Effects of cutoff functions of Tersoff potentials on molecular dynamics simulations of thermal transport

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Abstract
Past molecular dynamics studies of thermal transport have predominantly used Stillinger–Weber potentials. As materials continuously shrink, their properties increasingly depend on defect and surface effects. Unfortunately, Stillinger–Weber potentials are best used for diamond-cubic-like bulk crystals. They cannot represent the energies of many metastable phases, nor can they accurately predict the energetics of defective and surface regions. To study nanostructured materials, where these regions can dominate thermal transport, the accuracy of Tersoff potentials in representing these structures is more desirable. Based upon an analysis of thermal transport in a GaN system, we demonstrate that the cutoff function of the existing Tersoff potentials may lead to problems in determining the thermal conductivity. To remedy this issue, improved cutoff schemes are proposed and evaluated.

(Some figures in this article are in colour only in the electronic version)
a few [14–16] used Tersoff/Brenner types of potentials. Recently, we published a series of papers on MD simulations of thermal transport in GaN [10–12]. While these studies employed a Stillinger–Weber GaN potential [29, 30], significant efforts were also made to explore the Tersoff GaN potential [31] during the course of the work. With this particular parameterization of the Tersoff potential, we found it difficult to ensure energy conservation during a ‘constant energy’ MD simulation unless the time step size was significantly reduced from the 0.001 ps we normally used for other potentials, and the thermal conductivities obtained were more than one order of magnitude smaller than the values we would otherwise obtain from the Stillinger–Weber potential [29, 30].

From a physics point of view, Stillinger–Weber potentials are empirically designed for diamond-cubic-like bulk environment and they do not work well in defective and surface regions. For instance, the angular term in Stillinger–Weber potential is essentially a positive parabolic energy penalty for deviations of bond angles from the tetrahedral angle. As this positive energy term is repulsive, any structures with non-tetrahedral bond angles would have longer bond lengths than those in diamond-cubic-like crystals or dimers. This is not always true in reality. Furthermore, under the condition that the diamond-cubic-like crystal has the lowest energy, the angular term in Stillinger–Weber potential must be constrained above a certain level. As a result the potential cannot correctly describe the trend of energies in many other metastable phases. Tersoff potentials, on the other hand, inherit the quantum mechanics-based bond order concept [32–34]. They are therefore well suited for treating defects and surfaces. In particular, we note that the GaN Tersoff potential [31] was carefully parameterized using cohesive energies, atomic volumes, defect properties, melting temperatures and solubility limits of a variety of stable and metastable phases. Its fidelity has also been validated in MD simulations of vapor deposition that correctly showed the crystalline growth of the lowest energy phase [35].

The energy non-conservation and the abnormally low thermal conductivity are not transparent problems. Intuitively, they cannot be attributed directly to the potential format. Resolving these significant problems is important to the materials modeling community, as it will both promote the use of Tersoff potential in future MD simulations and improve the atomistic simulations of semiconductor systems. Understanding the abnormally low thermal conductivity predicted by the GaN Tersoff [31] potential may also result in the discovery of a new thermal scattering phenomenon that can be utilized to engineer thermal conductivity of materials. This paper will address these issues.

Following the format of the GaN paper [31], the Tersoff potential is expressed as

$$E = \sum_i \sum_{j>i} [\phi_{ij}(r_{ij}) - \tilde{B}_{ij} \cdot \psi_{ij}(r_{ij})]$$

(1)

where the bond order $\tilde{B}_{ij}$ is defined as

$$\tilde{B}_{ij} = \sqrt{1 + \chi_{ij} + \sqrt{1 + \chi_{ji}} \over 2}$$

(2)

with the local angular-dependent variable $\chi_{ij}$ calculated as

$$\chi_{ij} = \sum_{k \neq i, j} f_{ik}(r_{ik}) \cdot g_{ik}(\theta_{jik}) \cdot \exp[2\mu_{ik}(r_{ij} - r_{ik})].$$

(3)

Equations (1) and (3) involve three pair functions $\phi_{ij}$, $\psi_{ij}$ and $f_{ik}$ representing, respectively, the $i−j$ repulsion, the $i−j$ attraction and the $i−k$ cutoff (in the angularly dependent $\chi$ term). Here the symbol $r_{ij}$ represents the usual relative distance between atoms $i$ and $j$ and $\theta_{jik}$ is the angle between the triplet $jik$ with $i$ at its vertex. The cutoff function $f$ is taken to be a
sinoidal spline:

\[
f_{ij}(r_{ij}) = \begin{cases} 
1, & r_{ij} \leq R_{ij} - D_{ij} \\
\frac{1}{2} \frac{1}{2} \sin \left( \frac{\pi (r_{ij} - R_{ij})}{2D_{ij}} \right), & R_{ij} - D_{ij} < r_{ij} \leq R_{ij} + D_{ij} \\
0, & r_{ij} > R_{ij} + D_{ij}.
\end{cases}
\] 

(4)

Here \( r_s = R - D \) is the cutoff starting radius and \( r_c = R + D \) is the cutoff distance at which the point interactions go to zero. To impose the cutoff of the \( \phi \) and \( \psi \) functions, the Tersoff potentials simply define \( \phi_{ij}(r_{ij}) = f_{ij}(r_{ij}) \cdot V^R_{ij}(r_{ij}) \) and \( \psi_{ij}(r_{ij}) = f_{ij}(r_{ij}) \cdot V^A_{ij}(r_{ij}) \), where \( V^R(r) \) and \( V^A(r) \) are two exponentially decaying functions \([26–28, 31]\) that are not subject to the discussions here. Due to the use of equation (4), the three functions \( \phi \), \( \psi \) and \( f \) have continuous values and the first derivatives, but their second derivatives abruptly change at the junction points \( r_s \) and \( r_c \). This is contrary to the Stillinger–Weber potentials whose high order derivatives are always continuous.

By dividing the \( r_s-r_c \) range evenly into three sections with two internal points \( r_1, r_2 \in (r_s, r_c) \), a cubic spline cutoff approach can be used to remove the discontinuous second-derivatives of the \( \phi \), \( \psi \) and \( f \) functions. Using \( \phi \) as an example, we can write,

\[
\phi_{ij}(r_{ij}) = \begin{cases} 
V^R_{ij}(r_{ij}), & r_{ij} \leq r_{s,ij} \\
\sum_{n=0}^{n=2} \frac{V^{(n)}_{ij}(r_{s,ij})}{n!}(r_{ij} - r_{s,ij})^n + a_3(r_{ij} - r_{s,ij})^3, & r_{s,ij} < r_{ij} < r_{1,ij} \\
\sum_{n=0}^{n=3} b_n(r_{ij} - r_{2,ij})^n, & r_{1,ij} \leq r_{ij} \leq r_{2,ij} \\
c_3(r_{ij} - r_{c,ij})^3, & r_{2,ij} < r_{ij} \leq r_{c,ij} \\
0, & r_{ij} > r_{c,ij}.
\end{cases}
\] 

(5)

equation (5) is continuous up to the second derivative at \( r_s \) and \( r_c \). It involves six parameters \( a_3, b_0-b_3 \) and \( c_3 \) that can be solved by requiring the values as well as the first and the second derivatives to be continuous at the two added junction points \( r_1 \) and \( r_2 \). For an example comparison, the modified and unmodified \( \phi_{GaGa} - \psi_{GaGa} \) and \( f_{GaGa} \) functions are shown as the black and red dashed lines, respectively, in figure 1. Note that equating the bond energy with \( \phi_{GaGa} - \psi_{GaGa} \) implies a bond order of \( \bar{B}_{GaGa} = 1 \). This does not represent the real scenario but is sufficient for the discussion here. It can be seen that the modified potential does not significantly differ from the original potential. In fact, equation (5) should be applicable to any existing Tersoff potentials without a need to re-parametrize. This cubic spline cutoff scheme has been implemented in the MD simulator LAMMPS [36].

We suspect that the discontinuous second-derivatives are likely to be the source of the problems with the Tersoff potentials. To explore this, we calculate the bond energy \( \phi_{ij}(r_{ij}) - \bar{B}_{ij} \cdot \psi_{ij} \) as a function of bond length \( r_{ij} \) for different bonds \( ij = GaN, GaGa, NN \) using a fixed bond order \( \bar{B}_{ij} \) estimated from the equilibrium wurtzite GaN and equation (2). The results are shown in figure 2 using black, long red dashed and short blue dashed curves to represent, respectively, the Ga–N, Ga–Ga and N–N interactions. The radial distribution of atoms was also determined from a GaN wurtzite equilibrated at a temperature of 300 K, and the result is included in figure 2 as the shaded area. Figure 2 indicates that the third- or higher-nearest neighbors do not contribute to material properties as the corresponding radial distributions do not fall within ranges of any of the three interaction curves. Similarly, the N–N interaction does not contribute to properties because the N–N energy curve only overlaps with the nearest neighbor radial distribution which is between Ga and N. In fact, only the nearest
Figure 1. GaGa pair interaction functions ($\phi_{\text{GaGa}}$, $\psi_{\text{GaGa}}$, and $f_{\text{GaGa}}$).

Figure 2. Different pair interactions in wurtzite GaN crystal

neighbor Ga–N and the second-nearest neighbor Ga–Ga interactions contribute to properties. However, because the cutoff starting point $r_{c, \text{GaN}} (=2.7 \text{ Å} [31])$ is well above the upper limit of the first radial distribution peak, how the Ga–N interaction is truncated has no effect on properties. Clearly, the effect due to a discontinuous second-derivative, if any, must come from the Ga–Ga interaction.

In addition to the cubic spline cutoff modification, figure 2 suggests numerous other ways to remove or mitigate the discontinuous second-derivatives of the functions. As indicated by the circle in the figure, the Ga–Ga interaction has an insignificant contribution to the energy near the cutoff distance. In fact, there is no energy contribution at all at 0 K because the second neighbor (Ga–Ga) distribution would then reduce to a single line at approximately the peak position outside of the Ga–Ga interaction range. This means that neglecting the Ga–Ga interactions would only cause a negligible energy change and would not alter the relative phase stabilities. Similarly, a reduction of the cutoff starting point $r_{c, \text{GaGa}}$ (at a constant $r_{c, \text{GaGa}}$ cutoff distance) also does not significantly change the energy. A reduced $r_{c, \text{GaGa}}$, however, increases
Table 1. Results of temperature drift $\Delta T$ (K) and thermal conductivity $\kappa$ (W K$^{-1}$ m$^{-1}$) obtained from MD simulations over a 10 ns period using different combinations of GaGa cutoff function, GaGa cutoff starting point $r_{c,\text{GaGa}}$ (Å), reneighboring and time step sizes $d_{t}$ (ps).

| Schemes | A     | B     | C     | D     | E     | F     |
|---------|-------|-------|-------|-------|-------|-------|
| Cutoff function | Sinoidal | Sinoidal | Sinoidal | Sinoidal | None ($f \equiv 1$) | Cubic spline |
| $r_{c,\text{GaGa}}$ | 2.72  | 2.72  | 2.32  | 2.72  | N/A   | 2.72  |
| Reneighboring | Yes   | Yes   | Yes   | No    | No    | Yes   |
| $d_{t}$ | 0.0010 | 0.0005 | 0.0010 | 0.0010 | 0.0010 | 0.0010 |
| $\Delta T$ | 27    | 3     | 23    | 3     | $<1$  | $<1$  |
| $\kappa$ | $5.4 \pm 0.1$ | $6.2 \pm 0.04$ | $19.0 \pm 0.3$ | $13.9 \pm 0.1$ | $14.6 \pm 0.1$ | $12.1 \pm 0.1$ |

the cutoff transition range and therefore can be used to reduce magnitude of the second-derivative near the transition. When no Ga–Ga interactions are considered, the only remaining interactions are between Ga and N, whose radial distribution is near the Ga–N interaction energy minimum which is far away from the cutoff distance. Consequently, the Ga–N neighbors do not change during thermal transport simulations where no phase transformation occurs. Hence, we can initialize the Ga–N neighbors at the start of simulations and not perform reneighboring calculations during the rest of simulations. It should be noted that the purpose of cutoff in atomistic simulations is to define the neighbor lists. When the correct Ga–N neighbors are initialized and are not recalculated, there is really no need to apply the cutoff algorithm to the Ga–N interaction functions. Hence, we can simply set $f_{\text{GaN}} \equiv 1$ to remove the discontinuous second-derivatives of the Ga–N interactions.

Based upon these observations, several schemes (as illustrated in table 1) are designed to test the effects of the discontinuous second-derivatives of the Ga–Ga functions near their cutoffs: A, the original potential without modifications (time step size 0.0010 ps unless indicated otherwise); B, the original potential simulated at a reduced time step size of 0.0005 ps; C, a reduced $r_{c,\text{GaGa}}$ value to reduce the second-derivatives (and hence the extent of the discontinuity) of the Ga–Ga pair functions at $r_{c,\text{GaGa}}$; D, with only Ga–N interactions that are initialized without reneighboring; E, same as D with a further condition of $f_{\text{GaN}} \equiv 1$, and F, the cubic spline modification of the potential with other conditions the same as in scheme A. All these schemes were explored in thermal transport simulations.

The ‘direct method’ MD approach [10–12] was employed to calculate the thermal conductivities of GaN wurtzite crystal along the [0001] direction. The computational system used for the simulations is shown in figure 3, where the red and blue colors indicate, respectively, the hot and cold regions. The systems are 136, 50 and 6 cells in the $x$-, $y$- and $z$-directions, corresponding approximately to a $708 \times 276 \times 18\text{Å}^3$ material volume. Four voids are evenly created between the hot and the cold regions by removing six Ga and six N atoms as shown in figure 3. All simulations were carried out at a temperature of 300 K using periodic boundary conditions in all three coordinate directions. The simulated system therefore represents an infinite GaN crystal containing uniform defects. Thermal conductivities were averaged over 10 ns. The resulting temperature drift $\Delta T$ (energy drift) and thermal conductivity are compared as a function of simulation conditions in table 1 for various schemes.

Table 1 indicates that all simulations that involve discontinuous second-derivatives of the Ga–Ga interactions, such as schemes A and C, have an energy conservation problem at a time step size of 0.0010 ps (the temperature drift during the 10 ns simulation is $\Delta T > 20$ K). This finding agrees well with the previous result [37] that non-smoothness of the potential functions causes energy drift. Reducing the time step to 0.0005 ps can significantly improve the energy conservation, as in scheme B. The thermal conductivities obtained from simulations with large
energy drift may not be accurate. Nonetheless, table 1 clearly shows that the finite second-
derivatives of the Ga–Ga functions at the cutoff distance also contribute to the abnormally
low thermal conductivities, as with schemes A and B. Reducing the second-derivatives by
reducing the cutoff starting point \( r_{s,\text{GaGa}} \) increases thermal conductivity, as in scheme C.
All simulations that remove the discontinuous second-derivatives, schemes D–E, have good
energy conservation and reasonably large thermal conductivities. Note that both schemes D
and E ignore the Ga–Ga interactions and use the Ga–N neighbors determined at the start of
simulations. Scheme E further assumes \( f_{\text{GaN}}(r_{\text{GaN}}) \equiv 1 \). However, this change of the Ga–N
cutoff does not have a significant effect because the Ga–N spacing of the crystal is well below
the cutoff starting point \( r_{s,\text{GaN}} \) as mentioned above. As a result, schemes D and E are expected
to produce similar results. Because the reduction in thermal conductivity due to non-smooth
cutoff function is an unphysical artifact, and because scheme E does not apply any cutoff
modifications, the good agreement between the results of schemes E and F strongly validates
the cubic spline cutoff approach.

In summary, we discovered that the existing Tersoff potential formats do not always
produce the correct results due to the discontinuous second-derivatives of the cutoff functions.
This problem can be solved by applying the cubic spline cutoff modifications. In some thermal
transport simulations where atomic neighbors do not change, one can initialize the neighbor
lists at the start of simulations and not perform reneighboring. This is not only computationally
efficient, but also eliminates the need to apply the cutoff algorithms to the functions and thereby
removes the problem of the Tersoff potential. When the discontinuous second-derivatives come
from an insignificant second neighbor interaction, the problem can be simply solved by ignoring
that interaction. Finally, we discovered the fundamental fact that the finite second-derivatives
of the interaction between atoms near the cutoff distance can significantly change the thermal
conductivity of the lattice. This observation calls further studies of the fidelity of interatomic
potentials where the cutoff distance is often chosen rather than determined from fundamental
insights. \textit{Ab initio} studies to remedy this issue should enable MD to reliably predict properties,
such as thermal conductivity, at the nanoscale and promote new material discovery.

The discontinuous second derivatives lead to jumps in elastic constants. This would
prevent realistic studies of mechanical properties of semiconductors (in particular, the plastic

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**Figure 3.** Atomistic configuration for MD simulations.
deformation and the dislocation behavior). The proposed modification of the Tersoff potentials can therefore impact many problems including the mechanical properties of materials.

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