Ab initio Virial Equation of State for Methane

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Advances in computer technology make it possible to determine the thermophysical properties of simple fluids with high accuracy entirely from theory. For very low and very high temperatures and also for highly corrosive or toxic substances *ab initio* computations represent a reasonable way to obtain accurate values for thermophysical properties. Virial coefficients of gaseous and supercritical fluids up to high order can be calculated with the Mayer-sampling Monte Carlo procedure [1]. In a previous study we computed the virial coefficients of argon up the seventh using highly accurate *ab initio* two-body and nonadditive three-body potentials [2] as well as a new method to systematically account for nonadditive contributions in the calculation of virial coefficients [3]. The resulting EOS shows excellent agreement with the best experimental data in the regions where the virial expansion up to the seventh order is converged. For methane we will present preliminary results for the virial EOS up the seventh order based on a two-body potential obtained from quantum-chemical *ab initio* calculations [4] and a semi-empirical nonadditive three-body potential. Since quantum effects are of importance at low temperatures, we have computed the second, third, and fourth virial coefficients with the first-order translational and rotational quantum corrections. Eventually we want to apply an *ab initio* three-body potential instead of a semi-empirical one to further improve the accuracy of the EOS.

[1] J. K. Singh, D. A. Kofke, Phys. Rev. Lett. 92, 220601 (2004)
[2] B. Jäger, R. Hellmann, E. Bich, E. Vogel, J. Chem. Phys. 135, 084308 (2011)
[3] R. Hellmann, E. Bich, J. Chem. Phys. 135, 084117 (2011)
[4] R. Hellmann, E. Bich, E. Vogel, J. Chem. Phys. 128, 214303 (2008)