The Ratio $D_{int}/D$ between the Coefficients for the Diffusion of Internal Energy and of Self Diffusion in Thermal Conductivity Data Correlations for Gases of Linear Molecules

E. Vogel, E. Bich, and S. Bock

Highly consistent sets of generalized cross sections are used to judge critically correlations of the thermal conductivity in the limit of zero density for nitrogen, carbon monoxide, and carbon dioxide. The correlations were developed by Millat, Vesovic, and Wakeham some years ago using restricted experimental information in order to deduce a set of generalized cross sections as consistent as possible for the extrapolation beyond the temperature range of the primary experimental data. Recently, the generalized cross sections needed have been evaluated by means of classical trajectory calculations for rigid rotors on the basis of accurate anisotropic \textit{ab initio} potential energy hypersurfaces including a new improved way to take into account the vibrational degrees of freedom. It is shown that the ratio between the coefficients of internal energy and of self diffusion $D_{int}/D$ was not appropriately chosen and that this effect was extensively compensated in a fortuitous way in the course of the development of the data correlations by a likewise unsuitable choice of the ratio $A^*$ between the effective cross sections of viscosity and self-diffusion.

KEY WORDS: carbon monoxide; carbon dioxide; data correlation; diffusion coefficient of internal energy; nitrogen; thermal conductivity.


\textsuperscript{2}Universität Rostock, Fachbereich Chemie, Albert-Einstein-Str. 3a, D–18059 Rostock, Germany.

\textsuperscript{3}To whom correspondence should be addressed. E-mail: eckhard.vogel@uni-rostock.de.
1. INTRODUCTION

The formal exact kinetic theory of dilute polyatomic gases [1], which relates the transport and relaxation phenomena to a number of generalized cross sections, is well developed, but essentially more complicated than the theory for monatomic gases [2]. The complications are due to the additional internal degrees of freedom introduced by the internal energy states and to the potential energy hypersurfaces of the molecules. Nevertheless, extensive classical trajectory (CT) calculations using accurate intermolecular interaction potentials have been performed for such phenomena, and the properties and behavior of such systems have been investigated to a great extent. However, the vibrational modes of motion can be neglected, because the vibrational state of a molecule does not practically influence the transport of mass and momentum. Collisions characterized by an exchange of vibrational energy with translational or rotational energy are rare. However, in the case of thermal conductivity which measures the transport of energy through the gas, vibrational excitation of the molecule representing stored energy becomes important and the rigid-rotor approximation is much more questionable.

Heck and Dickinson as well as Heck et al. [3–5] performed rigid-rotor CT calculations for nitrogen and carbon monoxide using anisotropic ab initio potential energy hypersurfaces of van der Avoird et al. [6] (nitrogen) and of van der Pol et al. [7] (carbon monoxide). But in the following calculation procedure for thermal conductivity, they did not completely consider the effects of vibrational modes.

Bich et al. [8] proposed recently a distinctly improved way for the inclusion of the vibrational degrees of freedom into rigid-rotor calculations of the thermal conductivity of linear molecules and presented a re-evaluation of the results for nitrogen and carbon monoxide. The CT calculations were extended to carbon dioxide [9,10], since new ab initio potential-energy hypersurfaces for CO$_2$ were developed [11–13] and the effects of the vibrational modes on thermal conductivity have been expected to be of greater importance.

Correlations of thermal conductivity data in the limit of zero density for nitrogen and carbon monoxide were developed by Millat and Wakeham [14] and another one for carbon dioxide by Millat et al. [15] and by Vesovic et al. [16], all more than ten years ago. Unfortunately, the temperature range of selected primary experimental thermal conductivity data determined by means of the transient hot-wire technique was rather restricted (from 300 to 470 K for nitrogen and carbon dioxide and from 300 to 430 K for carbon monoxide). Hence, these authors included in