Computational approaches for aerosol/mineral composition based on non-Equilibrium Thermodynamics

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The composition of material in equilibrium is not only constrained by the available building blocks (i.e., molecules and atoms of a mixture, solution, melt, etc.) but also thermodynamic state variables such as temperature and pressure. However, transitions and changes of the chemical composition of materials are generally also affected by additional constraints in Earth System Science, e.g. transport limitations on various scales such as diffusion and advection. This results in the fact that the often assumed equilibrium approaches are only valid under certain circumstances.

Therefore, the different time scales of the individual processes should explicitly be considered, e.g., atmospheric aerosol particles of a few µm size equilibrate only after a few hours to days due to diffusion limitations. In case the chemical composition of the air mass changes due to other processes such as advection and mixing of different air masses, or irreversible redox-chemistry the particles actually never equilibrate with their environment.

In the solid Earth geosciences, minerals and melts generally have transport coefficients (viscosity, diffusivity etc) with characteristic timescales of thousands or millions of years. This leads to the fact that geological systems are most of the times out of equilibrium as documented by the incomplete mineral reactions in the metamorphic-rock record. However, high-temperatures and hydrous fluid presence can drastically increase the reaction rates and therefore knowledge of the spatial and temporal evolution of a system's thermodynamic parameters is essential for the accurate prediction of the stable and metastable mineral assemblages.

The traditional approach to describe the composition of aerosol particles, but also minerals is the application of thermodynamic equilibrium models, which are based on the principle of the minimisation of Gibbs Free Energy of the whole system. This is supposed to describe the thermodynamically preferred phase state of the constituents. Due to the limitations of the equilibrium approach and the difficulties to provide accurate solutions for complex chemical composition systems, the current project plans to follow an alternative approach (which can be derived theoretically from this state of minimum energy), namely the formulation of reaction kinetics. In this case, equilibrium processes can be described with the help of a formation and a decay chemical reaction with reaction kinetics appropriate for the time scales of the system and the reaction enthalpies (which are also reflected in the Gibbs Free energy of the system). If these reaction systems are simulated

sufficiently long, a dynamic equilibrium will evolve, which is supposed to be comparable to the state derived from Gibbs free energy. However, depending on the stability of the system also metastable states could be achieved which are beyond the limits of most classical thermodynamic equilibrium models which usually determine the absolute minimum of the free energy. Additionally, this approach has the potential to also include non-equilibrium processes such as degassing from the system and "quasi- irreversible" redox-chemistry. In comparison to simple thermodynamic equilibrium schemes this approach can be computationally more expensive, however due to the sparsity of the resulting differential equation system the numerical costs can be reduced. Particularly , once a near-equilibrium state is reached the changes due to modifications of temperature, pressure or composition mixing are often relatively small resulting in a reduced numerical effort compared to a complete recalculation of the minimum Gibbs energy of the system.

The project aims to develop a joint framework to determine chemical composition modules for both atmospheric aerosols and minerals, building on the principles of reaction kinetics. With the help of the KPP software a system of coupled ordinary differential equations is created semi-automatically from a set of chemical reactions (either equilibrium or non-equilibrium processes). This system can then be formulated as either FORTRAN code (as required for atmospheric models) or C (as required by the geophysical models) and can be easily embedded into 3D transport models. The software already comes with a set of numerical accurate solvers for this equation system, allowing to optimise accuracy versus computational costs. Additionally, it is planned to convert this reaction system either into a CUDA code or using OpenACC directives into a model suitable to run on GPUs or booster's of the next generations of supercomputers.

Within the project in the first phase the joint framework is planned and designed. This includes close collaboration between the PIs Tost, Moulas and Kaus defining the common principles of the reaction systems, but also identifying distinct differences between the systems. These will include, e.g.:

– aerosol-water interactions and hence size of the particles due to water uptake which influences directly the equilibrium time scale
– the sometimes not well defined stochiometric coefficients in minerals and melts which are highly dependent on the temperature and pressure conditions.

After some simple test cases, the new system will be benchmarked against state-of-the-art reference models from both fields of science.

In phase 2 of the project the transfer of the newly developed computer modules to hybrid architectures will be tackled with support of the PI Brinkmann. As current models in both atmospheric and geoscience are mostly using classical multicore architectures a pure transfer of the module to a GPU type computer is not useful, as the classical components of these models require parallel CPU machines.

In the third phase of the project the new module will be implemented in 3D

models for the atmosphere (PI Tost) and solid earth (PI Kaus) to allow a more accurate description of the chemical composition in the respective domains.

The PhD candidate should ideally have some experience in computing science and ideally some chemical background knowledge. Alternatively, theoretical geosciences or atmospheric sciences would strengthen the corresponding part of the project. However, it is highly important that the developed method will be applied to both fields of science, allowing a cross-discipline collaboration based on the newly developed computing tool.