Equilibrium Born-Oppenheimer molecular-dynamics exploration of the lattice thermal conductivity of silicon clathrates

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ABSTRACT

Thermal conductivity plays a critical rôle in determining the performance of a thermoelectric material. However, the computation of thermal conductivity from first principles is a challenging and laborious process, with pitfalls galore. Here, we present results on the calculation of the lattice thermal conductivities of silicon clathrates using a very efficient scheme based on the Einstein relationship for the energy moment, sampled from *ab initio* Born-Oppenheimer molecular dynamics employing linear-scaling Density Functional Theory. Both sI and sII silicon clathrates were studied using systems consisting of up to thousands of atoms. Instead of more glass-like behaviour reported for an empty sII clathrate, the present accurate first-principles calculations predict a thermal-conductivity temperature dependence more in keeping with that of a normal crystal for both clathrates polymorphs, essentially in agreement with a previous theoretical study on sI clathrate. Over the temperature range from 50 to 600 K at ambient pressure, it is found that the sI-structure thermal conductivity is somewhat lower than sII, due probably to the greater proportion of larger tetrakaidecahedral $5^{12}6^2$ cavities (vis-à-vis smaller dodecahedral 5^{12} cages) therein leading to more substantial dissipation of heat-carrying acoustic phonons. However, the absolute conductivity of sII clathrate is itself limited due to the larger number of atoms per unit cell (136 versus 46 for sI) leading to significant zone-edge damping of acoustic phonons.

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1. Introduction

Thermal conductivity (TC) is a fundamental and important property of a material, particularly for thermoelectric applications. Theoretical calculations of thermal conductivity are often performed using equilibrium molecular dynamics (MD) *via* the Green-Kubo relationship. This method requires calculations of heat-flux correlation functions and, therefore, can only be applied to systems that can be described by pairwise interaction potentials. Straightforward extension of GK to first-principles electronic-structure-based MD is not possible. An alternative computational method is to employ the semi-classical Boltzmann transport equation (BTE). In this case, phonon relaxation times may be computed from phonon frequencies, and group velocities determined either from lattice-dynamics calculations or from direct analysis of the MD trajectory. Indeed, such a procedure to provide reliable estimates of phonon relaxation times is painstaking, laborious and prone to technical pitfalls. Recently, it has been recognised that the physics of heat transport is inherently present in equilibrium

MD calculations (whether propagated via pairwise or *N*-body potentials, or potentially via electronic-structure methods) [1]. Furthermore, it was pointed out, in an analogous manner to the relationship between the Einstein relationship and the correlation-function formalism, that the heat current in a solid can be estimated from the energy moments, from which the heat-flux vector can be computed numerically [1]. Indeed, this statistical-mechanics *tour de force* circumvents elegantly direct calculation of the heat-flux correlation function for periodic systems, increasing precision substantially from the Einstein-relationship route, heralding an era of relatively facile TC determination with unprecedented precision regardless of the nature of the potential (pairwise, *N*-body or determined from electronic-structure methods). Here, we apply this Einstein-relationship procedure to predicting the lattice thermal conductivity of silicon clathrates, a class of potentially efficient thermoelectric materials, from Born-Oppenheimer MD simulation of large systems.

Silicon clathrates represent an important class of semiconducting materials, possessing an open-framework crystal structure. Their relatively low lattice thermal conductivity fostered by this open lattice [2,3] has spawned a great interest in potential applications in thermoelectrics [4]. Clathrates resemble the

non-stoichiometric crystalline inclusion compounds of clathrate hydrates, in which a water host lattice encages small guest atoms or molecules in cavities; the clathrate lattice structure adopts identical common polymorph clathrate structure types of sI and sII, with $Pm\bar{3}n$ and $Fd\bar{3}m$ space groups, respectively. In type I clathrate (or hydrate), the unit cell is formed from two small 5^{12} pentagonal dodecahedral cavities and six slightly larger tetrakaidecahedral $5^{12}6^2$ cages, with 46 silicon atoms. A unit cell in sII consists of 136 atoms forming sixteen small 5^{12} cages and eight large hexadecahedral $5^{12}6^4$ cages. These cavities may also accommodate 'rattlers' of guest atoms, e.g., sodium or barium, which, in principle, may serve to reduce conductivity further by 'resonant scattering' of phonons [2–4], along the lines of the phonon glass-electron crystal paradigm [5,6]. In a recent molecular-dynamics (MD) examination of thermal-conduction processes in (inter alia) 'filled' sI, sII, and 'empty' sI methane hydrates [7,8], which observed amorphous, glass-like thermal-conductivity behaviour above ~150 K due to rattling in the filled case and crystal-like behaviour in the empty sI lattice, it has been conjectured [7,8] that both the rigidity of the clathrate's lattice framework as well as guest-host interactions (and resonant scattering) determine TC. Clearly, to rationalise (relatively low) lattice TC in empty clathrates, it is only framework effects (e.g., rigidity) that apply. It was hypothesised [7–9] that the relatively subdued level of resonant scattering observed in practice in some skutterudites [10] and silicon clathrates [11,12], together with low lattice TC in empty silicon clathrate [2] may be explained by the notion of lattice rigidity.

Bearing this intriguing conjecture in mind, it would appear that a detailed ab initio (AI-) MD exploration of the lattice thermal conductivity (TC) of (empty) silicon-clathrate polymorphs is now timely. In this regard, Tang et al. carried out Density Functional Theory (DFT)-Local Density Approximation (LDA) study for sII clathrate, coupled with harmonic lattice dynamics, to estimate Grüneisen parameters, phonon properties, heat capacities and thermal-contraction properties [13]. Härkönen and Karttunen have performed lattice dynamics studies of phonon and thermal-contraction properties of the entire gamut of known clathrate polymorphs [14]. Schopf et al. have made very impressive progress recently, applying force-matching to LDA calculations to fit an angular-dependent potential (ADP) for subsequent use in conjunction with the Green-Kubo approach and ADP-based MD to estimate the thermal conductivity of sI clathrate [15]. However, it is difficult to assess the accuracy of forcefield-based MD, and there was no experimental lattice TC value for sI with which to compare the TC estimate of Schopf et al.; unfortunately, the Ba_8Si_{46} sI TC was over-predicted by a factor of ~3.5 using ADP-based MD/GK [15], and there was no comparison for empty sII clathrate TC with respect to the experimental data of Nolas et al. [2]. Therefore, the present study seeks to apply AI-MD to estimate lattice TC properties for both sI and sII, and compare to available sII experimental data. Although de Koker [16], Thomas et al. [17] and Hellman and Abrikosov [18] have made substantial progress in recent years in the application of phonon spectral energy density [16,17] and fitting second- and third-order force [18] to the analysis of AI-MD, here we use the very recent Einstein relationship of the energy moment of Kinaci et al. [1] applied to Born-Oppenheimer (BO-) MD to compute TC without any model approximation, and retrieve the full arsenal of GK [19,20] via numerical differentiation of the energy moment to obtain the heat-flux vector [1].

2. Methodology

Owing to potential size and electrostatics dependence of the thermal conductivity in clathrates and clathrates [15,21,22], systems containing 1, $2 \times 2 \times 2$ and $3 \times 3 \times 3$ sI and $1 \times 1 \times 1$ and

$2 \times 2 \times 2$ of sII were simulated (containing, respectively, 46, 368 and 1242 atoms for sI and 136 and 1088 for sII). The initial lattice parameters were obtained from experimental densities of Ramachandran et al. [23]. Given the comparatively large system sizes, linear-scaling DFT [24] permits the accurate study of larger system sizes to thousands of atoms [25–28], and we used the ONETEP package for BO-MD [29,30], which exploits "near-sightedness" of the density matrix [24]. The Perdew-Burke-Ernzerhof (PBE) functional [31,32] of the generalised gradient approximation (GGA) was used. Non-orthogonal generalised Wannier functions (NGWFs), localised in real space at four per atom, were used to represent the density matrix, with truncation radii of 6 Å. The NGWFs were expanded in a basis of periodic cardinal sine (psinc) functions [25] with a kinetic energy cut-off of 800 eV, and a norm-conserving pseudopotential was used. During 1 ps NVT equilibration runs at each desired temperature, the lattice constant was varied until the stress yielded a pressure of approximately 1 bar. Approximately 20 ps of BO-MD was carried out with a time step of 1 fs over the 50–600 K temperature range at ambient pressure (with three independent runs for each condition following Maxwell-Boltzmann velocity randomisation [33]) using velocity-Verlet propagation [33], including Pulay forces [34,35], in the NVT ensemble with relatively light Nosé-Hoover coupling (with period of 0.5 fs) [36]. For the larger systems featuring over a thousand atoms (the $3 \times 3 \times 3$ sI and $2 \times 2 \times 2$ sII), computational expediency motivated the use of the time-reversible scheme of re-using NGWF history for efficient self-consistent field (SCF) calculation, in which the BO Lagrangian is extended by additional degrees of freedom representing initial NGWF guesses [37,38]. The energy moment $\mathbf{R}$ was computed, as detailed by Kinaci et al. [1],

$$\mathbf{R} = \sum_{i=1}^{n} \mathbf{r}_i \int_0^t \mathbf{f}_i \cdot \mathbf{v}_i \mathrm{d}t \tag{1}$$

and the Einstein relationship used to determine TC, without any model approximation. Here, $\mathbf{r}_i$ refers to the position of each atom i (taking care to correct for periodic-image 'jumps' across the lattice imposed by periodic boundary conditions, in view of the non-convective nature of the system and calculation approach), whilst $\mathbf{f}_i$ and $\mathbf{v}_i$ refer to the force on i and its velocity, respectively. $\mathbf{f}_i$ was computed from the Hellman-Feynman approach within the strictures of DFT, including Pulay forces [34,35], as available during propagation of BO-MD.

To validate the energy-moment approach, BO-MD simulations were performed on crystalline and amorphous silicon at 298 K using 64-atom systems. The Vienna Ab initio Simulation Package (VASP 5.2) [39,40] was used for NVT BO-MD simulations. The face-centered cubic structure of crystalline silicon was optimised at ambient pressure prior to MD. The amorphous silicon structure was constructed by melting crystalline silicon followed by slow cooling. The projected augmented wave (PAW) method was used to represent electron-ion interactions [40], in conjunction with PBE exchange. After relaxation, 100 ps of production NVT MD was performed with a 1 fs time step. The temporal energy moments were computed from the corresponding positions and forces of the MD trajectory (cf. Eq. (1)). Numerical differentiation of the energy moment $\mathbf{R}$ was carried out to obtain the heat-flux vector $\mathbf{J}$, via $\mathbf{J} = \mathrm{d}\mathbf{R}/\mathrm{d}t$ [1]. Using this method, the thermal conductivity for crystalline silicon was found to be ~123 ± 8 W m^{-1} K^{-1}: this value is in good agreement with the result of 145 W m^{-1} K^{-1} of Jain and McGaughey [41] using the same PBE/PAW approach at ambient temperature for a larger system, and the experimental value of 153 W m^{-1} K^{-1} [41]. The discrepancy may be attributed to the well-known sensitivity of thermal conductivity to system size [21], as discussed previously. For amorphous silicon, the TC was estimated to be 0.98 ± 0.11 W m^{-1} K^{-1}, in agreement with the