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Heat transport through a solid-solid junction: the interface as an autonomous thermodynamic system

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We perform computational experiments using nonequilibrium molecular dynamics simulations, showing that the interface between two solid materials can be described as an autonomous thermodynamic system. We verify local equilibrium and give support to Gibbs description of the interface also away from global equilibrium. In doing so, we reconcile the common formulation of the thermal boundary resistance as the ratio between the temperature discontinuity at the interface and the heat flux with a more rigorous derivation from nonequilibrium thermodynamics. We also show that thermal boundary resistance of a junction between two pure solid materials can be regarded as an interface property, depending solely on the interface temperature, as implicitly assumed in some widely used continuum models, such as the acoustic mismatch model. Thermal rectification can be understood on the basis of different interface temperatures for the two flow directions.

Introduction—The autonomous or self-contained thermodynamic nature of the interface has long been a topic of discussion.1–4 This is not surprising as the interface between two material phases ceases to exist in the absence of the materials that make it up. While some studies5,6 support the idea that it is a two-dimensional thermodynamic system1,4, others reject it2,3.

The discussion originates in the formulation first made by Gibbs.7 He proposed that the interface was an autonomous thermodynamic system, when described by excess densities, and that thermodynamic relations can be written for these variables. The interface is autonomous in the sense that all its properties are unequivocally determined by such local variables. The description was developed for equilibrium conditions, but later it has been used successfully out of global equilibrium as well8 to model, in particular, the liquid-vapor phase transitions.5,6,9 In nonequilibrium, these assumptions imply that an interface can sustain a temperature, which is both compatible with its thermodynamic definition and is a local (i.e. different from the surroundings) property that follows from its autonomous character. All excess densities of an autonomous interface will depend on this temperature alone and not on the temperatures in the adjacent phases. The autonomous nature of a solid-solid interface provides a rigorous justification for tabulating the Kapitza resistance as a junction property, which is independent of the applied thermal bias and where the relevant variable is the interface temperature.

The reluctance in adopting this picture, rather than conceptual, was mostly due to the difficulty of measuring such an interface temperature. Accordingly, in nonequilibrium conditions it was natural to assign to the interface an average temperature, hiding its autonomous nature and hinting that its properties depend on the overall thermodynamic conditions, e.g. the thermal bias, rather than on its own thermodynamic variables.

Numerical simulations have supported the formulation of Gibbs, which implies local equilibrium at the interface.5,6,9 Support has also been obtained from diffuse interface theories10–12. However, all these results were obtained for the liquid-vapor interface. In this paper we provide evidence that this property also holds for solid-solid interfaces by performing a controlled set of computational experiments of the Si/Ge interface, namely the prototypical semiconductor heterojunction in many nanotechnology applications of current interest. In doing so, we also give a
rigorous theoretical foundation to the common formulation of the Kapitza resistance.

Computational methods—We perform nonequilibrium molecular-dynamics (NEMD) simulations of a Si/Ge interface with a bond-order potential\(^1\).\(^2\).\(^3\) We use a timestep of 0.7 fs and run the simulation for 5.25 ns. The nonequilibrium condition when performing our investigation is achieved by connecting the ends of the computational cell with two Nosé-Hoover thermostats at interface temperature,\(^4\)\(^5\)\(^6\)\(^7\)\(^8\) the interface temperature, \(T_{\text{I}}\), along the heat transport direction \((T_H = 500 \text{ K} \text{ and } T_C = 100 \text{ K}, \text{in this case})\). The interface temperature, \(T_{\text{I}}\), is calculated from the average kinetic energy \(H\), with \(T = 200 \text{ K}\), in this case). The \(T_{\text{I}}\) and \(T_{\text{S}}\) (see text), are estimated extrapolating the linear fit of \(T(x)\) in the Si and Ge region up to the interface boundaries (see the magnified views of the insets).

This procedure gives an estimate of the interface thickness of 16.6 Å, i.e. 12 layers of the diamond lattice. It also leads to the interesting result that the interface region lies entirely in the Si half of the system, i.e. the last Ge bilayer, right before the heterojunction, has the same structural features as bulk Ge and relaxation effects all take place in Si. Therefore, the chemical interface (where the chemical identity of the atoms that occupy the zinc-blende lat-
tic changes, dashed line in Figure 1b) and the thermodynamic interface (defined through the variation of a suitable property $P(x)$, shaded area in Figure 1b) do not match. Notice that this conclusion is not general and depends on the specific conditions (choice of lattice parameter, constant volume), that nevertheless reflect a possible experimental situation, of these calculations. Yet, these results show that such a decoupling is at least in principle possible.

Thermodynamic autonomy of the interface—Once the interface has been defined, we verify the hypothesis of local equilibrium. We have studied the internal energy $U^s$ at different thermodynamic conditions. We first run a series of equilibrium MD runs. In order to allow comparisons with nonequilibrium calculations we use the NEMD configuration illustrated in Figure 1a also at equilibrium, but set both thermostats at the same temperature. Next, we perform a similar set of calculations, but this time we apply a $\Delta T = 200$ K. The values of the mean temperature $(T_H + T_C)/2$ are then set the same as in the equilibrium calculations. In both cases we calculate the average internal energy of the interface

$$
\langle U^s \rangle = \langle E^s_k \rangle + \langle E^s_p \rangle,
$$

where $E^s_k$ and $E^s_p$ are obtained by summing the kinetic and potential energy per atom over all the atoms that we established belonged to the interface region, thus obtaining the kinetic and potential energy of the interface region. The temperature of the interface region, $T^s$, is determined from the average kinetic energy $\langle E^s_k \rangle$ of the atoms therein as:

$$
T^s = \frac{2\langle E^s_k \rangle}{k_B};
$$

where $k_B$ is the Boltzmann constant (of course in the equilibrium calculations $T^s = T_H = T_C$, within numerical errors). All time averages are taken over the last 3 ns of the simulation.

In Figure 2 we plot the internal energy of the interface as a function of the interface temperature for both the equilibrium and nonequilibrium conditions, which result in qualitative and quantitative agreement, within the accuracy of the calculation. This result strongly supports the view of the solid-solid interface as an autonomous thermodynamic system. Our calculations show that no matter what the overall thermodynamic conditions of the system are –and we tested this hypothesis in conditions as different as equilibrium and nonequilibrium–, the internal energy of the interface only depends on its temperature and not on the overall thermal bias conditions. These results also support that local equilibrium, one of the underlying assumption of nonequilibrium thermodynamics and thermodynamic modeling at large, holds. In other words, one can define a small enough piece of material which can be considered in equilibrium and assign to it a temperature, obeying $T = (\partial U/\partial S)_{V,N}$, even in considerably out-of-equilibrium conditions. In what follows, to further test the hypothesis of local equilibrium, we calculate the thermal boundary resistance under different nonequilibrium conditions. Notice that the derivative of the internal energy with respect to the temperature at constant volume is the heat capacity, i.e. the amount of heat required to change the temperature of a given system by one degree. We can therefore define and calculate the heat capacity of the interface as

$$
C^s = \left( \frac{\partial U^s}{\partial T} \right)_V
$$

We found that the heat capacity of the interface was the same at equilibrium and nonequilibrium, and for the system studied, we estimated $C^s$ to be 29 J K$^{-1}$ mol$^{-1}$. We performed the same calculation, but restricting this time to a region of Si sufficiently far from the interface and the cell boundary, obtaining a value of 33 J K$^{-1}$ mol$^{-1}$. We understand that both values of the heat capacity calculated at the interface and far away from it are not accurate since the present simulations are missing of any quantum features, as instead included in the more precise prediction of Ref. 19 for bulk–like Si. Furthermore, the structure here investigated structure has, by construction, a pseudomorphic lattice meaning that both Si and Ge slabs are in fact under strain, so that the actual value of their heat capacity is expected to differ from the bulk–like one. Nevertheless, we remark that their relative difference (as large as 15 %) is in fact meaningful, carrying an important qualitative information, namely: the additional proof of the thermodynamic autonomy of the interface with respect to the neighboring bulk–like regions.

If the interface is an autonomous thermodynamic system, its thermal resistance can be treated as a system variable that depends solely on the interface temperature. To calculate the interface thermal resistance we need the temperature discontinuity across the the interface. We then extrapolate the linear dependence of $T(x)$ in the Si and Ge regions to the interface boundaries and obtain $T^i$ and $T^0$ (see Figure 1c); the linear fits are performed conveniently far from the thermostats and from the interface. The

![Fig. 3](image-url)
resulting force-flux relations read

\[ \Delta T^g = T^0 - T^i, \]  

and the heat flux is the Kapitza resistance and it is customary used as a measure of interface thermal resistance. The present nonequilibrium thermodynamics approach proceeds along a different path. At the interface, the entropy production associated to the transport of heat is

\[ \sigma^s = J^i \left( \frac{1}{T^i} - \frac{1}{T^0} \right) + J^0 \left( \frac{1}{T^0} - \frac{1}{T^s} \right) \]  

where \( J^i (J^0) \) is the heat flux entering (exiting) the interface and \( T^i \) and \( T^0 \) are the temperatures of the boundaries of the interface, as defined in Figure 1c. In the stationary state, \( J^i = J^0 = J \) and the resulting force-flux relations read

\[ \frac{1}{T^0} - \frac{1}{T^s} = r^{s,0} J \]  

\[ \frac{1}{T^0} - \frac{1}{T^i} = r^{s,i} J \]  

The coefficients in these equations are interface resistivity coefficients and have the dimensionality of a resistivity of a bulk homogeneous phase times a length (the interface thickness); \( r^{s,i} (r^{s,0}) \) is the resistivity to heat flux between the material on the left (right) side and the interface. It follows that the interface thermal resistance is

\[ r^s = r^{s,i} + r^{s,0} = \frac{1}{J} \left( \frac{1}{T^0} - \frac{1}{T^i} \right) + \frac{1}{J} \left( \frac{1}{T^0} - \frac{1}{T^s} \right) = \frac{1}{J} \left( \frac{1}{T^0} - \frac{1}{T^i} \right) \]  

emphasizing the fact that the actual thermal driving force is the inverse temperature.

We use Eq. 8 to calculate \( r^s \) for different nonequilibrium conditions. We apply \( \Delta T \) of 200 and 400 K and a reverse bias of \( \Delta T = -400 \) K. In each case we consider several average temperatures \( \langle T_H + T_C \rangle / 2 \) in order to sample many interface temperatures, \( T^s \). In Figure 3 we plot \( r^s \) as a function of \( T^s \). This plot shows clearly that \( r^s \) indeed depends only on \( T^s \); irrespective of the overall thermodynamic conditions, each value of \( T^s \) is associated with a corresponding \( r^s \). We make the same plot for the more common Kapitza resistance, \( r^K = \Delta T^s / J \) (bottom panel), and obtain very similar conclusions. Indeed, \( r^K \) can be obtained, to lowest order in the temperature difference, from \( r^s \) by multiplying it by \( (T^s)^2 \), as shown in Table 1.

If one writes Fourier's law, in its integral form, for the entire system

\[ \Delta T = -\Delta T^\text{tot} S J \]  

where \( \Delta T^\text{tot} \) is the total thermal resistance and \( S \) the cross-section, and compares it with Eq. 8, it is straightforward to show that

\[ \Delta T^s = \frac{r^{s,i} T^0}{\Delta T^\text{tot} S} \Delta T \]  

Hence the temperature discontinuity, \( \Delta T^s \), should be linear in the applied temperature bias, \( \Delta T \), for a given value of the interface temperature \( T^s \) (notice that \( T^i T^0 \sim (T^s)^2 \)). To this purpose we performed an additional series of NEMD calculations where, for \( \langle T_H + T_C \rangle / 2 = 300 \) K, we varied \( \Delta T = T_H - T_C \). The results, displayed in Figure 4b, confirmed that also this additional condition was nicely fulfilled. Notice, however, that the interface temperature is only approximately constant throughout the investigated range of \( \Delta T \) (see Figure 4a); consequently, \( \Delta T^s \) exhibits a small, but non negligible superlinearly.

We conclude our study with a final remark on thermal rectification, i.e. the preferential flow of heat in one direction. Previous

| Table 1 | Comparison between the Kapitza resistance and the renormalized interface thermal resistance of Eq. 8 in the case of \( \Delta T = 200 \) K. A renormalization factor of \( T^s T^0 \) would yield strictly the same values. Here we use \( T^s T^0 \), a more consistent choice within the formalism of nonequilibrium thermodynamics, which gives only an approximate, (in general \( T^s \neq \sqrt{T^s T^0} \)) though excellent, agreement (unless at the lowest temperature studied). Resistance units are \( m^2KW^{-1} \).

<table>
<thead>
<tr>
<th>( T^s )</th>
<th>( r^K )</th>
<th>( r^s (T^s)^2 )</th>
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<tr>
<td>47.7</td>
<td>1.2 \cdot 10^{-8}</td>
<td>3.0 \cdot 10^{-8}</td>
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<td>101.4</td>
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<td>8.7 \cdot 10^{-9}</td>
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<td>2.4 \cdot 10^{-9}</td>
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<td>700.2</td>
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works have demonstrated that the different temperature dependence of the thermal conductivity of two materials result in some degree of rectification when they are brought together and form a junction.\textsuperscript{15,25–28} The role of the interface itself in the rectification, however, has been thus far neglected. Here we have shown that \( r \) depends univocally on \( T^s \). The latter, nonetheless, depends on how the overall thermal bias \( T_H - T_C \) is split between the two materials: the more their thermal resistances differ, the farther \( T^s \) will be from the mean temperature \( (T_H + T_C)/2 \) (see Ref.\textsuperscript{28} for a simple model). Consequently, a different temperature dependence of the thermal conductivity of the two materials results also in a different \( T^s \) upon forward or reverse bias. This is clearly seen in Figure 4, where we have plotted \( T^s \) also in the case of a reverse bias \( \Delta T = -400 \text{ K} \): the interface temperatures are different, if compared with the case of forward bias \( \Delta T = 400 \text{ K} \), thus the interface resistances \( r^s(T^s) \) will also be different and will contribute to the thermal rectification.

**Conclusions**—In summary, we have shown that a Si-Ge solid-solid interface can be regarded as an autonomous thermodynamic system, with interface properties that depend solely on the interface temperature. On the basis of structural relaxation it was possible to identify the interfacial region as a 16.6 Å thick layer in the Si adjacent to the chemical junction between Si and Ge. The interface temperature is obtained from the average kinetic energy of this region. The results follow from application of the thermodynamic driving forces as defined in nonequilibrium thermodynamics for this region. We have also shown that the commonly used Kapitza resistance can be related to the thermal boundary resistance rigorously derived within nonequilibrium thermodynamics.

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**References**

16. In this case study we do not consider dislocations or other line defects that often form in Si/Ge interfaces to release the stress induced by the lattice mismatch. Atomically abrupt, defect-free Si/Ge interfaces, however, can be obtained in nanowire axial junctions.\textsuperscript{29,30}