Kapitza thermal conductance at the interface between Lennard-Jones crystals using non-equilibrium molecular dynamics simulations

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Abstract. We characterize the thermal Kapitza conductance between Lennard-Jones solids using non-equilibrium molecular dynamics simulations. We consider a series of perfect interfaces between mass-mismatched solids. We show that both the acoustic mismatch model (AMM) and the diffuse mismatch model (DMM) fail to predict the interfacial conductance even for large acoustic mismatched solids. This poor agreement may be explained by the use of equilibrium distributions of phonons in the expression of the conductance. On the other hand, we show that an extension of AMM taking into account the out-of-equilibrium phonon distribution on both sides of the interface leads to a good agreement with the simulation results, even for interfaces between almost similar materials. This opens the way to understand interfacial heat transport across real semi-conductors and dielectrics.

1. Introduction
The existence of a finite thermal conductance between two dissimilar materials is known since the pioneering experimental work of Kapitza on superfluid Helium/solid interfaces [1]. The interface between solids at room temperature has been considered in the seventies [2]. More recently, with the development of fast thermal techniques, the Kapitza conductance between a number of metal/dielectrics solids has been characterized [3, 4]. Despite decades of research, there is no theoretical framework which succeeds in predicting the value of the Kapitza conductance between dissimilar solids. Among the most popular models, let us mention the acoustic mismatch model (AMM) [5] and the Diffuse Mismatch Model (DMM) introduced by Swartz and Pohl [2]. In the former, phonons are assumed to behave as plane waves experiencing specular transmission at the interface, while in the DMM, phonon scattering is supposed to be governed by the density of states mismatch between the two solids [6]. Both models fail to predict the thermal conductance measured experimentally [3]. Note however, that both models assume perfect interfaces where only elastic phonon-phonon scattering take place. In reality, the interface between solids is far from being perfect and several phenomena may occur such as scattering.
from asperities, interface dislocations or scattering due to plasticity generated by the lattice mismatch between the two solids. Hence, it is highly desirable to obtain information about the Kapitza conductance of perfect interfaces. Molecular dynamics (MD) simulations have established oneself in the determination of the Kapitza conductance between Lennard-Jones solids [7], Silicium/Germanium interfaces [8] and also between metals and dielectrics [9]. To the best of our knowledge, there is no theoretical model which provides a good description of the MD data of the simplest LJ solids. In particular, the DMM model has been found to underestimate the conductance between Lennard-Jones solids [7]. In this article, we show that both the AMM and the DMM models can not predict the Kapitza conductance obtained with MD, even for large acoustic impedance ratios between the solids. We propose a generalisation of the AMM model inspired by Simons [10] which accounts for the out-of-equilibrium distribution of phonons on both sides of the interface. We show that this model provides a good description of the interfacial conductance between Lennard-Jones solids over a broad range of acoustic impedance ratios. Finally, we quantify the relative importance of out of equilibrium phonons in the value of the thermal conductance.

2. Theory
In this section, we present two expressions of the interfacial Kapitza conductance: one which is commonly used and which assumes the phonon on both sides of the interface to follow Bose-Einstein distribution; and the other one proposed by Simons where the phonons have a non-equilibrium distribution consistent with the flux flowing across the interface. We then discuss how to calculate this latter conductance if we assume both elastic and specular scattering at the interface.

Consider the interface between two media 1 and 2. The interfacial conductance $G$ between these two media is defined in terms of the ratio

$$G = \frac{q}{T_2 - T_1}$$

where $q$ is the heat flux flowing across the interface from medium 2 to 1, and $T_i$ denotes the temperature of the medium $i$ in the vicinity of the interface. The interfacial conductance eq. 1 can be related to the phonon distribution in each medium if the heat flux $q$ is expressed in terms of transmitted phonons:

$$q = \frac{1}{V} \sum_{j,k_x>0} v_{1x}(j, \vec{k}) \hbar \omega(j, \vec{k}) f_1(j, \vec{k}) t_{12}(j, \vec{k})$$

$$- \frac{1}{V} \sum_{j,k_x<0} v_{2x}(j, \vec{k}) \hbar \omega(j, \vec{k}) f_2(j, \vec{k}) t_{21}(j, \vec{k})$$

where $V$ is the volume of each medium supposed to be equal, $v_{ix}$ is the group velocity in medium $i$ projected along the direction $x$ normal to the interface, $f_i$ is the mode dependant phonon distribution function in medium $i$, $t_{ij}(\vec{k})$ is the wave vector dependant transmittivity from medium $i$ to medium $j$, and the sums runs over all polarizations indexed by $j$, and over wavevectors in the first Brillouin zone corresponding to phonons crossing the interface. A common assumption in the calculation of the interfacial conductance is to assume that the phonon population may be described by the Bose-Einstein equilibrium distribution $f_{eq}$:

$$f_{eq}(\omega, T) = \frac{1}{\exp (\hbar \omega / k_B T) - 1}$$
at the temperature $T_i$ in the vicinity of the interface. It is then a simple exercise to show that under this assumption, the interfacial conductance is given by the Landauer formula [11]:

$$G_L = \frac{1}{V} \sum_{j,k_x>0} \hbar \omega v_{1x} t_{12} \frac{\partial f_{eq}}{\partial T}$$

(4)

where in the derivation we have used the fact that when the two materials are at the same temperature the interfacial flux in eq. 2 vanishes. The expression above is widely used in the context of transport phenomena, and serves as a basis for the AMM and DMM models. Its limitations are well known [10, 13, 12, 8]: equation 4 predicts a finite conductance when the two materials are identical, i.e. when $\forall \vec{k} \ t_{12}(\vec{k}) = 1$, which is of course unphysical: for an interface between identical media, the temperature drop should vanish whatever the flux $q$, leading to an infinite conductance. Obviously, the problem is related to the use of two equilibrium distribution functions in the flux eq. 2. The previously mentioned paradox may be solved using the actual distribution function consistent with the interfacial heat flow $q$. Following Simons [10], we write the out-of-equilibrium phonon distribution in the medium $i$:

$$f_i(\vec{r}) = f_{eq}(T(\vec{r})) + \delta f_i(\vec{r})$$

(5)

where $T(\vec{r})$ is the local value of the temperature and $\delta f_i$ is given by [14]:

$$\delta f_i(\vec{r}) = -\tau_i \frac{\partial f_{eq}}{\partial T} \vec{v}_i \cdot \vec{\nabla} T = \tau_i \frac{\partial f_{eq}}{\partial T} |\vec{v}_i| \cos \theta \frac{q}{\lambda_i}$$

(6)

where $\tau_i$ is the mode dependent phonon relaxation time, $\theta$ is the angle between the phonon propagation axis and the direction of the temperature gradient. We have assumed in the last equation that the flux $q$ is proportional to the temperature gradient with the conductivity $\lambda_i$ describing diffuse transport in the medium. Introducing the excess phonon population in the expression of the interfacial flux eq. 2, it is easy to obtain the expression of the interfacial conductance first derived by Simons:

$$G_{neq} = G_L \frac{1 - \beta_{12} - \beta_{21}}{1 - \beta_{12} - \beta_{21}}$$

(7)

where we have introduced the fractions:

$$\beta_{12} = \frac{1}{V} \sum_{j,k_x>0} \tau_{1x} v_{1x}^2 \hbar \omega \frac{\partial f_{eq}}{\partial T} t_{12}/\lambda_1$$

(8)

and a similar equation for $\beta_{21}$. The physical signification of $\beta_{12}$ is clear: it is a measure of the fraction of the energy flux flowing across the interface which is transmitted. These coefficients vary typically between 0 when all the phonon modes of medium 1 are reflected by the interface to 1/2 when all the modes of medium 1 are transmitted. In particular, the latter expression solves the paradox of the thermal resistance between similar materials since the interfacial conductance eq. 7 diverges to infinity as can been shown using the Peierls expression for the thermal conductivity [14]:

$$\lambda_1 = \frac{1}{V} \sum_{j,\vec{k}} \tau_1 v_{1x}^2 \hbar \omega \frac{\partial f_{eq}}{\partial T} \rightarrow \beta_{12}(t_{12} = 1) = \frac{1}{2}$$

(9)

where the last equality applies to the case of an interface which transmits all the phonon modes, $\forall (j, \vec{k}), t_{12} = 1$. Thus at least, eq. 7 solves the paradox of the conductance of
the interface between identical materials. In the following, it will be useful to express the interfacial conductance in terms of the vibrational density of states $g_{i,j}(\omega)$ of the material $i$ and characterizing the polarization state $j$:

$$G_L = \frac{1}{2} \sum_j \int_0^{\omega_{\text{max}}} g_{1,j}(\omega)|v_1(\omega)|^2 \hbar \omega \frac{\partial f_{\text{eq}}}{\partial T} \int_0^{\pi/2} t_{12}(\omega, \theta) \cos \theta d\theta d\omega$$  \hspace{1cm} (10)$$

and the fraction $\beta_{12}$ becomes:

$$\beta_{12} = \frac{\frac{1}{2} \sum_j \int_0^{\omega_{\text{max}}} g_{1,j}(\omega)|v_1(\omega)|^2 \hbar \omega \frac{\partial f_{\text{eq}}}{\partial T} \int_0^{\pi/2} t_{12}(\omega, \theta) \cos \theta d\theta d\omega}{\frac{1}{2} \sum_j \int_0^{\omega_{D1}} g_{1,j}(\omega)|v_1(\omega)|^2 \hbar \omega \frac{\partial f_{\text{eq}}}{\partial T} d\omega}$$  \hspace{1cm} (11)$$

where $\omega_{D1}$ is the Debye frequency of medium 1 and $\omega_{\text{max}}$ is the maximal frequency transmitted by the interface and its value will be discussed below. A similar expression holds for $\beta_{21}$. So far the two expressions derived for the interfacial conductance are general and we have not made any assumption on the transmission coefficient. The value of the transmission coefficient depends on the model retained to describe phonon scattering at the interface. In the AMM model, the transmission coefficient is assumed to depend only on the two acoustic impedances $Z_i = \rho_i c_i$ given by the product of the mass density $\rho_i$ by the acoustic velocity in the medium $i$. The transmission coefficient writes then [5]:

$$t_{12}(\mu_1) = \frac{4Z_1 Z_2 \mu_1 \mu_2}{(Z_1 \mu_1 + Z_2 \mu_2)^3}$$  \hspace{1cm} (12)$$

where we have introduced the cosine of the incident angle $\mu_i = \cos \theta_i$. This expression is assumed to hold when the incident angle is smaller than the critical angle corresponding to total reflection, and for phonon frequencies smaller than the Debye frequency of the softer solid. On the other hand, in the DMM model the transmission coefficient depends only on the relative density of states $g_i(\omega)$ of the two materials:

$$t_{12}(\omega) = \frac{c_2 g_2(\omega)}{c_1 g_1(\omega) + c_2 g_2(\omega)}$$  \hspace{1cm} (13)$$

and again we assume that $t_{12}$ vanishes above the Debye frequency of the softer solid. In all the following, we will assume Debye solids with a DOS given by [20]: $g(\omega) = \omega^2/2\pi^2c^3$ for the three polarization states relevant to bulk crystals in three dimensions. We will also assume classical solids as it is the regime relevant to molecular dynamics simulations. The AMM and DMM conductances of classical Debye solids are thus respectively given by:

$$G_L^{\text{AMM}} = \frac{3}{2} n_1 k_B c_1 \left( \frac{c_2}{c_1} \right)^3 \int_0^{1} t_{12}(\mu_1) \mu_1 d\mu_1$$  \hspace{1cm} (14)

where $n_1$ denotes the number density of medium 1 and $t_{12}(\mu_1)$ is given by eq.12. We have supposed without loss of generality that the medium 2 has the lowest Debye frequency. As for the DMM conductance, we have:

$$G_L^{\text{DMM}} = \frac{3}{2} n_1 k_B \frac{c_2^3}{c_1^2 + c_2^2}$$  \hspace{1cm} (15)$$

To obtain tractable expressions for the non-equilibrium eq. 7 which depends on the fractions eq. 11, we need to do an hypothesis regarding the frequency-dependance of the phonon
lifetime $\tau_i(\omega)$. The simplest is to assume that the phonon lifetime $\tau_i$ is controlled by Umklapp processes obeying Callaway model [16]:

$$
\tau_i(\omega) = A_i \omega^{-2} \tag{16}
$$

where $A_i$ is a material parameter which depends on the temperature. Note that with the previous functional form eq. 16, the conductance is independent of the constant $A_i$. Under this assumption, the non-equilibrium conductances take the form:

$$
G_{\text{neq}}^{\text{AMM}} = \frac{G_{L}^{\text{AMM}}}{1 - \frac{3}{2}(c_2/c_1)\left(\int_0^1 \mu_1^2 t_{12}(\mu_1)d\mu_1 + \frac{c_2}{c_1} \int_0^1 \mu_1 \mu_2 t_{12}(\mu_1)d\mu_1\right)} \tag{17}
$$

where $\mu_2$ denotes the cosine of the refracted angle [17]; $\mu_2 = \sqrt{1 - (c_2/c_1)^2(1 - \mu_1^2)}$. For the sake of comparison, we will also consider the non-equilibrium conductance predicted using the DMM transmission coefficient (eq. 13):

$$
G_{\text{neq}}^{\text{DMM}} = \frac{G_{L}^{\text{DMM}}}{1 - (c_1 c_2 + c_2^2)/2(c_1^2 + c_2^2)} \tag{18}
$$

In the following, we will compare the four expressions for the interfacial conductance eq (14), (15), (17) and (18) to the results of molecular dynamics simulations of heat transport across the interface between Lennard-Jones solids.

3. Molecular dynamics simulations

We compare now the previous theoretical predictions to the results of non-equilibrium molecular dynamics (NEMD) simulations. To this end, we have considered a series of mass-mismatched Lennard-Jones FCC solids having the same lattice constant. A sketch of the simulation cell studied is shown in fig. 1. The cross section of the simulation cell is $6a_0 \times 6a_0$ where $a_0 \simeq 1.58\sigma$ is the lattice parameter of the FCC LJ solids at the temperature considered $T = 40$ K and $\sigma$ is the atomic diameter. The interface is oriented along the crystallographic [100] direction. Periodic boundary conditions are used in all spatial directions parallel to the interface. All the atoms of the system interact through a Lennard-Jones potential $V_{LJ}(r) = 4\epsilon ((\sigma/r)^{12} - (\sigma/r)^6)$ truncated at a distance $2.5\sigma$. A single set of energy $\epsilon$ and diameter $\sigma$ characterizes the interatomic interaction potential. As a result, the two solids have the same lattice constant $a_0$, and the interface may be considered perfect. To introduce an acoustic mismatch between the two solids, we have considered a mass mismatch between the masses of the atoms of the

![Figure 1](image-url). Snapshot of the configuration studied. Red and blue atoms denote respectively the cold and hot thermostats. The temperature profile across the system is schematically depicted with black solid lines.
two solids, characterized by the mass ratio $m_r = m_2/m_1$, which will take typical values between 1 and 6. From now on, we will use real units where $\epsilon = 1.67 \times 10^{-21}$ J; $\sigma = 3.4 \times 10^{-10}$ m and $m_1 = 6.63 \times 10^{-26}$ kg, where these different values have been chosen to represent solid Argon. With this choice of units, the unit of interfacial conductance is $G = k_B/\tau \sigma^2 \approx 56$ MW $\cdot$ m$^{-2}$ $\cdot$ K$^{-1}$.

The different systems have been equilibrated at the final temperature $T = 40$ K as explained in previous publications [18, 21] except that we have imposed a vanishing pressure. Once the system is equilibrated, we impose a thermal flux in the direction perpendicular to the interface by thermostatting in each medium the two monolayers of atoms the most remote from the central interface at the respective temperatures $T_C = 36.4$ K and $T_H = 43.6$ K. The interfacial conductance $G$ is obtained as the ratio of the steady-state heat flux $q$ over the temperature jump $\Delta T$ measured at the interface as schematically shown in fig. 1. In particular, we have considered long enough simulation cells so that the measured conductance was found to be independent of the length of the system, as shown in fig. 2.

In figure 3, we compare the results of the NEMD simulations to the different theoretical predictions discussed in the previous section. The total length of the system has been chosen to be $L = 200a_0$ and we have made the mass ratio varying between 1.2 and 6 so as to change the acoustic impedance ratio between the two solids $Z_1/Z_2 = \sqrt{m_1/m_2}$. In evaluating the different theoretical expressions eqs. 15, 14, 17 and 18, we have used a mean sound velocity $c_1 = 1250$ m $\cdot$ s$^{-1}$ in the harder solid and a number density $n = 2.57 \times 10^{28}$ m$^{-1}$. Figure 3 shows that both the AMM and DMM models fail to predict the interfacial conductance measured in molecular simulations. This is true when the acoustic impedance ratio $Z_1/Z_2 \rightarrow 1$ as the two models predict a finite conductance while the measured conductance should diverge as we explained previously.

However, even when the acoustic ratio is $\approx 0.7$ a value which is typical of the Si/Ge interface, the theoretical models are wrong by a factor larger than 3! When the acoustic ratio is $\approx 0.8$, which is typical of the interface between AlAs and AsGa, the AMM and the DMM underpredict the real conductance by a factor 5 and 9 respectively! On the other hand, the conductance eq. 17 seems to give a good description of the measured conductance over a broad range of acoustic impedance ratio. Hence, we conclude that it is very important to correctly account for the actual out-of-equilibrium phonon distribution across the interface, but not only! Indeed, we also conclude from figure 3 that the DMM generalisation eq. 18 also fails to describe the MD data. Fortuitously, this equation predicts values of the conductance close to the classical AMM model. Indeed the generalisation eq. (18) suffers from the same limitations as the original DMM model, as the conductance is predicted to remain finite (and equal to $2G_L^{DMM}(Z_1/Z_2 = 1) = G_L^{AMM}(Z_1/Z_2 = 1)$) when the two materials are identical. This
is related to the fact that the transmission coefficient eq. 13 tends towards 1/2 in this limit. We think that indeed interfacial phonon scattering is rather specular and not diffuse in our MD simulations, because the majority of incoming phonons that are transmitted by the interface have a wavelength larger than the interfacial roughness which in our case is atomic. Finally, the relative importance of the deviation of the phonon distribution from the local equilibrium distribution may be discussed considering the two fractions $\beta_{12}$ and $\beta_{21}$ which are a measure of the out-of-equilibrium phonons which participate in the conductance. The evolution of $\beta_{12}$ and $\beta_{21}$ with the impedance ratio may be understood using the following qualitative arguments valid asymptotically for very dissimilar materials: consider first phonons coming from medium 1 and travelling across the interface. Because medium 1 is harder than medium 2, only a fraction $(c_1/c_2)^3$ of modes will be transmitted. However the modes transmitted have very large wavelengths and according to Callaway’s model very long relaxation times and the total contribution to $\beta_{12}$ will be $\propto (c_2/c_1)$. Now we have to account for the transmission coefficient $t_{12} \sim 4Z_1Z_2/(Z_1 + Z_2)^2 \sim Z_1/Z_2$ which yields the scaling $\beta_{12} \sim (Z_1/Z_2)^2$. When it comes to evaluate $\beta_{21}$, we need to consider phonons coming from the medium 2. As this medium is softer than medium 1, all the incoming modes are transmitted. However, the phonons effectively transmitted should have an incidence angle smaller than the critical angle $\arcsin(c_2/c_1)$. The corresponding fraction is $\sim (c_1/c_2)^2$, and since the transmission $t_{12} \sim Z_1/Z_2$, it comes: $\beta_{21} \sim (Z_1/Z_2)^3$. From this analysis, we conclude that both fractions are increasing functions of the impedance ratio. When the two materials are highly dissimilar, these two fractions are negligible not only because there are relatively few modes which are transmitted across the interface, but also because the transmission coefficient is very small. We conclude also that $\beta_{21}$ is smaller than $\beta_{12}$ essentially because of the restriction on the angle of incidence which severely hinders the transmission of phonons from the soft to the hard material.

4. Conclusion

In conclusion, we have compared the results of molecular dynamics simulations regarding the Kapitza conductance at the interface between Lennard-Jones solids. The advantage of the Lennard-Jones solids is the relative simplicity of the potential, the fast computational times as compared to semi-conductors which require the use of many body potentials, and the absence of optical modes. This allows to assess in a simple way the generic character of interfacial heat transport across solids. We have considered a series of mass-mismatched LJ solids with identical lattice constant so as to make the acoustic impedance ratio vary and to consider a atomically “perfect” interface. Results of the non-equilibrium simulations have been compared to different
theoretical expressions eq. (14), (15) (17) and eq. (18). We have shown that the classical AMM and DMM models fail to predict the conductance measured in the simulations for impedance ratios typical of real interfaces. This discrepancies have been traced back to the assumption made in these models that phonons on both sides of the interface have the equilibrium distribution corresponding to the local temperature. On the other hand, the non-equilibrium generalisation eq. (17) inspired by Simons yield to a good agreement with the MD data over a broad range of impedance ratio. The reasons for this good description are twofold: first, the interfacial scattering is supposed to be specular. Indeed, the generalisation eq. 18 which assumes diffuse scattering describes as poorly the MD data as the AMM model. Secondly, it is accounted for the out-of-equilibrium distribution of phonons close to the interface; the relative importance of these out-of-equilibrium phonons have been measured by the two fractions \( \beta_{12} \) and \( \beta_{21} \), which are found to be negligible only for highly dissimilar materials, and we have found that they are somehow dominated by the phonons travelling from the hard to the soft material.

As a perspective of this work, we may consider the case of more realistic interfaces, such as Si/Ge. We need also to elucidate the link between the conductance measured in non-equilibrium simulations and the one obtained in equilibrium simulations [22, 21].

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