DEVELOPMENT OF NUMERICAL METHODS FOR PHASE EQUILIBRIA CALCULATION INVOLVING MODELS WITH INTERNAL DEGREES OF FREEDOM

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Multicomponent systems often include non-stoichiometric phases that require complex thermodynamic models based on sublattices, ions, associates etc. In this case phase models often have internal degrees of freedom, i.e. number of independent components is less than the number of species. And computation of Gibbs energy of phase requires its minimization. It may require specialized approaches, especially in the case of the convex hull method. And the aim of this work is to suggest such methods for further usage during further development in the Laboratory of Chemical Thermodynamics of Lomonosov MSU.

Each phase can be characterized by molar fractions of independent components ($\vec{x}$) and species ($\vec{y}$). The $\vec{x}$ vector can be unambiguously calculated from $\vec{x}$ as $\vec{x} = f(\vec{y})$ where f is a model-specific function. But if internal degrees of freedom are present and f is not bijective then computation of $G(\vec{x})$ will require the solution of the next nonlinear minimization problem:

$$G(\vec{x}) = \min_{\vec{y}} G(\vec{y}) ; \vec{x} = f(\vec{y})$$

In the case of convex hull method that is used for robust search of an initial approximation two approaches were suggested:

1) Solve the *G* minimization problem at each point of the grid used by the convex hull method during the Gibbs energy discretization. It makes the method not derivative free.
2) Monte Carlo approach with generation of large amounts of $\vec{y}$ pseudorandom or quasi-random vectors with their further projection to $\vec{x}$ coordinates. The procedure is continued until the $G(\vec{x})$ with the desired discretization step is stabilized. It may be computationally extensive but doesn't require derivatives.

Both methods allow to reduce the number of dimensions in the convex hull method; it is important because it may slow down at grids with more than 4 components.

In the case of phase equilibria computation based on an explicit minimization of *G*, e.g. by means of Lagrange multipliers method, the minimization procedure can either directly integrate $\vec{y}$ into the problem or assume optimization of $\vec{y}$ vectors inside thermodynamic models of phases. Both variants require the analytical $\partial G / \partial y_i$ and $\partial^2 G / \partial y_i \partial y_j$ derivatives, especially for sublattice models. Their addition to the developed software complex allowed us to increase numerical stability.

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