Statistical Molecular Thermodynamics

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Video 3.8

Review of Week 3

Critical Concepts from Week 3

- The probability of a state in an ensemble being populated decreases exponentially with its energy; temperature dictates the rapidity of that exponential decay
- The canonical ensemble involves fixed number (N), volume (V), and temperature (T)
- The partition function Q is a measure of the number of "accessible" states at a given temperature
- The ratio of, the exponential of the energy of a given state divided by $k_{\mathrm{B}}T$, relative to Q, provides the probability of a member of the ensemble *being* in that state
- Various macroscopic properties can be computed as averages of properties weighted by ensemble probabilities

Critical Concepts from Week 3

- For non-interacting particles, the partition function of an ensemble can be written as the product of partition functions for the individual particles.
- The macroscopic internal energy of a monatomic ideal gas is related to the ensemble average energy for an appropriate partition function (so, too, is the molar heat capacity)
- The macroscopic pressure of a monatomic ideal gas is related to the ensemble average pressure for an appropriate partition function and predicts the ideal gas equation of state
- Another partition function for a gas can be shown to be consistent with the van der Waals equation of state

Critical Concepts from Week 3

- Partition functions for *distinguishable* vs *indistinguishable* non-interacting particles differ by a factor of $(N!)^{-1}$
- Molecular partition functions can themselves be expressed as products of translational, rotational, vibrational, and electronic partition functions
- Partition functions expressed over states can be related to partition functions expressed over energy levels through inclusion of the degeneracy in the partition function sum