Thermodiffusion in liquid binary alloys computed from molecular-dynamics simulation and the Green-Kubo formalism

William C. Tucker and Patrick K. Schelling¹

¹*Advanced Material Processing and Analysis Center and Department of Physics*

University of Central Florida

4000 Central Florida Blvd.

Orlando, FL 32816

Phone: (1)-407-882-1016

Fax: (1)-407-823-5112

email: patrick.schelling@ucf.edu

Abstract

In the presence of a temperature gradient, the components of a binary liquid tend to segregate. This phenomena, generally referred to as thermodiffusion or the Soret effect, is usually quantified by the heat of transport. We report heat of transport values Q_c^* for NiAl and NiCu melts computed using molecular-dynamics simulation and the Green-Kubo formalism. Thermal conductivities are also reported. To develop a clear picture of the phenomena, we determined contributions to Q_c^* due to the convective and virial components of the heat current, which were then compared to the related terms in the partial enthalpy. It is shown that the contribution to Q_c^* from the convective component of the heat current is comparable to the average energy of the diffusing atoms, differing by an amount comparable to the activation energy for diffusion. The contribution to Q_c^* from the virial heat current is closely related to the pressure-volume term $p_c\Omega$ in the partial enthalpy. It is established that the virial heat current plays a dominant role in determining the sign of the reduced heat of transport $Q_c^{*'} = Q_c^* - h_c$. By comparing results obtained with different empirical potentials, a trend emerges. Specifically, it is found that the sign of the reduced heat of transport is correlated with the sign of the partial pressure associated with the low-mass component. It is also shown that two different empirical potentials for the NiAl system give vastly different results for $Q_c^{*'}$. The results indicate that in developing a potential that might accurately predict $Q_c^{*'}$, the distribution of the partial energy and partial pressure between the two components is critical. Based on these observations, it would appear that existing empirical potentials may not be able to generate reliable predictions for $Q_c^{*'}$ without additional validation.

I. INTRODUCTION

Thermodiffusion is the coupled transport of heat and matter [1]. In the presence of a temperature gradient, the components of a liquid binary alloy are expected to segregate, with one component driven towards the hot end of the system, and the other component driven towards the cold end. At present, there is no simple picture that suggests which component is driven towards higher temperatures, and which is driven towards lower temperatures. In the case of binary organic fluids, there is now an extensive and systematic experimental database[2]. Analysis of the experimental results has demonstrated that the behavior of the components in a binary fluid can be characteristic in terms of a pure component property, termed the thermophobicity[2, 3]. However, there is only a limited understanding of the physical nature of thermophobicity. Similarly, significant computational work has been reported, primarily to describe thermodiffusion in binary liquids modeled using Lennard-Jones potentials[4–6]. In the case of metallic binary liquids, an equivalent experimental database does not yet exist, and computational studies are also fairly rare. In principle, one approach towards developing a database for liquid binary alloys is using molecular-dynamics simulation. In addition, this approach might serve as an additional way to develop a more clear physical understanding of thermodiffusion. The reduced heat of transport $Q_c^{*'}$ is essentially the heat transported by the species during interdiffusion. This is an important quantity as it is proportional to the ratio of the concentration gradient to the temperature gradient, both of which can be measured. In terms of the driving force for the segregation, it determines the entropy generated as interdiffusion occurs in the presence of a temperature gradient.

In liquids, or any system that where diffusion happens rapidly on a molecular-dynamics (MD) timescale, the Green-Kubo method[7, 8] has been shown to be a reliable approach. Recently, Evteev and coworkers [9] have used Green-Kubo to compute thermodiffusion in $\text{Ni}_{0.50}\text{Al}_{0.50}$ liquids. In their study, by computing the relevant heat of transport, they were able to show that segregation in the presence of a temperature gradient should proceed with Ni driven in the direction of increasing temperature, and Al driven in the direction of decreasing temperature.

In this paper, we report computed transport coefficients using embedded-atom model (EAM) potentials for NiAl and NiCu binary liquid alloys. Details of the approach closely follow the work reported in Ref. [9]. From the transport coefficients, the reduced heat of transport $Q_c^{*'}$ was determined. Two different empirical potentials for NiAl are found to result in very different predictions. This provides insight into what aspects of the empirical potentials might be correlated with thermodiffusion and the value of $Q_c^{*'}$, including the sign which determines direction of the

segregation. From analysis of the results, a consistent picture emerges. First, in agreement with previous studies[10, 11], it was found that the convective and virial contributions to Q_c^* are closely related to corresponding terms in the partial enthalpy h_c . Second, it was found that there is a close connection between the sign of the partial pressure of the low-mass component, which should dominate the heat and particle transport, and the sign of Q_c^{*} . Finally, the sensitivity of Q_c^{*} to specific details of the empirical potential and the resulting partial pressures of the components suggests a way forward for the development of empirical potentials that might accurately predict thermodiffusion phenomena, and moreover provides a hypothesis on the physical interpretation of thermophobicity.

II. APPROACH

The most important theoretical details developed in Ref. [9] are reprised here. We first consider a binary system with N_1 particles of component 1, and N_2 particles belonging to component 2. The particle currents $\vec{J}_1$ and $\vec{J}_2$ are defined in a center-of-mass reference frame by,

$$\vec{J}_1 = \sum_{i=1}^{N_1} \vec{v}_i \quad (1)$$

$$\vec{J}_2 = \sum_{i=N_1+1}^{N_1+N_2} \vec{v}_i \quad (2)$$

Here we have assumed that atoms $i = 1$ to $i = N_1$ are component 1, and atoms $i = N_1 + 1$ to $i = N_1 + N_2$ are component 2. In a center-of-mass reference frame, the two mass currents are not independent. If the atoms of component 1 each have mass m_1 , and the atoms of component 2 each have mass m_2 , then the two particle currents satisfy, by conservation of momentum,

$$m_1 \vec{J}_1 + m_2 \vec{J}_2 = 0 \quad (3)$$

The fact that the two particle currents are not independent suggests that we should instead consider the interparticle current defined by,

$$\vec{J}_c = c_2 \vec{J}_1 - c_1 \vec{J}_2 \quad (4)$$

where $c_1 = N_1/N$, $c_2 = N_2/N$, and N is the total number of particles $N = N_1 + N_2$. This choice of $\vec{J}_c$ can easily be shown to be invariant with respect to the choice of reference frame. Given

this definition, we can see that $\vec{J}_c$ can also be related to $\vec{J}_1$ or $\vec{J}_2$ determined in the center-of-mass reference frame using,

$$\vec{J}_c = \frac{\bar{m}}{m_2} \vec{J}_1 = -\frac{\bar{m}}{m_1} \vec{J}_2 \quad (5)$$

where $\bar{m} = c_1 m_1 + c_2 m_2$. Thus, knowledge of $\vec{J}_c$ is enough to determine the particle currents in any reference frame, including $\vec{J}_1$ and $\vec{J}_2$ as defined in the center-of-mass reference frame.

In the results presented here, we use embedded-atom model (EAM) potentials[12]. The total energy for an EAM potential is given by,

$$E_{tot} = \frac{1}{2} \sum_i m_i \vec{v}_i \cdot \vec{v}_i + \sum_i F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{\langle ij \rangle} \phi_{ij}(r_{ij}) \quad (6)$$

where the local charge density at site i is,

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij}) \quad (7)$$

In order to obtain a microscopic definition for the heat current, it is necessary to define a local energy associated with each site. The local energy is chosen to be given by,

$$\epsilon_i = \frac{1}{2} m_i \vec{v}_i \cdot \vec{v}_i + F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) \quad (8)$$

In this expression, the embedding energy $F_i(\bar{\rho}_i)$ is assigned to site i , and the pair-potential energy $\phi_{ij}(r_{ij})$ is evenly divided between sites i and j . As explained in Ref. [13], this choice is not at all unique. However, given this choice, the energy current is given by[13],

$$\vec{J}_q = \sum_i \epsilon_i \vec{v}_i - \frac{1}{2} \sum_i \sum_{j \neq i} \vec{r}_{ij} \left[\frac{1}{r} \frac{d\phi_{ij}}{dr} \right]_{r=r_{ij}} (\vec{r}_{ij} \cdot \vec{v}_i) - \sum_i \sum_{j \neq i} \vec{r}_{ij} \left[\frac{dF_j}{d\rho} \right]_{\rho=\bar{\rho}_j} \left[\frac{1}{r} \frac{d\rho}{dr} \right]_{r=r_{ij}} (\vec{r}_{ij} \cdot \vec{v}_i) \quad (9)$$

which is also consistent with the expression used in Ref. [9]. The heat current $\vec{J}_q$ is comprised of convective and virial contributions, with $\vec{J}_q = \vec{J}_q^{(conv)} + \vec{J}_q^{(vir)}$, with these defined by,

$$\vec{J}_q^{(conv)} = \sum_i \epsilon_i \vec{v}_i \quad (10)$$

$$\vec{J}_q^{(vir)} = -\frac{1}{2} \sum_i \sum_{j \neq i} \vec{r}_{ij} \left[\frac{1}{r} \frac{d\phi_{ij}}{dr} \right]_{r=r_{ij}} (\vec{r}_{ij} \cdot \vec{v}_i) - \sum_i \sum_{j \neq i} \vec{r}_{ij} \left[\frac{dF_j}{d\rho} \right]_{\rho=\bar{\rho}_j} \left[\frac{1}{r} \frac{d\rho}{dr} \right]_{r=r_{ij}} (\vec{r}_{ij} \cdot \vec{v}_i) \quad (11)$$

The formal transport theory is defined in terms of $\vec{J}_c$, the energy current $\vec{J}_q$, and the driving forces $\vec{X}_c$ and $\vec{X}_q$,

$$\vec{J}_c = \frac{\Omega}{k_B T} \left[L_{cc} \vec{X}_c + L_{cq} \vec{X}_q \right] \quad (12)$$

$$\vec{J}_q = \frac{\Omega}{k_B T} [L_{qc} \vec{X}_c + L_{qq} \vec{X}_q] \quad (13)$$

where Ω is the system volume. The thermodynamic driving forces are given by the expressions,

$$X_c = -T \nabla \left(\frac{\mu_c}{T} \right) \quad (14)$$

$$X_q = -\frac{1}{T} \nabla T \quad (15)$$

The chemical potential μ_c for interdiffusion, which can be related to the chemical potentials μ_1 and μ_2 defined for the two components (see Ref. [9]), depends in general on the thermodynamic variables describing composition, temperature, and pressure. To compute the transport coefficients L_{cc} , $L_{cq} = L_{qc}$, and L_{qq} , the Green-Kubo approach was used [7, 8]. The integrated time-correlation functions, as a function of the integration limit τ , are given by,

$$\zeta_{cc}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_c(\tau) \cdot \vec{J}_c(0) \rangle d\tau \quad (16)$$

$$\zeta_{cq}(\tau) = \zeta_{qc}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_c(\tau) \cdot \vec{J}_q(0) \rangle d\tau \quad (17)$$

The transport coefficients are then formally given by,

$$L_{cc} = \lim_{\tau \rightarrow \infty} \zeta_{cc}(\tau) \quad (18)$$

$$L_{cq} = L_{qc} = \lim_{\tau \rightarrow \infty} \zeta_{cq}(\tau) \quad (19)$$

In practical calculations, the integration limit is chosen to be large enough so that correlations are absent, but yet not so large that numerical error begins to dominate.

The heat of transport is defined by the ratio of L_{cq} and L_{cc} ,

$$Q_c^* = \frac{L_{cq}}{L_{cc}} \quad (20)$$

The reduced heat of transport $Q_c^{*'} = Q_c^* - h_c$ is the quantity most directly measured by experiment, since it correlates directly to the segregation of components in the presence of a temperature gradient. To determine $Q_c^{*'}$, we require calculation of the partial quantity h_c , which was computed using the expression developed in Ref. [9] ,

$$h_c = \frac{m_2}{\bar{m}} h_1 - \frac{m_1}{\bar{m}} h_2 \quad (21)$$

where h_1 and h_2 are partial enthalpies of the individual component. The specific definitions of those quantities in terms of the interatomic potential will be given later. One important requirement is that the partial enthalpies add to give the total system enthalpy H_{tot} ,

$$H_{tot} = N_1 h_1 + N_2 h_2 \quad (22)$$

To obtain more insight, we also separately compute individual contributions to the enthalpy $h_c = u_c + p_c \Omega$. Specifically, following the approach above,

$$u_c = \frac{m_2}{\bar{m}} u_1 - \frac{m_1}{\bar{m}} u_2 \quad (23)$$

$$p_c \Omega = \frac{m_2}{\bar{m}} p_1 \Omega - \frac{m_1}{\bar{m}} p_2 \Omega \quad (24)$$

where Ω is the system volume and p_1 and p_2 are partial pressures for component 1 and 2. The energies u_1 and u_2 are determined from time averages of the site energies ϵ_i given in Eq. 8,

$$u_1 = \frac{1}{N_1} \left[\sum_{i=1}^{N_1} \langle \epsilon_i \rangle \right] \quad (25)$$

$$u_2 = \frac{1}{N_2} \left[\sum_{i=N_1+1}^{N_1+N_2} \langle \epsilon_i \rangle \right] \quad (26)$$

The computation of the partial enthalpies h_1 and h_2 also requires a definition of the partial pressures p_1 and p_2 . The microscopic definition naturally emerges from how the local energy was partitioned between the two components, and hence is also consistent with the virial part of the heat current given in Eq. 11. The definition used for the components of the local stress tensor corresponding to atom i is,

$$\pi_{i,\mu\nu} \Omega = m_i v_{i,\mu} v_{i,\nu} - \frac{1}{2} \sum_{j \neq i} \left[\frac{1}{r} \frac{d\phi_{ij}}{dr} \right]_{r=r_{ij}} r_{ij,\mu} r_{ij,\nu} - \sum_{j \neq i} \left[\frac{dF_j}{d\rho} \right]_{\rho=\bar{\rho}_j} \left[\frac{1}{r} \frac{d\rho}{dr} \right]_{r=r_{ij}} r_{ij,\mu} r_{ij,\nu} \quad (27)$$

Then the contributions to the partial enthalpies, $p_1 \Omega$ and $p_2 \Omega$, are found from the time averages,

$$p_1 \Omega = \frac{1}{3N_1} \sum_{i=1}^{N_1} \sum_{\mu=1}^3 \langle \pi_{i,\mu\mu} \rangle \Omega \quad (28)$$

$$p_2 \Omega = \frac{1}{3N_2} \sum_{i=N_1+1}^{N_1+N_2} \sum_{\mu=1}^3 \langle \pi_{i,\mu\mu} \rangle \Omega \quad (29)$$

We also note the relationship describing the total pressure P ,

$$P = N_1 p_1 + N_2 p_2 \quad (30)$$

Then, the total stress contribution to the total enthalphy is,

$$P\Omega = N_1 p_1 \Omega + N_2 p_2 \Omega \quad (31)$$

Finally the partial enthalpies for component 1 and 2 are given by,

$$h_1 = u_1 + p_1 \Omega \quad (32)$$

$$h_2 = u_2 + p_2 \Omega \quad (33)$$

The results described in the next section were computed for the binary liquids NiAl and NiCu. For the NiCu system, we used the potential from Ref. [14]. In the case of the NiAl system, two different empirical potentials for the NiAl system were used [15, 16]. For each simulation, $N_1 = N_2 = 512$, for a simulation with a total of $N = 1024$ atoms. The system was prepared in an $L1_0$ lattice, with 256 non-primitive fcc unit cells. The system was first melted and equilibrated at the desired temperature in a constant volume and temperature (NVT) ensemble. The system volume was chosen so that the total pressure $p = p_1 + p_2$ was close to zero, although small deviations from $p = 0$ were tolerated. These pressures are reported in Table I. After equilibration, data was generated for Green-Kubo integration from a constant energy and volume (NVE) simulation. The amount of data used for time-averaging varied between the different systems, and will be discussed in the next section. In presenting the data, the lightest component is taken as component 1, and the heaviest as component 2. Thus, for NiAl, component 1 is Al, and component 2 is Ni. For NiCu, component 1 is Ni, and component 2 is Cu.

III. RESULTS AND ANALYSIS

In Table I, the simulation results are reported. First, the atomic volume Ω_a , defined as the volume per atom of the simulation cell, is shown for each potential and temperature simulated. After equilibrating the liquid for at least $40ps$ in the NVT ensemble at the desired temperature, heat and mass currents were output for calculation of the correlation functions. Correlation functions were averaged over the entire data set at each temperature, which involved several independent runs of varying length. For the NiAl potential from Ref. [15], correlation functions at each temperature were averaged from at least $2.93ns$ of data obtained from 16 independent runs. For the NiAl potential from Ref. [16], at least $1.28ns$ of data obtained from 8 independent runs was used to determine average correlation functions. Finally, for the NiCu potential in Ref. [14], averaging was

performed over $5.11ns$ of data obtained in 32 independent simulations. In each case error bars for the correlation functions were obtained from the statistical variance obtained from the independent simulations. This procedure results in estimated error for the computed heat of transport.

To calculate partial energies and pressures, 8 independent simulation runs were performed at each simulated temperature within the NVT ensemble. In each simulation, the system was allowed to equilibrate for at least $36ps$, followed by time averaging over at least $270ps$. The statistical error in the partial quantities was found to be significantly less than that of the time-correlation functions, and hence is not important for determining the error in the reduced heat of transport.

The results for $\zeta_{cc}(\tau)$ and $\zeta_{cq}(\tau)$ for the two empirical potentials used for the NiAl system as a function of integration time τ are presented first. Specifically, in Fig. 1 and Fig. 2, results obtained at $T = 2000K$ using the NiAl potential from Ref. [15] are shown. In Fig. 3 and Fig. 4, results for the NiAl system are also shown, but with $T = 2012K$ using the potential from Ref. [16], which was also the potential used in the transport calculations reported in Ref. [9]. Qualitatively, the results from the two potentials look quite similar. Both results show that an integration time of $\tau \sim 0.1ps$ is adequate to obtain converged transport parameters L_{cc} and L_{cq} . Correlations beyond $\sim 0.1ps$ are essentially absent. Consequently, to compute L_{cc} and L_{cq} , and also the heat of transport Q_c^* , the integration time $\tau = 0.25ps$ was used. The two potentials predict values for L_{cc} and L_{cq} which do not differ by large amounts. However, the small differences result in values for Q_c^* that are significantly different. In Table I, the computed values for Q_c^* are shown for both potentials. For the potential from Ref. [15], results were determined for five different temperatures, while for the potential from Ref. [16], Q_c^* is reported for only one temperature. For each simulated temperature and potential, Table I also includes the partial quantities h_c , u_c , and $p_c\Omega$, as well as the individual contributions from the two component u_1 , u_2 , h_1 , h_2 , $p_1\Omega$, and $p_2\Omega$. In these results, as noted previously, component 1 is Al and component 2 is Ni. Also shown in Table I are the contributions to Q_c^* arising from the convective ($Q_c^{*(conv)}$) and virial ($Q_c^{*(vir)}$) components of the heat current. Finally, the reduced heat of transport $Q_c^{*'} = Q_c^* - h_c$ is also given in Table I.

From Table I, one important result is that $Q_c^{*'}$ has a different sign for the two NiAl potentials considered, which indicates qualitatively different thermodiffusion. Specifically, the potential from Ref. [15] results in $Q_c^{*' < 0$, which means that Al is driven towards higher temperatures and Ni is driven towards lower temperatures. By contrast, when the potential for NiAl in Ref. [16] was used, $Q_c^{*' > 0$, which means that Al is driven towards lower temperatures, and Ni is driven towards higher temperatures. This indicates that the results for $Q_c^{*'}$ are very sensitive to details of the potential, and moreover that results obtained using EAM potentials are likely not predictive. To

obtain predictive results, it would be necessary to optimize empirical potentials, but the target properties for optimization are not entirely clear. We discuss this aspect later in this article.

In Figs. 5 and 6, results obtained for $\zeta_{cc}(\tau)$ and $\zeta_{cq}(\tau)$ using the EAM potential for the NiCu system are shown. The simulation temperature was $T = 2000K$. The correlation time appears to be slightly longer in this system, but nevertheless $\tau = 0.25ps$ appears to be long enough to obtain converged results. Results for the NiCu system are also included in Table I. As mentioned previously, for the NiCu system, component 1 is Ni, and component 2 is Cu. The value for $Q_c^{*'} is negative, with a rather small magnitude, which indicates a weak driving force for Ni to be driven towards higher temperatures, and Cu driven towards lower temperatures.$

It was found in Ref. [11] for Pd:H thermodiffusion that the convective and virial contributions to the heat of transport are closely linked to the relevant contributions to the partial enthalpy. In the results presented here, this observation would suggest that there should be a close connection between $Q_c^{*(conv)}$ and u_c , and also between $Q_c^{*(vir)}$ and $p_c\Omega$. This trend is examined in Table II, where we show values for $Q_c^{*(conv)} - u_c$ and $Q_c^{*(vir)} - p_c\Omega$. For the convective contribution, $Q_c^{*(conv)} - u_c$ is always found to be positive. This was also found in Ref. [11] for the Pd:H system. In the Pd:H system, thermodiffusion is largely due to the hydrogen, with the Pd unable to diffuse. In the liquid alloys, while both components diffuse, the lightest component should undergo the largest displacements. By choosing as component 1 the lightest of the two components, the values for $Q_c^{*(conv)} - u_c$ are all positive. Also, the very small value $Q_c^{*(conv)} - u_c = 0.09eV$ for the NiCu system is likely due to the fact that the mass difference between Ni and Cu is only $\sim 5amu$, which is significantly less than the difference between Al and Ni, $\sim 32amu$. Based on the results and discussion in Ref. [11], the hypothesis here is that the positive values for $Q_c^{*(conv)} - u_c$ reflect the excess kinetic and potential energy transported convectively by the diffusing component. In the liquids here, while both component diffuse, the lightest component more effectively transports this energy.

It is apparent from the results that virial heat current plays a dominant role in comparison to convective heat current. To provide evidence for this mechanism, we show in Figs. 7-9 results for Q_c^* , including contributions from the virial ($Q_c^{*(vir)}$) and convective ($Q_c^{*(conv)}$) components of the heat current. The quantity plotted in Figs. 7-9 corresponds to the heat of transport computed for different integration times τ . For example, the total heat of transport $Q_c^*(\tau)$ is defined as,

$$Q_c^*(\tau) = \frac{\zeta_{cq}(\tau)}{\zeta_{cc}(\tau)} \quad (34)$$

with the limit as $\tau \rightarrow \infty$ corresponding to the theoretical prediction for Q_c^* measured in experiment.

In each case, the virial contribution $Q_c^{*(vir)}$ changes significantly as a function of the integration limit τ , indicating strong correlation between mass transport and virial heat current. By contrast, dependence on τ is much weaker for the convective component. The timescale for this change is also coincident with the $\sim 0.1ps$ timescale for correlations in $\zeta_{cc}(\tau)$. In the case of NiAl described by the potential in Ref. [15], the results in Fig. 7 show a strong decrease in the virial contribution with integration time τ . Similar behavior is obtained from the NiCu potential, as shown in Fig. 9. In contrast to these results, the NiAl potential from Ref. [16], shows in Fig. 8 an increasing virial contribution with integration time τ . These results correlate with the reduced heat of transport values shown in Table I: an increasing virial contribution correlates with a positive reduced heat of transport, and a decreasing virial contribution correlates with a negative reduced heat of transport. In the case of NiAl, these observations also correlate with the partial pressure term $p_1\Omega$ for Al. Specifically, for the results in Fig. 7, $p_1\Omega$ is positive, while for the results shown in Fig. 8, $p_1\Omega$ is negative. For NiCu, both $p_1\Omega$ and $p_2\Omega$ are extremely small. Moreover the masses of Ni and Cu are extremely close, which would indicate that neither component should tend to dominate the heat transport. Temperature dependence of the reduced heat of transport is weak and is not outside the error bars for the reduced heat of transport. We note that there is no particular theory or existing understanding of how the reduced heat of transport might depend on temperature.

In a separate study [18], we have found that for Lennard-Jones potentials, short-range repulsive interactions, which always result in a positive contribution to the partial pressure, tend to dominate thermodiffusion via the resulting virial heat current. What was observed was that the positive stress due to short-range repulsion tends to decrease during an atomic hop, resulting in an overall negative contribution to the reduced heat of transport. This particular mechanism tends to result in the low-mass component being driven up the temperature gradient, and the high-mass component being driving down the temperature gradient. Similar observations were reported for the Pd:H system reported in Refs. [10, 11]. There, hydrogen is the diffusing component, and due to the nature of the particular interatomic potential, hydrogen always has a positive partial stress. During a hop of a hydrogen atom through a “gate” of Pd atoms, it was found that the stress along the direction of the hop was strongly reduced. By this mechanism, the virial contributions to the reduced heat of transport were found to be negative, and hence the hydrogen atoms were driven up the temperature gradient.

We propose in the present case, a similar mechanism applies, mainly due to correlation between atomic diffusion of the low-mass component and the local stress. If the partial pressure $p_1\Omega$ of the low-mass component is positive, short-range repulsive interactions likely dominate. When the

low-mass component diffuses, it should experience reduced stress along the direction of the hop and hence tend to exhibit a negative contribution to the heat of transport. This is the case for the NiAl system using the potentials from Ref. [15]. By contrast, for the NiAl potential in Ref. [16], $p_1\Omega$ is negative, which would be consistent with a dominant role for longer-range attractive interactions. In this case, it seems plausible that during diffusion, the magnitude of the stress along the direction of the hop would be reduced (i.e., become less negative), and hence correlates with a positive heat of transport. In the NiAl system, it is likely that the low-mass component Al plays a dominant role, although clearly the Ni does contribute. By contrast, for NiCu, the masses are very similar, and it is difficult to say which component might play a dominant role. Nevertheless, the behavior shown in Fig. 9 does at least indicate a dominant role for virial heat current. Furthermore, as examined in greater detail in [18], when the contributions of two different species to the virial stress are examined, it becomes apparent that the virial contributions dominate thermodiffusive behavior but often tend to cancel. However, in the NiCu potential, the mass difference between the two species is very small, and therefore no single species can be dominant.

Another way to consider the connection between the partial stress terms, $p_1\Omega$ and $p_2\Omega$, and Q_c^{*} , is found by examining the stress terms in Eq. 27 and the virial heat current terms in Eq. 11. For simplicity, consider a system with $m_1 \ll m_2$, so that component 1 carries most of the heat during diffusion. Consideration of Eq. 11 and Eq. 27 indicates that when $p_1\Omega > 0$, the virial heat current is parallel to the mass current. By contrast, if $p_1\Omega < 0$, then the virial heat current is antiparallel to the mass current. This represents a clear qualitative difference between the two NiAl systems modeled here. In both instances, we propose that fluctuations in local atom density, which would be required to generate an open volume for interdiffusion to occur, would result in a reduction of stress along the direction of the mass diffusion. When $p_1\Omega$ is positive, it seems likely that short-range repulsion dominates the heat transport. By contrast, when $p_1\Omega$ is negative, there is likely a greater role for attractive interactions that operate over larger distances. This suggests that future potentials must consider these details in order to most correctly describe the stress in a binary alloy.

In the case where m_1 and m_2 are very close, it is likely that neither component plays a dominant role. This corresponds to the NiCu system, where the mass of Ni is only slightly less than that of Cu. Here we expect the correlations between $p_1\Omega$, $p_2\Omega$, and Q_c^{*} to be more subtle. We have found this to be true for Lennard-Jones potentials[18], where simulations with $m_1 = m_2$ displayed relatively small values for Q_c^{*} whose sign had no simple explanation. In the case of NiCu, the two components are similar in not just their masses. Specifically, the partial pressures $p_1\Omega$ and

$p_2\Omega$ are quite both small and nearly zero. In this case, it seems more difficult to formulate a simple picture that can explain the results.

The Green-Kubo results also permit the thermal conductivity to be computed. The thermal conductivity itself requires the partial enthalpy h_c to be subtracted from the heat current. Hence, we consider here the integrated correlation function,

$$\zeta'_{qq}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}'_q(\tau) \cdot \vec{J}'_q(0) \rangle d\tau \quad (35)$$

where the reduced heat current $\vec{J}'_q = \vec{J}_q - h_c \vec{J}_c$. The transport parameter is then given by,

$$L'_{qq} = \lim_{\tau \rightarrow \infty} \zeta'_{qq}(\tau) \quad (36)$$

which is related to thermal conductivity κ by,

$$\kappa = \frac{L'_{qq}}{k_B T^2} \quad (37)$$

In Fig. 10, $\zeta'_{qq}(\tau)$ is plotted as a function of integration time τ for the NiAl system at $T = 2000K$ with the empirical potential from Ref. [16]. It is evident that correlations extend only to times τ comparable to those previously found for ζ_{cc} and ζ_{cq} . The results for the other potentials look qualitatively similar to Fig. 10 and are hence not shown here. The thermal conductivity values we obtain obtained for the two NiAl potentials are somewhat similar at $T = 2000K$. Specifically, for the NiAl potential in Ref. [15], we obtained $\kappa = 3.53 W m^{-1} K^{-1}$ for $T = 2000K$, while for the NiAl potential in Ref. [16] we obtained $\kappa = 4.26 W m^{-1} K^{-1}$ at $T = 2012K$. The NiCu potential [14] results in a smaller thermal conductivity $\kappa = 1.12 W m^{-1} K^{-1}$. To obtain these values, L'_{qq} was taken from $\zeta'_{qq}(\tau)$ at $\tau = 0.25 ps$. These results suggest that timescales for thermal conduction are comparable to those associated with mass diffusion. These thermal conductivities are far lower than what would be expected in experiment due to the neglect of electronic contributions. Finally, our result for the NiAl potential in Ref. [16] is in fair agreement with previous results for thermal conductivity using the same potential [17].

We note that the results reported here using the potential from Ref. [16] show some disagreement with those reported in Ref. [9]. Specifically, at $T = 2012K$, Ref. [9] reports a value $Q_c^* = -0.59 eV$, in contrast to the value from Table I, $Q_c^* = -1.55 eV$. While both values are negative, this is a significant difference that we cannot explain. In Ref. [9], partial enthalpies were computed using both a thermodynamic definition and also using the same approach applied here based on the microscopic definition. In Ref. [9], the reduced heat of transport $Q_c^{*'} = 0.67 eV$ was computed using the thermodynamic definition of the partial enthalpy, which is different from the value $Q_c^{*'} = 0.49 eV$

reported in Table I. The sign of the values reported in Ref. [9] are altered here because in Ref. [9], component 1 was Ni, in contrast to the choice here where component 1 was Al. Though these results differ, the basic prediction that Ni is driven from lower to higher temperatures, and consequently Al is driven from higher to lower temperatures, is consistent between this work and Ref. [9].

Finally, we have provided values for L_{cc} , L_{cq} , L_{qq} , and L'_{qq} in Table I. By comparing with values for these transport coefficients given in Ref. [17] (where it was found that, in our units, $L_{cc} = 0.035 \text{ \AA}^{-1} \text{ ps}^{-1}$, $L_{qq} = 0.930 \text{ eV}^2 \text{ \AA}^{-1} \text{ ps}^{-1}$, and $L_{cq} = -0.020 \text{ eV \AA}^{-1} \text{ ps}^{-1}$) with our values obtained using the same potential, it seems that our values for L_{cc} and L_{qq} are in agreement, while we find a value for L_{cq} significantly larger in magnitude than the value found in Ref. [17]. This seems to account for the difference in values for Q_c^* between this work and Ref [9].

IV. CONCLUSIONS

Based on MD simulations, it was established that there may exist a correlation between partial pressures of the components in a binary liquid and the computed reduced heat of transport Q_c^{*} . The results indicate a dominant role for virial heat current in comparison to convective heat current. When there is a substantial difference in the atomic masses, the low-mass component plays a dominant role. In that case, the partial pressure of the low-mass component is strongly correlated with the value of Q_c^{*} . As with previous work on Pd:H [13], stress reduction along the direction of the diffusion event is proposed as the main determining factor for Q_c^{*} .

This suggests that there is a balance between the roles of short-range repulsive interactions, which correlate with positive stress, and long-range attractive interactions, which correlate with negative stress. We propose that the physical nature of thermophobicity is determined by these factors, and is likely correlated with the partial pressures of the components in a binary liquid. In the case where there is a large mass difference between the two components, we propose that the partial pressure of the low-mass component (component 1) is the most important, with $p_1\Omega < 0$ correlated with $Q_c^{*} > 0$, and $p_1\Omega > 0$ correlated with $Q_c^{*} < 0$. In other words, the thermophobicity of the low-mass component is the most important. When there is only a small difference in mass, then both components are important. We suggest that the relative importance of attractive and repulsive interactions acting over different length scales should be correlated with whether a component is “thermophobic” or “thermophilic”. While these details remain to be clarified and firmly established, we suggest that if the properties of a component are dominated by short-range

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4 repulsive interactions it should be more thermophilic (i.e. driven up a temperature gradient),
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6 whereas if long-range attractive interactions are dominant it should trend towards thermophobic
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8 (driven down a temperature gradient). The balance between both components in a binary mixture
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10 is important, as are the relative masses of the two components.

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TABLE I: Partial thermodynamic quantities and heat of transport values computed for NiAl and NiCu alloys. In each case, the component with the smallest mass is taken as component 1. Specifically, for the case of NiAl alloys, component 1 is Al, and component 2 is Ni. For NiCu, component 1 is Ni and component 2 Cu. The reference for the EAM potential used to compute the data in each column is given. Each energy is given in units of eV. The last row shows volume per atom Ω_a for each potential in units of $\text{\AA}^3$.

	NiAl	NiAl	NiAl	NiAl	NiAl	NiAl	NiCu
T (K)	2000	2125	2250	2375	2500	2012	2000
EAM	Ref. [15]	Ref. [15]	Ref. [15]	Ref. [15]	Ref. [15]	Ref. [16]	Ref. [14]
Ω_a ($\text{\AA}^3$)	14.46	14.46	14.46	14.46	14.46	14.73	13.38
u_1	-3.55	-3.52	-3.48	-3.44	-3.40	-2.62	-3.50
u_2	-3.64	-3.61	-3.58	-3.54	-3.51	-4.65	-2.96
h_1	-3.37	-3.28	-3.19	-3.08	-3.00	-3.31	-3.51
h_2	-4.12	-4.05	-3.97	-3.87	-3.80	-3.97	-2.99
$p_1\Omega$	0.18	0.24	0.29	0.36	0.41	-0.70	-0.01
$p_2\Omega$	-0.48	-0.44	-0.39	-0.33	-0.29	0.68	-0.03
u_c	-2.58	-2.55	-2.52	-2.48	-2.45	-0.65	-0.80
h_c	-2.02	-1.94	-1.87	-1.78	-1.71	-2.04	-0.78
$p_c\Omega$	0.55	0.60	0.65	0.70	0.74	-1.39	0.02
L_{cc} (1 / $\text{\AA} ps$)	0.05	0.06	0.06	0.07	0.08	0.04	0.02
L_{cq} (eV / $\text{\AA} ps$)	-0.12	-0.13	-0.14	-0.15	-0.16	-0.05	-0.02
L_{qq} (eV ² / $\text{\AA} ps$)	1.03	1.15	1.28	1.40	1.57	1.01	0.26
L'_{qq} (eV ² / $\text{\AA} ps$)	0.76	0.87	0.98	1.09	1.24	0.93	0.24
$Q_c^{*(total)}$	-2.35 ± 0.02	-2.28 ± 0.05	-2.23 ± 0.05	-2.25 ± 0.10	-2.12 ± 0.05	-1.55 ± 0.07	-0.94 ± 0.05
$Q_c^{*(conv)}$	-2.22 ± 0.01	-2.18 ± 0.02	-2.14 ± 0.02	-2.12 ± 0.02	-2.10 ± 0.02	-0.40 ± 0.02	-0.71 ± 0.01
$Q_c^{*(vir)}$	-0.13 ± 0.02	-0.09 ± 0.04	-0.10 ± 0.04	-0.13 ± 0.09	-0.02 ± 0.04	-1.15 ± 0.06	-0.24 ± 0.03
$Q_c^{*'}$	-0.33 ± 0.02	-0.34 ± 0.05	-0.36 ± 0.05	-0.47 ± 0.10	-0.41 ± 0.05	0.49 ± 0.07	-0.16 ± 0.05

TABLE II: Comparison of energies in eV for the convective and virial contributions to Q_c^* with relevant terms in the partial enthalpy h_c . The values for the contributions to Q_c^* , and also u_c and $p_c\Omega$, are given in Table I.

Potential	T (K)	$Q_c^{*(conv)}$	$Q_c^{*(vir)}$	$Q_c^{*(conv)} - u_c$	$Q_c^{*(vir)} - p_c\Omega$
NiAl (Ref. [15])	2000	-2.22	-0.13	0.36	-0.68
NiAl (Ref. [15])	2125	-2.18	-0.09	0.37	-0.69
NiAl (Ref. [15])	2250	-2.14	-0.10	0.38	-0.75
NiAl (Ref. [15])	2375	-2.12	-0.13	0.36	-0.83
NiAl (Ref. [15])	2500	-2.10	-0.02	0.35	-0.76
NiAl (Ref. [16])	2012	-0.40	-1.15	0.25	0.24
NiCu (Ref. [14])	2000	-0.71	-0.24	0.09	-0.22

Figure Captions

Figure 1 The integrated correlation function $\zeta_{cc}(\tau)$ as a function of integration time τ for $T = 2000K$ for the NiAl potential reported in Ref. [15].

Figure 2 The integrated correlation function $\zeta_{cq}(\tau)$ as a function of integration time τ for $T = 2000K$ for the NiAl potential reported in Ref. [15].

Figure 3 The integrated correlation function $\zeta_{cc}(\tau)$ as a function of integration time τ for $T = 2012K$ for the NiAl potential reported in Ref. [16].

Figure 4 The integrated correlation function $\zeta_{cq}(\tau)$ as a function of integration time τ for $T = 2012K$ for the NiAl potential reported in Ref. [16].

Figure 5 The integrated correlation function $\zeta_{cc}(\tau)$ as a function of integration time τ for $T = 2000K$ for the NiCu potential reported in Ref. [14].

Figure 6 The integrated correlation function $\zeta_{cq}(\tau)$ as a function of integration time τ for $T = 2000K$ for the NiCu potential reported in Ref. [14].

Figure 7 Contributions to the integrated heat of transport Q_c^* as a function of integration time τ for the NiAl potential contained in Ref. [15]. Thickness of the lines indicates statistical error.

Figure 8 Contributions to the integrated heat of transport Q_c^* as a function of integration time τ for the NiAl potential contained in Ref. [16]. Thickness of the lines indicates statistical error.

Figure 9 Contributions to the integrated heat of transport Q_c^* as a function of integration time τ for the NiCu potential contained in Ref. [14]. Thickness of the lines indicates error.

Figure 10 The integrated correlation functions $\zeta_{qq}(\tau)$ (solid black line) and $\zeta'_{qq}(\tau)$ (dotted red line) as a function of integration time τ for the NiAl system using the potential in Ref [15].

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 6

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Figure 9

Figure 10