# Title: Accurate atomic and molecular interactions for thermophysical standards

## Abstract

Future metrology standards will increasingly be based on physical quantities computed from first principles rather than measured. Previous progress made in the calculation of the thermophysical properties of helium reduced their uncertainty well below that of their experimental determinations, leading to novel metrological applications such as primary standards of pressure, temperature and viscosity. Extending this computational capability from He to more complex systems, like heavier monatomic gases and molecules, could improve our understanding of the fundamental physics of these systems with a deep positive impact on the metrology of fluids. The accuracy of the calculations should be compared with results from state-of-the-art experiments.

## Keywords

Theoretical interatomic and intermolecular potentials, polarisability, virial coefficients, transport properties, primary thermometry, atomic pressure standard, hygrometry, thermophysical standards

## Background to the Metrological Challenges

New primary methods for measuring temperature (and/or pressure) based on the determination of the speed of sound, the dielectric constant and the refractive index of gases have been previously developed to reduce the uncertainty in the determination of the Boltzmann constant in support of the International Committee for Weights and Measures (CIPM) redefinition of the kelvin in 2018. After this date, the same methods will constitute the fundamental core of the Mise en Pratique of the kelvin (MeP-K) as currently envisaged by the Consultative Committee for Thermometry (CCT). It is thus essential that these methods are further improved to reduce their uncertainty over an extended working temperature (and/or pressure) range. A reduction in the uncertainty associated with the calculated thermophysical properties which are used as essential input data for these methods is a crucial requirement. If achieved for a broader class of more-complex systems, like interacting polar and non-polar molecules, the advances of the theoretical capability to calculate gas properties would have a strong positive impact on fundamental hygrometry.

A benchmark comparison of the current capabilities of theory and experiment to achieve an accurate determination of the polarisability and thermophysical properties of different substances shows the best performance of theory for helium, a balanced situation for neon and argon, and the superiority of experimental determinations for more complex systems like heavier atoms and molecules. However, the rapidity by which ab-initio calculations are making progress indicates that the computational and theoretical difficulties of increasingly complicated systems may soon be successfully overcome. Experiments to determine low uncertainty values of thermophysical properties of more complex gaseous systems are used to validate theory, which currently has larger uncertainties. From the results of custom-designed experiments, agreement with theory, or lack of it, will provide the feedback needed to drive the selection of advanced theoretical tools.

In primary thermometry, research is underway to simplify the experimental practice of thermodynamic thermometry and increase the operating range of several experimental methods. The success of these attempts are dependent on the availability of accurate theoretical predictions of the polarisability, the density virial coefficients and the transport properties of monatomic gases like He, Ne and Ar over extended ranges of temperature and pressure. Similar requirements and improvements are shared and expected by pressure metrology, where novel primary standards based on capacitors, microwave and optical cavities are currently being developed. For instance, a He-filled microwave cavity has already been demonstrated to be competitive with traditional standards, though over a limited working pressure range. To overcome this limit at higher pressure, the uncertainty of higher density and dielectric virial coefficients of He must be reduced. To overcome this limit at lower pressure, the uncertainty of the calculated properties of gases like Ne or Ar, having a polarisability larger than He, must be reduced. Last, improved predictions of high-order density and acoustic virial coefficients of He and Ar will promote their use, instead of water, as the calibrating fluid for apparatus used to measure density and speed-of-sound at moderate to high pressure. Increasing the accuracy of these methods will provide improved datasets which are needed to develop fundamental reference equations of state of several substances.

## Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on improving the theory and experimental practice as needed to develop novel standards of temperature, pressure, humidity, flow and gas transport properties.

The specific objectives are

1. To improve the methods used for the calculation of the pair potential and three-body interactions for systems of increasing complexity such as light monoatomic gases (He, Ne, Ar) and linear molecules (e.g., $H_2$, $N_2$, $O_2$, $CO_2$). To reduce (by at least a factor of 5) the uncertainty associated with the calculation of the density virial coefficients of these substances.
2. To validate and drive the theoretical improvements in modelling by accurate measurements of the thermophysical and electromagnetic properties of the same systems listed in objective 1 and of more complex systems such as heavier monoatomic gases (Kr, Xe) and polar molecules (e.g., $H_2O$, CO).
3. To reduce (by at least a factor of 10) the uncertainty associated with the calculation of the polarisability of Ne and Ar and to reduce the uncertainty associated with the calculation of the dielectric and refractivity virials of He, Ne and Ar. To reduce (by at least a factor of 5) the uncertainty associated with the calculation and the measurement of the viscosity and thermal conductivity of selected systems (e.g. Ar between 100 K and 200 K). To calculate the first density correction to the viscosity and thermal conductivity of He and of Ar.
4. To measure the virial coefficients of gaseous mixtures of interest for fluid metrology and hygrometry (such as binary mixtures of the relevant constituents of air and water vapour). To measure the static polarisability of water vapour over a wide temperature range (up to 200 °C) reducing the uncertainty associated to the Debye constants by at least a factor of 2.
5. To facilitate the take up of the technology developed in the project by end users

Proposers shall give priority to work that aims at excellent science exploring new techniques or methods for metrology and novel primary measurement standards, and brings together the best scientists in Europe and beyond, whilst exploiting the unique capabilities of the National Metrology Institutes and Designated Institutes.

Proposers should establish the current state of the art, and explain how their proposed project goes beyond this.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 1.5 M€, and has defined an upper limit of 1.8 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 40 % of the total EU Contribution to the project.

## Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the “end user” community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,

You should detail other impacts of your proposed JRP as specified in the document “Guide 4: Writing Joint Research Projects (JRPs)”

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work

## Time-scale

The project should be of up to 3 years duration.