A Fully Nonlinear Bellman PDE for Inferring Gibbs Free Energies from Light Scattering Data

David S. Ross
Rochester Institute of Technology

ABSTRACT

Differences in *free energies* are the driving forces in chemical changes. The current project originated in our desire to understand phase changes in the protein mixtures in the lens of the human eye; such changes cause cataract disease, the leading cause of blindness. Our methods apply much more generally, to liquid mixtures.

George Thurston has proposed a new method of measuring free energies as functions of mixture composition: measure the intensity of light scattered by mixtures of various compositions and solve the PDE

$$\min_{\substack{\text{all}\\ \text{directions}}} \frac{\dfrac{\partial^2 G}{\partial s^2}}{\left(\dfrac{\partial \varepsilon}{\partial s}\right)^2} = \frac{1}{R}$$

which relates the free energy, G, regarded as a function of composition, to the Rayleigh ratio, R, of the scattered light. Here, s is arc length in the composition simplex and ε is the dielectric coefficient of the mixture. Our goal is to make a practical measurement device based on this mathematical theory.

In this talk we will formulate a well-posed problem for this equation with singular boundary conditions based on the Widom asymptotic form of the free energy. We will present computations done with a code based on a numerical method we have devised for solving the PDE. We will relate our PDE to the convex hull equation, to which it reduces in multi-phase regions, i.e., when $\frac{1}{R} \to 0$. We will describe the interpretation of the standard analytic tools of multi-phase thermodynamics—critical points, spinodals, cloud points, tie-lines, and tie-polygons—in terms of our PDE.

The perturbation theory of the nonlinear PDE yields a problem of Fichera for a degenerate parabolic equation. We will discuss the characteristics of this linear equation as a dynamical system, and we will analyze information flow using these characteristics.

As time permits, we will discuss open problems:

- Other well-posed problems; accommodating experimental restrictions.
- Designing data-acquisition methods to minimize errors in computed free energies.
- Second-derivative discontinuities.