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***Ab initio* calculation of thermal conductivity: application to molecular nitrogen**

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A novel method to compute the thermal conductivity of a dilute gas from stochastic particle methods is described. The proposed approach is inspired by the Müller-Plathe method, in that the heat flux is imposed on the system and is precisely known, whereas the temperature gradient is sampled during the simulation. In this manner, the issue of large statistical scatter associated with sampling the heat flux is circumvented. The modified Müller-Plathe (MMP) method is first verified with standard variable hard sphere direct simulation Monte Carlo. Then, it is used in Direct Molecular Simulation (DMS) equipped with an *ab initio* N₂+N₂ potential energy surface. The most significant sources of uncertainty are clearly identified and discussed. The DMS results for molecular nitrogen thermal conductivity agree remarkably well with the experimental evidence up to 2,000 K. The proposed MMP technique is applicable to arbitrary interatomic potentials and gas compositions, and it provides a direct way to evaluate thermal conductivity without relying on empirical extrapolations to high temperatures or approximations based on viscosity.

Introduction Hypersonic flows are characterized by temperatures that may reach thousands of degrees in the near-stagnation region, where molecular collisions are energetic enough to cause a significant transfer of the free stream kinetic energy into internal energy modes of the gas [1]. Depending on altitude, Mach number, and type of vehicle, the relevant flow physics include rovibrational excitation and dissociation of air molecules.

In recent years, there has been a significant effort to characterize air thermophysics from first-principles, because experimental characterization of gas phenomena at high temperatures is difficult and generally subjected to a large uncertainty. With the use of quantum mechanical methods, potential energy surfaces (PESs) have been constructed to describe atomic-level interactions between the various air components [2–10]. These PESs have then been used in several molecular dynamics studies to investigate some of the key quantities needed in thermochemical models for use in continuum descriptions and particle methods. Valuable insights into kinetic processes involving internal energy relaxation and its coupling to chemical reactivity have been obtained [3, 11–14] and the validity of this *ab initio* methodology, which does not rely on any empirical data, has been verified.

Another important aspect of high-temperature flows, however, is connected to the accurate determination of transport properties. There are two main difficulties with the construction of reliable models for transport coefficients at high temperatures. First, experimental measurements are often restricted to relatively low temperatures, usually not exceeding about 2,000 K [15–19] and suffer from significant uncertainty at high temperature [20]. Hence, the extrapolation of simple fitting functions to high temperatures is problematic, although not necessarily inaccurate. Second, the effect of thermal and chemical nonequilibrium on transport properties, if any, has to be carefully assessed.

To date, *ab initio* PESs have been widely used to investigate thermochemical processes, but far less is known about their ability to reliably predict transport properties for molecular and atomic nitrogen and oxygen, and their mixtures. Collision integral models used in computational fluid dynamics (CFD) [21, 22] were obtained from computations based on semi-empirical and simplified molecular interaction models [23, 24], many dating back several decades ago. Although not necessarily inaccurate, such interatomic potentials were too simplistic to accurately describe atom-diatom and diatom-diatom interactions and neglect chemical pathways during molecular collisions (e.g., exchange processes). For these reasons, the use of *ab initio* PESs to characterize transport properties is valuable to further refine or verify these semi-empirical models.

Only recently, researchers have started to revisit transport phenomena using some of the new and improved first-principles potential surfaces available in the literature, particularly focusing on viscosity. The methods have varied from (quasi-)classical trajectory based calculations [25, 26] to direct numerical quadrature of collision integrals using state-based potentials [27]. We have used the direct molecular simulation (DMS) method to obtain nitrogen viscosity up to 20,000 K [28]. Other studies have focused on thermal conductivity, but using relatively simple molecular models or standard direct simulation Monte Carlo (DSMC) [29, 30]. The Eucken relation [31] is frequently used to determine the thermal conductivity coefficient. However, this still represents an approximation based on simple arguments. To the authors' knowledge, however, no studies have been

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conducted to characterize thermal conductivity of air species using first-principles PESs. In general, “thermal conductivity has proved to be one of the most difficult transport coefficients to calculate” [32].

In this work, we present a simple but efficient computational technique applicable to the DMS method to reliably estimate thermal conductivity coefficients from first-principles PESs. Although the standard methods based on the direct evaluation of the heat flux from particles’ momenta (e.g., Fourier flow) are *directly* applicable to *ab initio* DMS, the computational cost becomes nearly prohibitive.

Numerical Method: Direct Molecular Simulation The DMS method has been described in detail elsewhere [33]. In summary, DMS can be envisioned as the *ab initio* variant of the DSMC technique, in that it replaces simplified collision models with actual molecular dynamics trajectories integrated on an *ab initio* PES. During the flow field computation, molecular trajectories are integrated on the fly and DMS simulated particles have the appropriate internal molecular structure of the gas molecule they represent, i.e., atomic, diatomic, or polyatomic phase-space coordinates. All molecular state transitions, solely governed by the PES and compatible with the local gas thermodynamic state, are permitted. DMS is therefore governed by all the well-known underlying dilute gas assumptions of DSMC (e.g., binary collisions, molecular chaos, etc.) but, remarkably, its overall accuracy is entirely traceable to the PES, which is the only molecular modeling input. The high fidelity nature of the method is reflected in its significant computational cost, primarily due to the integration of millions or billions of molecular trajectories on *ab initio* PESs. Only recently, DMS has been extended beyond simple zero-dimensional reactors [11–14, 34, 35] to flows in one or two dimensions [36–38]. Furthermore, it was shown to produce statistically identical solutions to deterministic molecular dynamics [33, 39]. DMS does not require any restrictions on molecular transitions or approximations on equilibration rates (e.g., rotranslational equilibrium). For these reasons, it has been used to verify reduced-order formulations [40, 41] that do have such approximations.

N₂+N₂ Potential Energy Surface In this work, we used the well-studied *ab initio* PES of Pauku *et al.* [2, 3] for ground state molecular nitrogen. Although a further refinement of this PES was recently produced [7], we have previously shown [37] that the solutions predicted by the original and new surface for a high-speed, reacting nitrogen flow around a two-dimensional cylinder do not differ significantly. Furthermore, we have verified with zero-dimensional chemical reactors that internal energy relaxation and dissociation rates are nearly identical between the two PESs. In the DMS calculations presented here, we set the maximum impact parameter for collisions to 6 Å and interactions are cut off when reaction products are separated by a distance of at least 20 Å. Trajectories are integrated with a fixed time step conservatively set to 0.05 fs using the velocity Verlet algorithm [42]. A thorough discussion on the proper choice of DMS simulation parameters is contained in previous works [33, 36, 37, 43].

Modified Müller-Plathe method Thermal conductivity κ is related to the heat flux vector $\mathbf{J}$ by the simple relation:

$$\mathbf{J} = -\kappa \nabla T, \quad (1)$$

where ∇T is the temperature gradient caused by the heat flux. For isotropic dilute gases, we will simplify Eq. 1 to consider the case of a scalar thermal conductivity dependent on temperature. Because of its temperature dependence, κ should be rigorously computed from a heat flux in the limit of a vanishing temperature gradient. For simplicity, we assume that the heat flux is in the x -direction, J_x , and, therefore, the limit $\partial T / \partial x \rightarrow 0$ should hold:

$$\kappa(T) = \frac{-J_x}{\partial T / \partial x}. \quad (2)$$

In particle methods, it is typically straightforward to impose a temperature gradient and sample the heat flux, for example by simulating a Fourier flow [29, 30, 44]. The difficulty with these strategies is that J_x represents a high-order moment of the velocity distribution function [29, 44]. As such, it is affected by poor statistical convergence, particularly in the high temperature regime. The difficulty with statistical scatter is further exacerbated by the need to impose a small temperature gradient. A different approach that does not require a finite perturbation is based on the calculation of integrals of time correlation functions of, for example, the stress tensor for viscosity and the energy current for thermal conductivity [42, 45]. These are known as Green-Kubo relations [32, 42, 45, 46] and are more frequently used in standard molecular dynamics, although their applicability to DSMC has been shown before [47–49]. Green-Kubo calculations “are notoriously difficult to perform” [32] as they suffer from the statistical convergence problems for the direct evaluation of the heat flux or the stress tensor.

A more efficient strategy is instead to reverse cause and effect, i.e., to *impose* the heat flux while sampling the resulting temperature gradient. In this manner, the heat flux is precisely known and temperature gradients are easily computed without large statistical scatter, as temperature is a lower order moment of the velocity distribution function. The classic method of Müller-Plathe (MP) [50] is, for these reasons, widely utilized in standard molecular dynamics and represents the inspiration for the method presented here.

Similar to the MP method, we subdivide the simulation box into n_s slabs of equal width Δx along the x -direction. At $x = 0$ and $x = L$, isothermal wall boundary conditions are imposed at T_w , and, for simplicity, $T_w(0) = T_w(L) = T$. Periodicity is used in the y and z directions. At each DMS time step Δt , particles located in the middle slab, i.e., whose $x \in [L/2 - \Delta x/2, L/2 + \Delta x/2]$ are

given additional center of mass kinetic energy $\delta\epsilon$ with a probability p_ϵ . If selected for the energy *kick*, the particle new center of mass velocity vector magnitude $|v_{new}|$ is corrected as

$$|v_{new}| = \sqrt{v_{old} \cdot v_{old} + 2 \frac{\delta\epsilon}{m}}, \quad (3)$$

where v_{old} is the old center-of-mass velocity vector and m is the particle mass. Then, the new center-of-mass velocity vector direction is assigned from a uniform distribution on a unit-radius sphere. In this way, the heat flux imposed on the system is given by:

$$J_x = \frac{1}{2} \frac{p_\epsilon N_{1/2} \delta\epsilon W_p}{A \Delta t}, \quad (4)$$

where $N_{1/2}$ is the number of particles contained in the central slab, W_p is the particle weight, and A the cross sectional area of the simulation domain perpendicular to the x axis. The factor $\frac{1}{2}$ accounts for the propagation of the energy added to the system in both x directions, a reasonable approximation for an isotropic gas. This mechanism produces an energy flux from the middle of the simulation box to the walls, which are kept at a constant temperature, and consequently a temperature gradient is established between the middle of the simulation box and the walls. The resulting thermal conductivity is then given by Eq. 2.

As stated, the MP and MMP methods share several similarities. However, a key difference is in the mechanism to impose the heat flux. In fact, in the MP technique, J_x is obtained by *swapping* the *hottest* (fastest) particle at one end of the domain with the *coldest* (slowest) particle in the middle slab of the domain [50]. Moreover, periodic boundary conditions are used in the direction of the heat flux. This mechanism, although applicable to DSMC and related stochastic particle methods, is not ideal for highly distributed computations, where domain decomposition must occur among hundreds or thousands of computing cores, as is the case for the first-principles calculations presented here. The addition of energy according to the MMP method, instead, is localized (middle of the channel) and does not require inter-core communications, thus greatly simplifying the implementation.

A few considerations must be made:

- i. For DSMC-like methods, the presence of walls does not alter the microscopic fluid structure in their vicinity, as conditions can be set to obtain near-continuum and no-slip. This is at variance with pure molecular dynamics, where walls must be modeled atomistically and, therefore, large density and temperature fluctuations are observed [45]. In this work, we assume diffuse scattering with full energy accommodation.
- ii. The temperature gradient is not known *a priori*. However, the total heat flux can be modulated by adjusting p_ϵ and $\delta\epsilon$ in order to achieve a small temperature variation, as discussed later.
- iii. Total momentum is conserved only in a statistical sense and total energy is not a conserved quantity. Similarly, the equations of motion are not derived from a modified Hamiltonian, like in other non-equilibrium techniques [45].

The MMP method is very easy to implement in stochastic particle methods for gas dynamic simulation and it does not depend on a particular molecular model, PES, gas type (monoatomic, diatomic, or polyatomic) or gas composition and density.

Verification with DSMC A preliminary verification of the MMP method was conducted with standard DSMC. Molecular nitrogen was modeled with the variable hard sphere (VHS) collision model of Bird [51]. The VHS parameters were set using DMS viscosity data from the PES described above [28], namely, a viscosity index of 0.662 and a reference diameter of 3.963 Å at 273 K were used. For simplicity, constant rotational and vibrational relaxation numbers were used and set to 4 and 1,000, respectively. Internal energy states were not quantized and were relaxed using the Borgnakke-Larsen model [52]. The simulation box consisted of 250 cubic cells aligned along the x axis, for a total length of 10 μm , while periodicity was used in the y and z directions. A total of 210,000 particles were used, with approximately 800 particles contained in each cell, whose side was set to about 0.9λ , where λ is the local mean free path estimated with the VHS model. A conservative time step of 5×10^{-12} s was used in the simulations and the particle weight W_p was set to 10^8 . The number of *slabs* used was 50. The kinetic energy added per particle was varied to obtain a relatively small temperature variation across the channel. The Knudsen number based on the channel width is estimated to be around 10^{-3} , hence negligible slip is seen at the walls. For all calculations, we set $p_\epsilon = 0.01$ and no chemical reactivity was considered.

Figure 1a shows an example of temperature profiles obtained at steady state for a wall temperature of 4,000 K. The temperature gradient in turn causes a modest density variation throughout the channel, as Fig. 1b illustrates. As expected, a reduction of $\delta\epsilon$ decreases the peak temperature in the channel (Fig. 1a). The temperature gradient used to evaluate κ is obtained from the average of linear fits of the temperature profiles at $x/L \in [0, 0.1]$ and $x/L \in [0.9, 1]$, where the gas temperature is closer to the nominal value at which $\kappa(T)$ is estimated. Samples were collected for at least 500,000 time steps after the system had reached steady state.

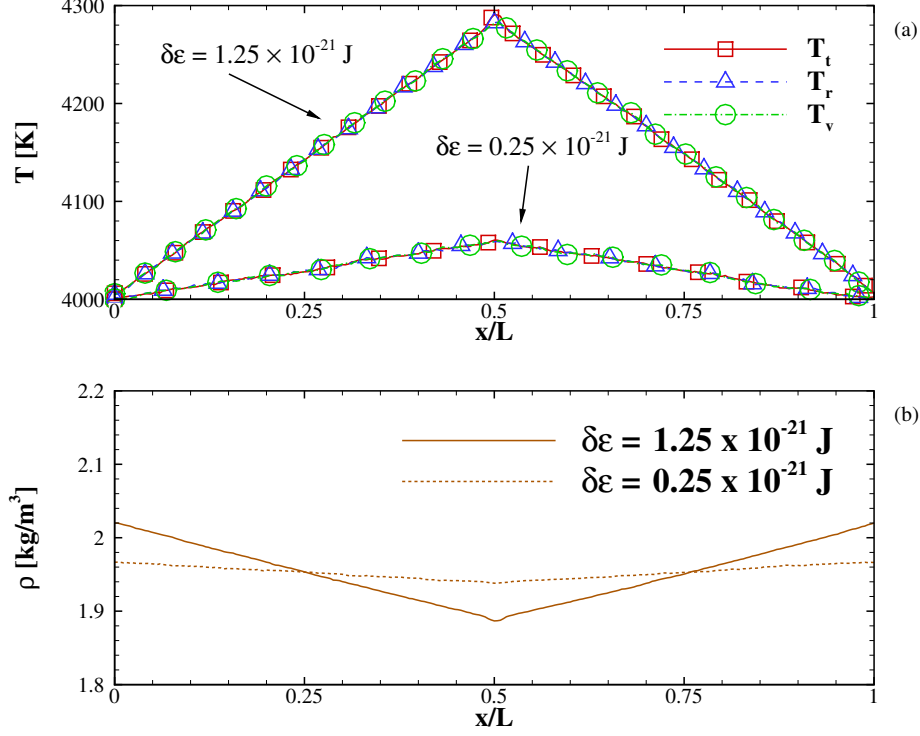


FIG. 1. (a) Temperature gradients obtained by modulating the imposed heat flux via Eq. 4; (b) corresponding density variations throughout the channel.

VHS thermal conductivities were obtained for a set of wall temperatures between 273 K to 10,000 K, as shown in Fig. 2. For reference, the results are compared with the correlation of experimental data of Lemmon and Jacobsen [17] for dilute molecular nitrogen and reasonable agreement is seen up to about 6,000 K. Although the fit of experiments of Lemmon and Jacobsen [17] is strictly valid up to about 2,000 K, its extrapolation to higher temperature remains fairly close to the VHS data up to about 6,000 K. In Fig. 2, we also plot the corresponding thermal conductivities using Eucken's relation [31]:

$$\kappa = \frac{15}{4} R \eta \left(\frac{4}{15} \frac{1}{\gamma - 1} + \frac{3}{5} \right), \quad (5)$$

where R is the gas constant and γ is the ratio of specific heats, assuming calorically perfect gas behavior for simplicity. The viscosity used in Eq. 5 is obtained from a fit of previous DMS calculations based on the same PES [28]:

$$\eta(T) = 17.1 \times (T/273)^{0.662} \mu\text{Pa}\cdot\text{s}. \quad (6)$$

As shown in Fig. 2, the best prediction of thermal conductivity using Eucken's equation is seen at $\gamma = 1.3$, i.e., close to $\gamma = 9/7$ which corresponds to the classical limit for vibrational degrees of freedom. The VHS DSMC computational results of Alves and Stark [53] are also reported and are in close agreement with the results obtained here up to about 4,000 K, even though the VHS parameter selection between the two studies is different. The rapid increase of κ beyond about 4,000 K shown by Alves and Stark [53] is not seen in our calculations.

Finally, we evaluated the thermal conductivity from a simple Fourier flow at the same number density than the previous cases. The left boundary was set at $T_w = 273$ K while the right boundary at $T_w = 373$ K. A total of 4.2 million particles were used, in contrast to about 210,000 particles used in the MMP method. To reduce statistical scatter, we collected samples for about 1,000,000 time steps at steady state, nearly twice as many as needed in a typical MMP run. The results for thermal conductivity obtained from both methods was nearly identical, namely 0.031 W/m-K, with a statistical uncertainty of less than 1% for both methods. The computational cost difference between the two methods derives entirely from the total number of particles needed in the simulation and the overall number of samples (time steps) required to bring the uncertainty below a prescribed value. The addition of energy to particles in the middle of the channel does not constitute a significant additional cost. On a single core and using the VHS model, we estimated the total cost of the MMP calculation at roughly 3 hours, whereas it was about 130 hours for

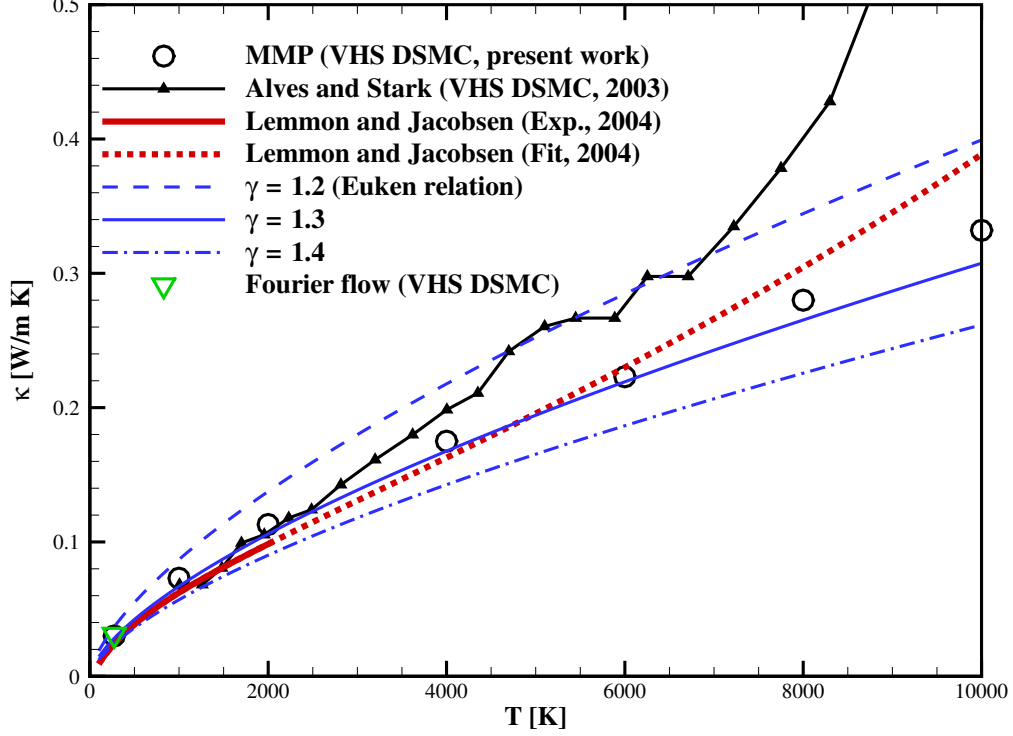


FIG. 2. . VHS molecular nitrogen thermal conductivity data obtained with the MMP method: comparison with experimental data [17], previous computations [53], Eucken relation [28, 31], and the Fourier flow method.

the direct computation of the heat flux. Finally, we emphasize that the issue with statistical scatter becomes considerably worse as the temperature is increased, and $T_w = 273$ K represents a relatively benign case.

Thermal Conductivity of Molecular Nitrogen from DMS. Molecular nitrogen thermal conductivity was obtained from DMS based on the *ab initio* PES of Paukku *et al.* [2, 3] for temperatures between 273 K and 10,000 K. At temperatures below about 6,000 K, dissociation is negligible [11], but becomes significant at higher temperatures. To maintain a fixed chemical composition, i.e., pure molecular nitrogen, we ignored simple and double dissociations by resetting the phase-space coordinates of the colliding molecules to their pre-collision states. However, exchange reactions were permitted, as they do not alter the chemical composition of the system.

The same simulation conditions and parameters as for the VHS results were used for the DMS cases. However, the particle weight was increased to $W_p = 10^9$, thus obtaining about 80 particles per cell. Samples were collected for at least 200,000 time steps (up to about 600,000 for the higher temperature cases) after the system had reached steady state.

Three primary causes of uncertainty were identified: (i) sampling, (ii) finite temperature gradient, and (iii) partial vibrational equilibration at low temperature. The error associated with (i) was estimated to be around 1-2 % by randomizing a subset of the collected samples and estimating their standard deviation. The uncertainty associated with (ii) was conservatively set to the amplitude of the temperature variation across the channel and can be reduced by decreasing $\delta\epsilon$ (Eq. 4). The final uncertainty (iii) relates to the extremely long relaxation times of vibrational modes at near-room temperature [54]. Below about 2,000 K, the time scale of vibrational relaxation is orders of magnitude larger than that associated with the heat flow from the middle of the channel to the walls. To estimate the magnitude of this error, we ran VHS DSMC calculations with a temperature-dependent vibrational relaxation number model [51]. The parameters for this model were informed by the same PES used in this work and resulted in a good match with the Millikan-White correlation [37, 54]. The resulting thermal conductivity at 273 K with only partial vibrational equilibration was about 15% lower than that corresponding to full equilibration of internal energy modes. In this regime, only the rotranslational temperature gradient is measured. At 2,000 K, the difference dropped to only about 4%. At even higher temperatures, the error becomes vanishingly small because the heat flow time scale becomes comparable to that of vibrational relaxation. This, however, is not an intrinsic limitation of the computational method.

Thermal conductivity data obtained from the selected PES agree well with the available experimental evidence, as illustrated in Fig. 3a and summarized in Table I with the comparison to a fit of a collapse of experimental data [17]. The difference of

about 20% seen at 273 K may be attributed to only partial vibrational energy equilibration and to the accuracy of this PES at low temperatures [36, 37], as the PES was tailored specifically to high-energy collisions, which are more representative of high-temperature gas environments. The agreement with the experiments of Faubert and Springer [19] and of Chen and Saxena

Temperature [K]	$\kappa(T)$ [W/m K] (DMS)	$\kappa(T)$ [W/m K] (Exp. fit)
273	0.029	0.024
1000	0.067	0.062
2000	0.105	0.099

TABLE I. Comparison between *ab initio* DMS predictions and experimental fit [17] for molecular nitrogen thermal conductivity.

[18], which contain data in roughly the widest temperature range and for dilute gas conditions [17], is also very good. The extrapolation of Lemmon and Jacobsen's fit [17] beyond 2,000 K follows the DMS data closely up to 10,000 K. Similar to the VHS results, the Eucken relation best agrees with the DMS predictions for $\gamma \simeq 1.3$. Finally, while the VHS and DMS results are in very close agreement at the lower end of the temperature range (up to 6,000 K), they markedly diverge at $T > 6,000$ K. This deviation from a simple constant-exponent power law is consistent with the Lemmon and Jacobsen fit, although the fit does not appear to have any physical justification for this high-temperature behavior. A similar trend was also shown by Alves and Stark [53]. The DMS data trend may be explained by a significant variation (increase) of the power law exponent at higher temperatures, indicative of a weakening of the N_2+N_2 repulsion at large collision energies.

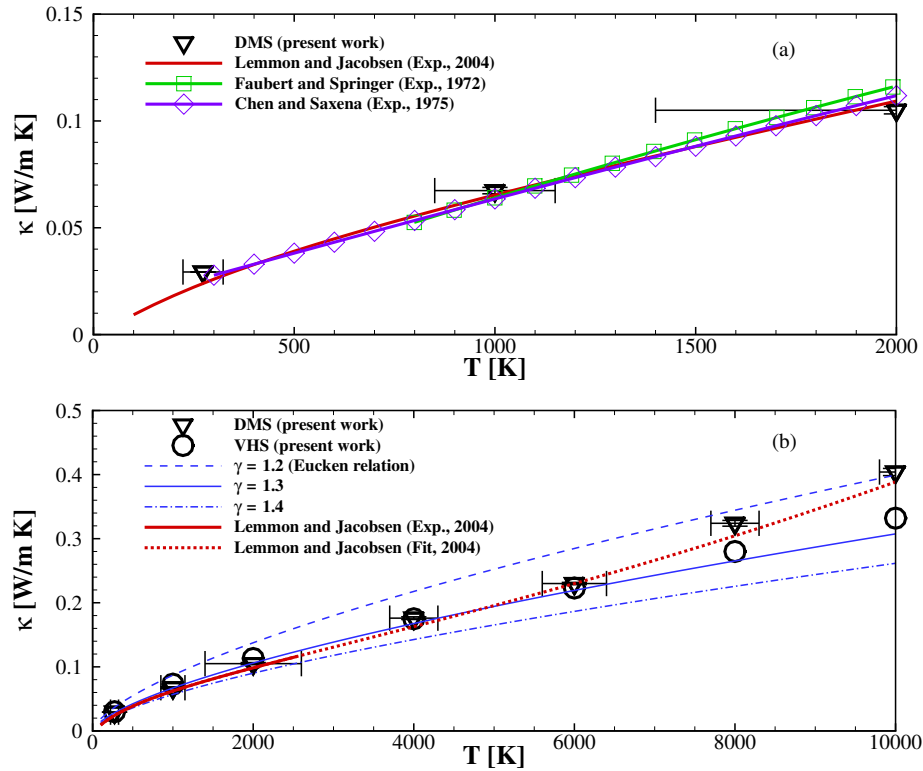


FIG. 3. . Thermal conductivity of molecular nitrogen from DMS calculations using the MMP method. (a) Low temperature comparison with experimental data [17–19]; (b) comparison with Eucken relation, fit of experimental data [17] and VHS DSMC between 273 K and 10,000 K.

Conclusions A novel method, named MMP, to compute thermal conductivity for a dilute gas using DSMC, DMS, or other stochastic particle method, is presented in this letter. Similar to the Müller-Plathe approach [50], the heat flux is imposed on the system and, consequently, it is precisely known. As such, it is the temperature gradient that must be sampled during the simulation. In this manner, the issue of large statistical scatter associated with sampling the heat flux in Fourier flows is overcome. This is particularly advantageous when applied to *ab initio* DMS based on computationally expensive PESs. The MMP method was first verified with standard VHS DSMC, whose parameters were taken from a previous nitrogen viscosity DMS study using the same PES as in this work [28]. The VHS DSMC results agree quite well with experimental data in

the low temperature range [17], with other VHS computations [53], and are consistent with the Eucken relation [31]. The method is then used in DMS calculations directly utilizing the N_2+N_2 PES of Paukku *et al.* [2, 3], and the most significant sources of uncertainty are identified and discussed. The DMS results for thermal conductivity agree remarkably well with the experimental evidence up to 2,000 K, and also with the high-temperature extrapolation of the dilute gas fit suggested by Lemmon and Jacobsen [17]. The MMP method is applicable to arbitrary PESs and gas compositions, and it provides a direct way to evaluate thermal conductivity without relying on empirical extrapolations to high temperatures or approximations based on viscosity, at a reasonable computational cost. The influence of thermal nonequilibrium was not investigated in this letter, but will be addressed in future work.

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