

Download Persian Version:

<https://daneshyari.com/article/1559866>

[Daneshyari.com](https://daneshyari.com)