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Molecular Dynamics Simulation of Thermal Accommodation Coefficients for LII Experiments

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ABSTRACT

Time-resolved laser-induced incandescence demands precise knowledge of the thermal accommodation coefficient, but little is known about the physics underlying this parameter. This paper presents the results of a molecular dynamics simulation that shows how the thermal accommodation coefficient is influenced by gas molecular mass and gas temperature. The MD results are also used to define scattering kernels that form boundary conditions in DSMC simulations of heat and momentum transfer between soot aggregates and surrounding gas molecules

INTRODUCTION

Accurate particle sizing by time-resolved laser-induced incandescence (TR-LII) requires an accurate model of heat transfer between the energized particles and the surrounding gas. In the majority of low-fluence TR-LII measurements on soot-laden aerosols this occurs mainly by free-molecular conduction, where gas molecules travel between the equilibrium gas and the particle surface without intermolecular collisions. In this regime heat transfer rate depends on the gas/surface collision kinetics specified by the thermal accommodation coefficient, α , defined as

$$\alpha = \frac{T_{g,o} - T_{g,i}}{T_s - T_{g,i}} \quad (1)$$

where T_s is the particle temperature, and $T_{g,i}$ and $T_{g,o}$ are the kinetic temperatures of the incident and scattered gas molecular streams, respectively. In the simplest case of a monatomic gas α can be rewritten in terms of the average translational kinetic energies of incident and scattered gas molecules,

$$\alpha = \frac{1/2 m_g [\langle \mathbf{v}_o \cdot \mathbf{v}_o - \mathbf{v}_i \cdot \mathbf{v}_i \rangle]}{2k_B (T_s - T_g)} \quad (2)$$

where \mathbf{v}_i and \mathbf{v}_o are the incident and scattered velocities, respectively. Accurate particle sizing through TR-LII data can only be carried out if the accommodation coefficient is known with certainty. Because the underlying physics of this parameter is poorly understood, the LII community treats the thermal accommodation coefficient more like a calibration constant than a physical parameter; there is almost no consensus of what may constitute a "reasonable" value for this coefficient, or how it may vary with experimental parameters including gas composition and temperature. This paper seeks to elucidate the thermal accommodation coefficient physics by simulating gas-surface scattering in LII using a classical mechanics-based molecular dynamics (MD) simulation. A comparison of the simulated and experimentally-measured α values shows good agreement between the two datasets. These promising results suggest that a broader understanding of the underlying physics of thermal accommodation in TR-LII is within reach.

MOLECULAR DYNAMICS SIMULATION

Soot aggregates consist of chains of roughly spherical primary particles that in turn contain flat graphite crystallites aligned parallel to the surface. Given the limited potential range between an incident gas molecule and a soot primary particle, free-molecular heat conduction can be modeled as a large number of independent scattering events between incident gas molecules and a graphite half-space having the same temperature as the laser-energized soot. The scattering events are simulated using a classical mechanics-based MD approach in which pairwise potentials are defined between bodies as a function of their relative locations and then differentiated to obtain the forces acting on each atom. Atomic and molecular trajectories are then calculated by integrating the equations of motion over time.

As shown in Fig. 1 (a), covalently-bonded carbon atoms form the graphene sheets, which in turn are held together by comparatively weak Van der Waals forces. The covalent bonds between carbon atoms are represented by a harmonic potential [1],

$$U_{cc}(r) = \frac{1}{2} k_{cc} (r - r_{o,cc})^2, \quad (3)$$

where r is the centre-to-centre distance between a C-C pair, $r_{0,CC}$ is the equilibrium bond length, and k_{cc} is the harmonic potential constant. The Van der Waals forces holding the graphene sheets together are modeled by the sum of Morse potentials between a carbon atom and its nearest neighbors in the upper and lower graphene sheets [2]. For atoms centered above or below a six-member ring as shown in Fig. 1 (b), the potential is given by

$$U_h = \sum_{i=1}^6 U_h^M(r_i), \quad (4)$$

where r_i is the centre-to-centre distance between the carbon atom and the i th carbon atom in the ring above or below and $U_h^M(r)$ is a Morse pairwise potential,

$$U_h^M(r) = D_h \left\{ \exp[-2a_h(r - r_{0,h})] - 2 \exp[-a_h(r - r_{0,h})] \right\}. \quad (5)$$

For carbon atoms centered directly above or below another carbon atom, as shown in Fig. 1 (c), the interplane potential is modeled as

$$U_c = \sum_{i=1}^3 U_h^M(r_i) + U_c^M(r) \quad (6)$$

where $U_c^M(r)$ corresponds to the potential between the carbon atom and the second atom directly above or below and has the same form as Eq. (5), and the summation terms pertain to the three next-nearest neighbors.

The potential well between the incident gas molecule and the soot surface is modeled as the sum of pairwise Lennard-Jones (L-J) 6-12 potentials between the gas molecule and the carbon atoms,

$$U_{gs}(r) = 4 \epsilon_{gs} \left[\left(\frac{\sigma_{gs}}{r_{gs}} \right)^{12} - \left(\frac{\sigma_{gs}}{r_{gs}} \right)^6 \right]. \quad (7)$$

The L-J model parameters are found by matching experimentally-reported atomic equilibrium distances and dissociation energies between different gas molecules and graphite [3] to values predicted by integrating the L-J potentials over the graphite half-space [2]. The interatomic potential parameters are summarized in Table 1.

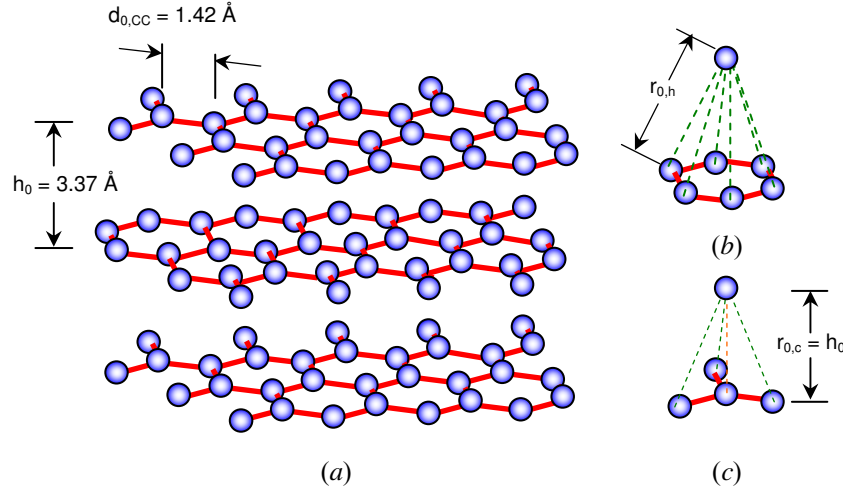


Fig. 1: Graphite consists of sheets of (a) covalently bonded carbon atoms in a hexagonal lattice, joined by weak Van der Waals forces. Lattice configurations corresponding to Eqs. (4) and (6) are shown in (b) and (c), respectively.

Table 1: Molecular Dynamics Simulation Parameters

Graphite Potential		Gas-Surface Potential [2, 3]		
Harmonic potential for in-plane covalent bonds [1]	$d_{cc} = 1.42 \text{ \AA}$	Species	$\epsilon_{gs} [\text{meV}]$	$\sigma_{gs} [\text{\AA}]$
	$k_{cc} = 44.44 \text{ meV}$	He	1.53	2.65
Morse potential for inter-plane Van der Waals forces [2]	$D_h = 6.72 \text{ meV}$	Ne	2.71	2.78
	$a_h = 1.399 \text{ \AA}^{-1}$	Ar	6.27	3.1
	$r_{0,c} = 3.37 \text{ \AA}$	Kr	7.61	3.2
	$D_c = 18.19 \text{ meV}$	Xe	9.20	3.3
	$a_c = 1.369 \text{ \AA}^{-1}$			

The molecular dynamics simulation described above forms the kernel of a Markov-Chain Monte Carlo (MCMC) integration for estimating α . At the beginning of the k th trial the carbon atoms are assigned random velocities so that the average speed corresponds to a surface temperature of 3000 K. The atomic trajectories are then solved with velocity-Verlet integration. The graphite surface is first “warmed up” for 40 time steps over which time an Andersen thermostat maintains the desired surface temperature. The thermostat is then turned off and a gas molecule is introduced into the simulation starting from $10 \cdot \sigma_{gs}$ above the graphite sheet, where the forces between the gas molecule and the carbon atoms are negligible. The initial velocity of the gas molecule is sampled from Maxwell-Boltzmann distributions for an equilibrium gas at $T_g = 300$ K. The attractive Van der Waals forces between the gas molecule and the carbon atoms accelerate the molecule towards the graphite sheet until it is repelled by the oscillating potential surface; in some cases, a single collision scatters the gas atom, while in other cases it “hops” along the surface until it gains enough energy to escape the potential well. The molecular

trajectories are tracked until the gas molecule stops decelerating, at which point the accommodation coefficient for the trial is calculated as

$$\alpha^k = \frac{1/2 m_g (\mathbf{v}_o^k \cdot \mathbf{v}_o^k - \mathbf{v}_i^k \cdot \mathbf{v}_i^k)}{2k_B(T_s - T_g)}. \quad (8)$$

A stable estimate of α is eventually obtained by averaging a large number of α^k trials.

RESULTS AND DISCUSSION

Figure 2 shows the simulated accommodation coefficients with error bars denoting three standard deviations of the mean, corresponding to the average of approximately 1500 independent trials. These results are plotted with two sets of α_T measurements derived by matching the modeled heat transfer rate to TR-LII experimental data for soot of known morphology [4]. One set is calculated by setting the heat transfer area of the soot aggregate equal to its 2-D projected area, denoted A_{cond} in the graph, following the premise that an approaching soot molecule “sees” a 2-D projection of the soot particle [5]. The second set of data was derived using a slightly larger area, $A_{cond}(\alpha)$, which accounts for gas molecules that reach “shielded” primary particles at the aggregate interior through scattering and incomplete accommodation with exposed primary particles [6]. The MD-simulated thermal accommodation coefficients lie between these two sets of experimental data, and show the same increasing trend of α with respect to molecular mass, μ_g .

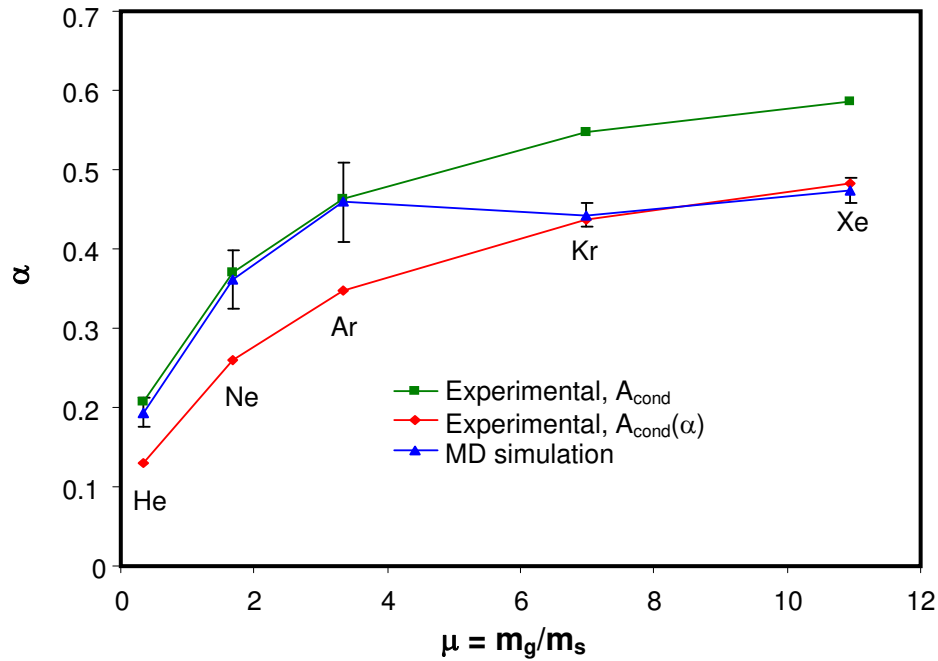


Fig. 2: Comparison between MD-simulated and experimentally-measured α_T values.

The MD simulation can be used to study other aspects of thermal accommodation in TR-LII experiments. A particularly important issue is how the gas temperature influences α through gas molecular approach velocity, since TR-LII experiments are performed on aerosols ranging from 300 K to 2000 K, and it is not clear how an accommodation coefficient measured at one gas temperature should compare to a value obtained at another temperature. Figure 3 shows that the

simulated α values increase with T_g for all species except argon; although these results pertain to monatomic gases, it does seem consistent with α values reported in the literature for in-flame soot, $\alpha = 0.37$ [6], and soot extracted from the same flame into nitrogen at ambient temperature, $\alpha = 0.18$ [4].

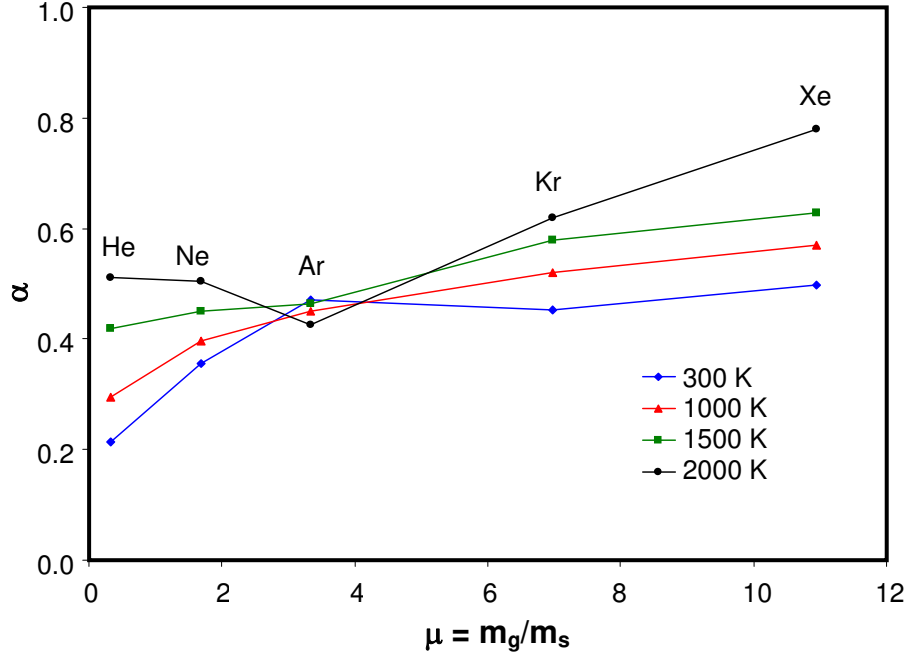


Fig. 3: Influence of aerosol gas temperature on MD-simulated α values.

Finally, the MD simulation can be used to investigate the veracity of different scattering kernels that form boundary conditions in DSMC simulations of heat and momentum transfer between soot particles and the surrounding gas (e.g. [6-8]). These kernels define the probability of a gas molecule having an approach velocity, \mathbf{v}_i , scattering with an exit velocity \mathbf{v}_o . The Maxwell kernel has been used in all DSMC simulations involving soot to date; it assumes that incident gas molecules equilibrate and are re-emitted diffusely with velocities sampled from a M-B distribution at T_s with a probability of α , and undergo specular, adiabatic scattering otherwise. A more sophisticated kernel is the Cercignani-Lampis-Lord (CLL) scattering kernel [9, 10]

$$R(\xi_i \rightarrow \xi_o) = \frac{2\xi_{o,n}}{\pi\alpha_n\alpha_t} \exp \left[-\frac{\xi_{o,n}^2 + (1-\alpha_n)\xi_{i,n}^2}{\alpha_n} - \frac{(\xi_{o,t} + \sqrt{1-\alpha_t}\xi_{i,t})^2}{\alpha_t} \right] \times I_0 \left(\frac{2\sqrt{1-\alpha_n}}{\alpha_n} \xi_{o,n}\xi_{i,n} \right), \quad (9)$$

where ξ_i and ξ_o are the incident and scattered molecular velocities normalized by the most probable speed at the surface temperature, $(2k_B T_s/m_g)^{1/2}$, subscripts n and t denote normal and tangential components, and α_n and α_t are corresponding accommodation coefficients, defined so that $\alpha = 1/2(\alpha_n + \alpha_t)$. [These parameters are obtained by averaging terms from the MD simulation similar in form to Eq. (8).] Figure 4 shows the scattering probabilities predicted by the CLL

kernel are in much better agreement with the MD simulation than the Maxwell kernel for the case of a beam of neon molecules traveling at the most probable speed at 300 K and striking the surface at 45° incidence. These results suggest that DSMC simulations of heat and momentum transfer between soot aggregates and the surrounding gas should be reevaluated using the CLL kernel in place of the Maxwell kernel.

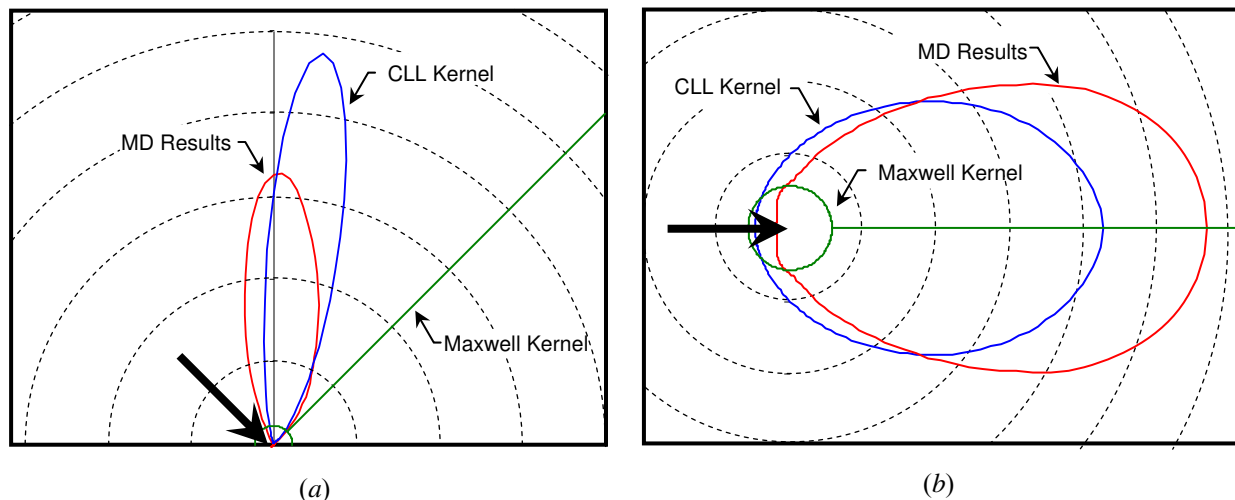


Fig. 4: Directional scattering probability for an incident molecular beam of neon molecules: (a) in the incidence plane, and (b) over all zenith angles.

CONCLUSIONS

This paper presents a molecular dynamics simulation that elucidates the gas-surface scattering that underlies free-molecular heat conduction in time-resolved laser-induced incandescence experiments. The simulated thermal accommodation coefficients agree with experimentally-measured values, which verifies that the interaction between the gas molecule and soot surface can be modeled using classical mechanics. The MD simulation was then used to investigate the effect of gas temperature on α , and finally to compare the accuracy of the Maxwell and CLL scattering kernels. Future work will focus on extending this treatment to polyatomic gases, and applying these results to enhance DSMC simulations involving soot aggregates.

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