Thermodynamics beyond molecules – Statistical mechanics of populations

Themis Matsoukas
Pennsylvania State University, University Park, United States

The central problem in statistical mechanics is the determination of the probability of microstate based on a small number of macroscopic state variables. The solution given by Gibbs is as elegant and it is simple: maximize a special functional, entropy, under a small number of constraints that represent our knowledge of the macroscopic state. The appeal of this approach is quite undeniable, a complex dynamic problem is reduced to an equivalent yet straightforward variational problem. Can this approach be extended outside statistical physics to any problem that involves an unknown distribution? In pursuit of this problem we formulate the "cluster ensemble", an ensemble that in the asymptotic limit contains every distribution. We construct a functional, W, that assigns a probability to each distribution in the ensemble and show that in the asymptotic limit the ensemble obeys "thermodynamics": the most probable distribution is overwhelmingly more probable than all others, it is a member of the exponential family, and its parameters obey the network of Legendre relationships of familiar thermodynamics. By proper construction of the functional W (selection functional) we may pick out any distribution of the ensemble to be the most probable distribution. The implication is that any process that involves an unknown distribution can be associated with a corresponding functional W, and thus shown to obey thermodynamics. We discuss certain problems in population balances, show how to construct the corresponding selection functional and demonstrate the conditions under which phase transitions are possible.