THE THERMODYNAMIC REGION OF NEGATIVE NONLINEARITY IN SELECTED SILOXANES PREDICTED BY MODERN THERMODYNAMIC MODELS

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A wealth of theoretical studies demonstrate that many interesting and often counter-intuitive gasdynamic phenomena can occur in vapor fluid flows of complex molecules in a thermodynamic region close saturation at high reduced pressures and temperatures [1]. For this reason the branch of fluid mechanics that studies these phenomena is known as nonclassical gasdynamics. The main thermodynamic parameter that, if negative, determines the possibility of nonclassical behavior is the fundamental derivative of gasdynamics Γ. The first studies on nonclassical gasdynamics employed the simple van der Waals polytropic model for the thermodynamic description of the fluid. Even if the qualitative results opened the way to this fascinating scientific field, it was known that the quantitative description of thermodynamic properties provided by this model is highly inaccurate in the thermodynamic region of interest. It is moreover important to note that the possibility of correctly predicting nonclassical gasdynamic phenomena is related to the value of a second derivative of main thermodynamic properties, therefore the accuracy and the functional form of the model is of primary importance. Further studies proved that, according to other cubic equations of state and multi-parameter equations of state, vapors of complex hydrocarbons and fluorocarbons exhibit regions of negative Γ [1,2,3]. Experiments aimed at proving nonclassical gasdynamic behavior were unsuccessful so far.

Initial studies on siloxanes [4] as a suitable class of BZT fluids lead to a research project which is ongoing at the Delft University of Technology aimed at the detection of a rarefaction shock wave moving in the dense, high temperature vapor of a cyclic siloxane. Siloxanes are a particularly attractive class of BZT fluids because of their thermal stability, nontoxicity, low flammability and, if compared to other potential BZT fluids, greater availability of reliable thermodynamic information. Siloxanes are employed as thermal fluids and as working fluids in organic Rankine turbines, a possible technical application of nonclassical gasdynamic effects. Major work has been recently accomplished which brought to the development of state-of-the-art equations of state (EoS) for several fluids of the siloxanes class and this paper presents a critical assessment of the region of negative nonlinearity as predicted by Peng Robinson-type cubic EoS, Martin Hou EoS and highly accurate Span-Wagner-type EoS for several linear and cyclic siloxanes. The thermodynamic models are briefly introduced and the Γ negative region as predicted by the various models for the different fluids is thoroughly analyzed. The consequences of the differences in the estimations of the models are also briefly addressed in connection with experiments and possible applications. As for all the classes of potential BZT fluids, a major source of uncertainty for the value of Γ is due to the relatively inaccurate estimation of the ideal gas isobaric specific heat of the molecules. The results of the associated uncertainty analysis are also presented.

References

[1] M. S. Cramer, "Negative nonlinearity in selected fluorocarbons," *Phys. Fluids A* journal = Phys. Fluids A, **11**, 1894-1897, 1989

[2] A. Guardone, L. Vigevano and B. M. Argrow. Assessment of thermodynamic models for dense gas dynamics. *Phys. Fluid*, **16**:11, 3878–388, 2004.

[3] A. Guardone and B. M. Argrow. Nonclassical gasdynamic region of selected fluorocarbons. *Phys. Fluid*, **17**:11, 116102-1–116102-17, 2005.

[4] P. Colonna and P. Silva. Dense gas thermodynamic properties of single and multicomponent fluids for fluid dynamics simulations. *ASME J. Fluids Eng.*, **125**, 414–427, 2003.

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